CHEMICAL STRATIFICATION OF THE CRUST:
ISOTOPE, TRACE ELEMENT, AND MAJOR ELEMENT CONSTRAINTS FROM
CRUSTALLY CONTAMINATED LAVAS AND LOWER CRUSTAL XENOLITHS
by
MARY RUTH REID
B.S. (Honors), A.B., University of California, Santa Cruz (1979)

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Signature of Author
Department of Earth, Atmospheric, and Planetary Sciences
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Certified by _____________________________
Stanley R. Hart
Thesis Supervisor

Accepted by _____________________________
Chairman, Department Committee on Graduate Students

WITHDRAWN
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Submitted to the Department of Earth, Atmospheric, and Planetary Sciences on November 7, 1986 in partial fulfillment of the requirements for the degree of Doctor of Philosophy

ABSTRACT

The dehydration of the lower crust and the assimilation of crustal materials into ascending magmas are two geologic phenomenon which lead to vertical mass transport and potentially, geochemical stratification of continental crust.

LOWER CRUSTAL XENOLITHS, KILBOURNE HOLE

This integrated Sr-Nd-Pb isotope study of paragneiss xenoliths from Kilbourne Hole maar, New Mexico, is the first of its kind applied to materials derived directly from the lower crust (6-10 kb). The pelitic paragneisses represent shales incorporated into the lower crust, in themselves exemplifying the importance of tectonic and sedimentary processes to the evolution of the lower crust. Because shales are rich in elements conventionally thought to be depleted in the lower crust, the pelitic paragneisses are an important geochemical reservoir to consider in the lower crust; their response to high grade metamorphism is pertinent to the problem of intracrustal stratification.

Sr isochrons determined from layers at a xenolith (decimeter) scale yield -1.6 Ga ages, coeval with metamorphic ages in basement rocks exposed at the surface. Locally, minerals are in isotopic equilibrium as a result of recent reheating of the lower crust related to Rio Grande rifting. Pb isochrons yield discordant ages as a result of this heating but are internally consistent with tectonothermal stability of the crust throughout the remainder of the Precambrian and most of the Paleozoic in spite of proximity to anorogenic plutonism at -1.4 Ga and orogenic activity at -1.0 Ga. Nd isochrons also yield discordant ages suggesting the heretofore unexpected possibility that effective diffusion rates for Nd are faster than Sr under dry crustal conditions.

The paragneisses exhibit a wide range in internal composition. A representative Sm/Nd ratio for the paragneisses as a whole is obtained by considerations based on their time-integrated Nd isotope evolution.
Other geochemical characteristics of the paragneisses are be correlated to Sm/Nd and a representative major and trace element composition for the paragneisses is determined. Although similar in many respects to typical shales, the paragneisses are significantly depleted in U and Cs and may have been depleted by a factor of ~2 in Th and the LREE relative to the protolith during metamorphism. High LREE abundances measured in the feldspars are unlikely to be maintained in the presence of a melt. Consequently, the paragneisses were probably depleted by means other than partial melting.

Relative to average crust, the pelitic paragneisses are radiogenic in $^{87}\text{Sr}/^{86}\text{Sr}$, are unradiogenic in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$, and have $^{143}\text{Nd}/^{144}\text{Nd}$ similar to middle Proterozoic crust. Existing data also show that they retain the relatively high $\delta^{18}O$ of their precursors. In contrast, isotopic data for orthogneisses from Kilbourne Hole indicate that they are unradiogenic in $^{87}\text{Sr}/^{86}\text{Sr}$ and may be more variable, albeit largely unradiogenic, in $^{143}\text{Nd}/^{144}\text{Nd}$. Consequently, representative isotope characteristics for the lower crust as a whole depend on the relative proportion of these different lithologies. If pelitic paragneisses are present at geologically reasonable 10-20% abundance levels in the lower crust, they reduce the heat flux required of the subcontinental mantle by up to 50%. They increase $^{87}\text{Sr}/^{86}\text{Sr}$ by up to 0.006 and incompatible elements abundances by 20-100% over previous estimates for the lower crust. On the other hand, the unradiogenic Pb isotopic signature of the lower crust, previously suspected from studies of granulites exposed at the surface, is confirmed.

CRUSTAL ASSIMILATION, KODIAK ISLAND, ALASKA, AND PARICUTIN VOLCANO, MEXICO

Crustal assimilation in two disparate tectonic settings is examined in order to understand its nature and timing. The Ghost Rocks volcanics (GRV) of Kodiak Island, Alaska are early Tertiary submarine basalts and andesites which erupted in a near-trench setting. Subduction of the Kula-Farallon spreading center beneath the Kodiak accretionary prism is proposed as the ultimate source of the GRV on the bases of tectonic considerations and MORB-like isotopic and trace element signatures in the basalts. Andesites which are conformably overlain by the basalts have less radiogenic Nd isotope signatures and arc-like chemical affinities. Inversion of selected trace element characteristics in light of the Nd isotope data shows them to be the product of mixing between the basalts and sediments of the accretionary prism.

The lavas of Paricutin volcano, a cinder cone in Mexico, exhibit linear trends in isotopic and incompatible element ratios consistent with crustal assimilation. However, they exhibit a tripartite trend in elemental abundances over time and more mafic lavas are richer in many of the incompatible elements than those which have undergone greater amounts of crustal assimilation. This is suggested to reflect the diachronous interplay of crystal fractionation with crustal
assimilation. Ratios between the U-series nuclides are not appreciably affected by crustal assimilation although $^{226}\text{Ra}$ is significantly enriched over $^{230}\text{Th}$ and $^{210}\text{Pb}$. Since the trend in $^{226}\text{Ra}$ abundance with time is correlated with that inferred to be the result of crustal assimilation, crustal assimilation must have occurred subsequent or consequent to Ra enrichment, or within the last 8000 years. If the $^{210}\text{Pb} - ^{226}\text{Ra}$ disequilibrium arose from Ra enrichment, crustal assimilation could have occurred within years of eruption.

Thesis Supervisor - Dr. Stanley R. Hart
Professor of Geology and Geochemistry
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Prelude

Years ago, when I was very young, I crossed the North Pacific from Vancouver to Japan; and one day, as our ship rounded the top of the great circle, I noticed a string of strange bare mountains rising out of the sea along the northern horizon. They resembled heaps of smoking slag; the sun, striking their sides, gave them a greenish cast like verdigris on copper. I asked a fellow passenger what they were. "Illusions," I thought he said, but now I realize he said they were Aleutians.

- Source unknown

Demetrio Toral, a laborer from Paricutin employed by Pulido as helper, was plowing land at Cuiyusuru. He had just completed a furrow and was about to turn his plow when the first outbreak of the volcano occurred almost in the exact furrow he had just drawn. This remarkable circumstance has led some people into the belief that Toral "plowed up the volcano." Toral, a deaf mute, died soon after in Caltzontzin.

...When they returned to San Juan Parangaricutiro, they related what they had seen, how the earth had opened and how smoke and small stones, like incandescent marbles and oranges were being cast out from a vent that continued growing bigger. The priest then consulted a book on Vesuvius in the church library, and they were convinced that they had seen a volcano.

- Birth and Devlopment of Paricutin Volcano, Mexico
  W.F.Foshag and J.Gonzalez R.
INTRODUCTORY NOTE

This dissertation concerns processes which shape the growth and evolution of continental crust. Together with a study of the source of island arc volcanism published recently with C. Nye (Nye and Reid, 1986), the scope of my dissertation research spanned many of reservoirs which contribute to the vertical growth and possible geochemical stratification of the continents: island arc mantle, lower crust, and crustal level magma chambers; the lithologies studied include igneous, sedimentary, and metamorphic.

This work consists of three autonomous parts. The first part consists of four chapters. These discuss the nature and scale of isotopic and geochemical heterogeneity in xenoliths, principally from the lower crust beneath Kilbourne Hole, New Mexico, and its implications for the chemical evolution of the deep crust. The contribution of metamorphosed sediments to the lower crust is considered in detail. This work is the result of collaborative efforts with S. Hart, E. Padovani, and S. Richardson. The first two chapters are intended for publication following minor revision: the first in Earth Planetary Science Letters and the second as a letter to Nature. The second two chapters are working drafts for publications pending streamlining.

The second part of this dissertation, Chapter 5, is an outgrowth of work begun when the author was an undergraduate at University of California, Santa Cruz. Based on isotopic and geochemical analyses of the Ghost Rocks volcanics, Kodiak Island, Alaska, I propose that this near-trench volcanism was the result of ridge subduction. This study illustrates the geochemical characteristics of magmas which arise from wholesale interaction of basalts and sediments. In addition, the origin of these volcanics contributes to the unravelling of terrane histories and trajectories in the North Pacific. The paper will be submitted to Journal of Geophysical Research.

The third part of this dissertation, Chapter 6, is a small part of ongoing research originally intended to be the chef-d'oeuvre of my dissertation. This work concerns the role of magma chamber processes in the geochemical evolution of volcanic arc magmas and ultimately the crust. In particular, I am interested in elucidating the operative time-scale of processes, such as crystal fractionation and crustal assimilation, inferred to occur in magma chambers and what constraints this imposes on their efficacy. The "magma chambers" studied were those emptied by relatively recent eruptions of Paricutin volcano, Mexico, and Volcan Arenal, Costa Rica. The approach taken involved U-series disequilibrium analyses of the lavas (and ultimately will include the hosted crystals) and ion microprobe studies of the crystals, in addition to other isotopic and geochemical studies. This tack explored so much uncharted territory that proper accounting of the results must await finalization of the data and much more cogitation on my part. For now, I offer the reader a progress report on Paricutin.
Chapter 1

VARIABLE SCALES OF Sr-Nd-Pb ISOTOPIC EQUILIBRIUM
AND TECTONOTHERMAL EVOLUTION OF THE LOWER CRUST,
KILBOURNE HOLE, NEW MEXICO
INTRODUCTION

In this study, we consider the scale of Sr, Nd, and Pb isotopic heterogeneity in crustal xenoliths from Kilbourne Hole maar located in southern New Mexico (Figure 1-1). Because basement lithologies of southern New Mexico are comprised of low to medium grade metamorphic rocks of 1.6 - 1.9 Ga age, this area appears to have been tectonically quiescent since the middle Proterozoic; their thermal history may be expected to be readily interpretable. The samples discussed here had a sedimentary heritage, thereby eliminating the possible interpretive wrinkle presented by igneous lithologies which may have been emplaced after crustal stabilization. These xenoliths were delivered to the surface on time scales of 3 days or less based on settling velocities of xenoliths of this size in magmatic liquids (Spera, 1980). Equilibration times for Pb, Sr, and Nd in the xenoliths at magmatic temperatures are considerably larger (ca. 30 years to 1 million years at the centimeter level). Thus, the isotopic characteristics of the xenoliths probably reflect those extant in the lower crust at the time they were transported to the surface. In spite of these favorable indicators, the xenoliths were extracted from the lower crust at a price. Their host basanite lava is one of many manifestations of mantle-crust thermal reactivation in the Rio Grande Rift province which, in turn, is characterized by an elevated geothermal gradient. High temperatures in the lower crust there are corroborated by phase equilibria in the xenoliths themselves (Figure 1-2; also Padovani and Carter, 1977a). Therefore, recent isotopic reequilibration at some scale is to be anticipated.
Figure 1-1

Map showing orogenic terranes of North American midcontinent and general location of Kilbourne Hole in southern New Mexico modified after Anderson (1983), Van Schmus and Bickford (1981), and Thomas et al. (1984). Shown in parentheses are proposed crustal extraction ages of Nelson and DePaolo (1985). Also shown are geologic features: M: Marathon region; FM: Franklin Mountains; and FI: Florida Island (aka Burro Mountain) uplift.
Thermal considerations in the study of the lower crust

The orogenic cycle is characterized by high crustal heat flow and may be accompanied by granulitization and dehydration of the lower crust, a phenomenon which appears to have been particularly true of the Archean (Moorbath, 1975; Hamilton et al., 1979; Moorbath et al., 1969). Thermal considerations suggest that crustal stabilization follows on the heels of crustal formation by a period of the order of 200 Ma (Sclater et al., 1980; Hamilton et al., 1979) and geothermal gradients subside to those of stable continental crust. As one can visualize from Figure 1-2, rocks in the upper crust must pass through the closure temperature for isotopic equilibration before those of the lower crust. Thus, one consequence of the orogenic cycle is that stabilization ages retained in the lower crust should be contemporary to somewhat younger than those of the upper crust.

However, mitigating circumstances to preservation of crustal stabilization ages abound and include the failure of minerals to close to radiogenic element migration, subsequent tectonic events, fluid migration, and retrograde mineral reactions. The first of these depends on temperatures at the base of the crust which are typically inferred from estimates of the geothermal gradient; hence, they are model dependent. Temperatures at 20-30 km in stable crust of Precambrian age are estimated to be 300 to 500°C today (Lachenbruch and Sass, 1977; Blackwell, 1971). As illustrated in Figure 1-2, this is close to or above the estimated closure temperatures of Sr equilibration between plagioclase and potassium feldspar for times on the order of 2 billion
Figure 1-2

Temperature-depth plot showing range of calculated temperatures and depths of origin for the Kilbourne Hole paragneisses analyzed by Padovani and Carter (1977a) (shaded field) and for two of the pelitic paragneisses discussed here. Two feldspar geothermometer of Stormer (1975) in conjunction with plagioclase-garnet-$Al_2O_3$-quartz applied as a geobarometer (Ghent, 1976) were used for consistency with Padovani and Carter (1977a). Also shown are geothermal gradients for: (1) RGR: the Rio Grande Rift (Decker and Smithson, 1975); (2) per: shield: stable continental crust (Blackwell, 1971); and (3) BR: the Basin and Range province (Decker and Smithson, 1975). Fields for vapor-present melting of muscovite pelite (dotted) and vapor-absent melting of muscovite pelite (horizontal ruling) are from Thompson and Tracy (1979). Stability fields for $Al_2SiO_5$ polymorphs are from Holdaway (1971). Finally, estimated closure temperatures for ~0.5 cm minerals (diagonal ruling) in thermally stable crust ($dT/dt=0$) over 1.6 billion years are shown for Rb-Sr systematics between two feldspars and for Sm-Nd systematics between feldspar and garnet. Left hand side of fields represents 10% time-integrated equilibration; right hand side represents 90% time-integrated equilibration. These were calculated from integration of the solution to Fick's second diffusion law for equilibration of spheres for zero surface concentration. Potassium feldspar and garnet are assumed to be rate-limiting phases and activation energies and pre-exponential factors for temperature dependence of diffusion coefficients taken from Misra and Venkatasubramanian (1977) and Harrison and Wood (1980) as summarized by Freer (1981). Diffusion rate used for garnet is average of pyrope and grossular data.
years. For Nd equilibration between garnet and the feldspars, the closure temperature is expected to be somewhat higher due to the generally more sluggish rate of Nd diffusion. Thus, if the crust has been relatively stable thermally, the scale of isotopic equilibrium in the lower crust may contain information about temperatures at the base of the crust.

Although many portions of the crust appear to have been relatively stable throughout much of their history, this is not the case everywhere, and particularly near continental margins. There, the crust is more readily assailable to reactivation during subsequent tectonic events, as tectonic provinces such as the Himalayas, the Alps, and the Great Basin of the western U.S demonstrate. Remobilization of the crust, as in instances such as these, may provide analogies for granulite occurrences where high grade metamorphism was significantly later than crust formation (e.g DePaolo et al., 1982; Jacobsen and Wasserburg, 1978; Montgomery and Hurley, 1978). The ensuing deformation may be laterally extensive, as numerical modelling by England and others (1985) quantifies: deformation at convergent and divergent margins may have aspect ratios in the neighborhood of 1:1. Areas undergoing compression or extension have higher geothermal gradients (e.g. as illustrated for extension in Figure 1-2) and therefore, temperatures in the lower crust affected by these events could conceivably exceed mineral closure to isotopic reequilibration on the time-scale of the event. In other words, because of relatively high ambient temperatures there, the base of the crust is nearer the thermal activation temperatures for mineral reequilibration during orogenesis.
As evident from Figure 1-1, the region in which Kilbourne Hole lies appears to have been near a Precambrian continental margin against which subsequent crustal amalgamation has occurred. Although crust formation in southern New Mexico was largely complete by ca. 1.6 Ga., this area was probably in the foreland of deformation during both Grenville- and Alleghenian-equivalent orogenies which occurred to the southeast (Garrison, 1981; Ross, 1979; Pindell and Dewey, 1982). As middle Proterozoic ages of the Central U.S. illustrate, the effect of emplacing younger age terranes is not always manifested by the obscuring of radiometric ages in adjacent upper crustal rocks.

Isotopic reequilibration in the lower crust would be greatly facilitated by the presence of water both as a medium of transport and by enhancement of ductile deformation and metamorphic recrystallization. Even where water is present only in hydrous minerals, isotopic reequilibration may be abbetted by the increased likelihood of partial melting during tectonothermal events. Although the lower crust is generally assumed to be anhydrous, quantification of this supposition rests largely on interpretation of geophysical data and is not currently definitive (see, for example, summaries by Kay and Kay, 1981; Smithson and Brown, 1977). Thus, the scale of isotopic equilibration in the lower crust may also reflect kinematic effects that are not strictly thermal.
GEOLOGIC CONTEXT

Kilbourne Hole maar lies near the southern terminus of the Rio Grande Rift (Chapin, 1979) where the rift merges with the Basin and Range Province near the international border between New Mexico and Mexico. Extensive geological and geophysical studies of the rift have shown it to be an area of high heat flow, recent volcanism, thinned crust and lithosphere, high seismicity, and active faulting (see, for example, Cordell, 1978; Riecker, 1979). In southern New Mexico, rift activity began at about 32 Ma (Chapin, 1979) and the maar itself erupted at about 0.125 Ma (Padovani, pers. comm. 1986).

The basement lithologies of southern New Mexico are comprised of Precambrian crystalline rocks and Paleozoic to Mesozoic sedimentary cover. Metamorphic and granitic rocks formed between 1.65-1.9 Ga and are themselves intruded by granitic rocks of predominantly 1.35-1.5 Ga age (Condie and Budding, 1979). The metamorphic rocks are principally of greenschist to amphibolite grade; granulites are unknown from either surface exposures or drill holes. Pennsylvanian strata, where present in southern New Mexico, are separated from older Paleozoic strata by an angular unconformity (Bachman, 1975). The extent of missing section diminishes southward such that the section may be largely continuous at Kilbourne Hole. Locally, the amount of Pennsylvanian subsidence may have been less than 500 feet (Plate 15, McKee et al., 1975) and total Paleozoic-Mesozoic sedimentary cover may be less than 4 km thick (Ramberg et al., 1978). Thus, to a first order, the crust has been stable with respect to uplift since formation.
SAMPLE DESCRIPTIONS

Only those garnet granulites containing sillimanite are reported. All are foliated, with planes of foliation being principally defined by garnet-rich layers (typically 3-5 mm across) alternating with wider, more felsic bands (variable dimensions up to 15 mm across), which sometimes contain macroscopically visible stringers of quartz and sillimanite (<3 mm across). Cross-folia compositional zonation from relatively garnet-rich to garnet-poor across the xenoliths is also evident. The dimensions of the xenoliths are shortest normal to the plane of foliation and range from 4 cm (sample 1975) to 6 cm (sample 79K6) to 11 cm (sample 1977).

The mineralogy of the Kilbourne Hole crustal xenoliths has been described by Padovani and Carter (1977a) who also present electron microprobe mineral analyses. The paragneisses described here belong to Group 2 garnet granulite classification of Padovani and Carter (1977a) and contain almandine garnet, sanidine with perthitic intergrowths, andesine, large, euhedral sillimanite, and quartz, with accessory rutile, apatite, and zircon. Other accessory minerals were not identified by Padovani and Carter (1977a) but may be present as discussed in Chapters 3 and 4. Caliche and minor host basalt veins are latter-day features. The garnets are rimmed with melts formed during adiabatic decompression (Padovani and Carter, 1977b). Mineral analyses for these and other xenoliths and their implications for geothermometry and geobarometry is in preparation (Padovani in prep., 1986). Pressure and temperature estimates for two of the xenoliths are shown in Figure 1-2 as well as the range reported for other crustal xenoliths from
Kilbourne Hole (Padovani and Carter, 1977a).

**ANALYTICAL SCHEME**

**Sample Preparation**

In view of the compositional heterogeneity within xenoliths, each xenolith was treated as a veritable outcrop. After first being cut transverse to foliation to create a working sample, the xenoliths were sawed parallel to the plane of foliation into 1-2 cm. Krogh-layers (Krogh and Davis, 1968; 1971). Layers were chosen to include paired garnet and felsic mineral bands. The resulting slabs were ground with corundum grit to remove saw marks, broken with hammer and chisel into gravel-sized pieces, and powdered in a tungsten-carbide shatterbox. Fragments containing veins of host basalt were discarded. In the case of sample 1977, the crushed layers were also leached in cold 0.1 N HCl in an ultrasonic bath for 10 minutes prior to powdering in order to dissolve caliche; several elements were analyzed in unleached aliquots for comparison (Table 1-1).

**Analytical Techniques**

Because of the coarse crystalline nature of these samples, larger than normal aliquots of sample powders were digested (typically 200 mg.) except in the case of the alkali and alkaline earths (50 mg.). Sample aliquots analyzed for Rb, Sr, K, Cs, and Ba concentrations by isotope dilution and Sr isotopes were digested in open beakers in an HF-HClO₄ mixture. Except as noted, sample aliquots analyzed for Pb isotopes and U, Th, and Pb concentrations and for Nd isotopes and Sm and Nd
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<th>Sr 87Rb/86Sr</th>
<th>87Sr/86Sr</th>
<th>147Sm/144Nd</th>
<th>143Nd/144Nd</th>
<th>Pb 238U/204Pb</th>
<th>235U/204Pb</th>
<th>232Th/204Pb</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
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<td>0.0903</td>
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**Notes:**

- a) 87Sr/86Sr corrected for fractionation using 86Sr/88Sr = 0.1194 and normalized to 0.7080 for DSA SrCO3. Analytical precision <0.005%. Rb/Sr reproducible to better than 1%.
- b) 143Nd/144Nd corrected for fractionation using 146Nd/144Nd = 0.7219 and normalized to 0.51264 for BCR-1. Analytical precision <0.004%. Sm/Nd ratios are reproducible to better than 1%.
- c) Pb isotopes normalized to NBS981. Errors assumed to be 0.05%/AMU; analytical precision <0.015%. U/Pb and Th/Pb ratios reproducible to better than 2%.
- E: Calculated from unweighted sum of the layers.
concentrations were digested with HF in hydrothermal bombs for at least 2.5 days at temperatures of 210°C, followed by dissolution in 6.2N HCl overnight in the bombs at 210°C. No recalcitrant minerals remained. Companion Nd and Pb isotopic analyses of open beaker digestions did not differ appreciably from those of bomb digestions, indicating that either refractory phases (rutile, zircon) were not a significant sink for these elements, were isotopically equilibrated, or were leached by the dissolution procedure. In all instances, spike solutions were added prior to dissolution. Preferential precipitation of spike isotopes into aluminosilicate fluorides produced during the digestion stage can be particularly severe for Th, but also for Nd and Sm (see also Sando and Gulen, submitted 1986) This problem was alleviated by subsequent and complete redissolution in 6.2N HCl.

Sr, Nd, and Pb isotope analyses and trace element isotope dilution analyses with the exception of U, Th, and Pb were performed using routine methods described in detail elsewhere (Hart and Brooks, 1977; Richard et al., 1976; Manhes et al., 1978; and summarized by Roden et al., 1984). U, Th and Pb concentrations were determined by spiking with 235U-, 230Th-, and 208Pb-enriched solutions which had been calibrated against standard solutions made from both metals and oxides. Separation of Pb followed routine anion exchange as for unspiked Pb (Manhes et al., 1978). The HBr effluent from the Pb columns was collected, converted to nitrates and U and Th were separated by anion exchange in 8N HNO3 on 2 cc DOWEX 1-X8 resin following conventional techniques. U and Th were collected together off the columns and purified by repeating this procedure. The purified Th and U were loaded together as phosphates on
the side filament of a double rhenium filament bead. Re emission from the center filament was usually held at approximately $1 \cdot 3 \times 10^{-13}$ amps. U emission precedes Th emission and ion beams of greater than $5 \times 10^{-13}$ amps and $2 \times 10^{-13}$ amps respectively were obtained. $\text{UO}_2^{2+}$ and $\text{ThO}_2^{2+}$ were typically measured and $^{232}\text{Th}^{16}_0$ corrected for $^{230}\text{Th}^{18}_0$.

Pb blanks were higher than normal, due to digestions in bombs with subsequent dissolution in copious HCl, and averaged 2 ng. Sample size was adjusted to keep the blank contribution less than 0.1% of total Pb. U and Th blanks for the same procedure were less than 25 pg. Most samples analyzed for Pb concentrations were slightly underspiked so that $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ could be duplicated in the spike runs. Reproducibility of these ratios between spiked and unspiked runs was generally better than reported fractionation errors, averaging 0.04% for both ratios.

RESULTS

Sr, Nd, and Pb isotopic data for three paragneiss xenoliths analyzed in detail are presented in Table 1-1 and Figures 1-3 to 1-7. Isochron ages are tabulated for all isotopic systems in Table 1-2. Individual isochron diagrams for the various isotopic systems except $^{235}\text{U}/^{204}\text{Pb}$-$^{207}\text{Pb}/^{204}\text{Pb}$ are shown for each of the three xenoliths (Figures 1-3 to 1-6). Where the data could plausibly be interpreted as an isochron, the age and errors implied by that isochron are given in the figure. For the others, an approximate apparent age is simply indicated. Also shown in these figures are summary diagrams comprised of summed whole rocks, individual layers, and, where possible,
<table>
<thead>
<tr>
<th></th>
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<th>79K6</th>
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<td>-1975</td>
<td>1.54 (0.19)</td>
<td>1.59 (0.86)</td>
<td>2.72 (0.44)</td>
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<td>1.58 (0.23)</td>
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<tr>
<td><strong>Sm-Nd (Ma)</strong></td>
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<tr>
<td></td>
<td>281 (129)</td>
<td>-142 (209)</td>
<td>846 (565)</td>
<td>271 (54)</td>
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<tr>
<td><strong>238U-206Pb (Ma)</strong></td>
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<td>-30 (508)</td>
<td>1357 (86)</td>
<td>130 (5)</td>
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<td><strong>235U-207Pb (Ma)</strong></td>
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<td>1883 (720)</td>
<td>315 (6)</td>
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<td><strong>232Th-208Pb (Ma)</strong></td>
<td>589 (154)</td>
<td>28 (708)</td>
<td>339 (142)</td>
<td>67 (15)</td>
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<td><strong>207Pb-206Pb (Ga)</strong></td>
<td>2.75 (± 0.68)</td>
<td>---</td>
<td>2.03 (± 1.4)</td>
<td>2.04 (± 0.67)</td>
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\*Numbers in parentheses are 2σ errors on isochron ages.*
additional paragneissic xenoliths (data to be presented elsewhere) and a similarly composed summary alpha-beta isochron diagram in Figure 1-7. Summed whole rocks were obtained from summation of the compositions of individual layers after accounting for volumetric contribution. Isochrons were calculated using a York regression (York, 1969). All isochron ages and their errors for the isotopic systems are summarized in Table 1-2; the better constrained isochron ages are shown in Figure 1-8.

Sr isochrons

Considering first the individual Rb-Sr isochrons (Figure 1-3), samples 1977 and 79K6 show large ranges in $^{87}\text{Rb}/^{86}\text{Sr}$ and rather well-defined isochrons. The best constrained isochron is from sample 1977 (Figure 1-3a) which gives an age of 1.59 (±0.09) Ga and a reasonable initial ratio of 0.7109(±8). In addition to layer 4 from the working sample, two portions of that layer from a different piece of the xenolith were also analyzed. Although the $^{87}\text{Sr}/^{86}\text{Sr}$ signatures are similar, some scatter about the $^{87}\text{Rb}/^{86}\text{Sr}$ axis is evident. In addition, all of the layers of sample 1977 were leached in dilute HCl to eliminate caliche (discussed above). The Sr content of caliche is appreciably higher than those of the layers, while its $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are lower (Table 1-1 and Figure 1-3a). Unleached aliquots of two layers (4 and 5) fall on the isochron but have somewhat lower $^{87}\text{Sr}/^{86}\text{Sr}$ than their leached equivalents. To a first approximation, the principal effect of caliche contamination on unleached samples is to shift the data points down the isochron.
Figure 1-3

$^{87}\text{Sr}/^{86}\text{Sr}$ - $^{87}\text{Rb}/^{86}\text{Sr}$ isochron diagrams for Kilbourne Hole pelitic paragneisses as labelled. Error bars shown where errors exceed the size of the symbol. Reference isochrons in figures b and c are from sample 1977 and in figure d is best fit to whole rocks. a-c: Layers from individual xenoliths as denoted. In (a), open circles are layers leached in weak HCl as described in text; half-shaded circles are unleached layers numbered in parentheses; circled +'s for mineral concentrates. Also shown is an analysis of caliche. In (b) and (c), symbols are unleached layers only. d: Whole rocks (closed symbols) and layers (open symbols); symbols as in a-c with additional whole rocks shown as diamonds. Also shown in this figure is field of orthogneisses (cf Chapter 3).
The layers of 79K6 (Figure 1-3b) show somewhat larger deviations from a true isochron, yielding an age of 1.71 (±0.18) Ga, relatively similar to that of sample 1977, but an almost certainly unreasonable initial ratio of 0.7017 (±24). Sample 1975 (Figure 1-3c) gives both a fictitious isochron age (2.7 Ga) and initial ratio (0.64) and appears to have undergone an recent episode of Rb enrichment. Deviations in these isochrons from that of sample 1977 cannot be explained by the effect of caliche contamination. Taking summed whole rocks together with whole xenoliths (Figure 1-3d) yields an isochron age of 1.54 (±0.19) Ga and an initial ratio of 0.7092 (±6). If we accept that sample 1975 has undergone recent Rb enrichment and omit it from the calculation, the resulting age is 1.58 (±0.23) Ga and the initial ratio is identical (0.7092 ±6).

In contrast to the Precambrian ages retained by the layer-layer and whole rock isochrons, most Rb-Sr mineral isochrons for the KH xenoliths are indistinguishable from equilibrium (Chapter 3). The only exception to this is a plagioclase-sanidine isochron from layer 2 of sample 1977 (Figure 1-3a) which yields an age of 34.1 ±17.8 Ma. This age probably represents incomplete attainment of equilibrium rather than a discrete thermal event as discussed later. Much of the scatter in the Rb-Sr layer-layer isochron of sample 1977 may be the result of sampling bias between more plagioclase-rich or more sanidine-rich portions of the layers. Thus, within individual layers, the feldspars are in or very nearly in equilibrium. As the major residence site for Sr in the rocks, on a xenolith scale, the feldspars cannot be in equilibrium.
Nd isochrons

In contrast to the Sr isochrons, layer-layer Nd isochrons are discordant between xenoliths and yield apparent ages from 0 to 0.8 Ga. The only apparent isochron which could be considered statistically significant is that of sample 79K6 (Figure 1-4b) which yields an age of 271 (±54 Ma). Most notably, with the exception of layer 1, the layers from sample 1977 are virtually in equilibrium (Figure 1-4a) in spite of the fact that this sample gave the tightest Sr isochron. Finally, three layers of 1975 (2-4) are in equilibrium such that the resultant errorchron is only a two-point one.

Summed whole rocks, together with an additional whole rock, yield an age of 281 (±129 Ma). In contrast to the whole rocks, virtual isotopic equilibria exists between the layers of both sample 1977 and sample 1975 indicating that the minerals must also be in equilibrium. Intralayer mineral isochrons of zero age (plagioclase-garnet and plagioclase-clinopyroxene) have been determined in other KH xenoliths (Chapter 3). Thus, both Sr and Nd isotopic equilibrium between the minerals sanidine, plagioclase and garnet exists on an intralayer scale but significant discordancy exists between these two isotopic systems on a xenolith scale.

Pb isochrons

Like Nd, the Pb isochrons exhibit a high degree of discordancy, both between isotopic systems as well as between samples. Radiometric ages determined from U-Pb and Th-Pb isochrons decrease in the order:
Figure 1-4

$^{143}\text{Nd}/^{144}\text{Nd}$-$^{147}\text{Sm}/^{144}\text{Nd}$ isochron diagrams for Kilbourne Hole pelitic paragneisses. Reference isochron drawn through bulk earth using parameters of Jacobsen and Wasserburg (1984). Topology and symbols analogous to Figure 1-3.
$^{207}\text{Pb}/^{204}\text{Pb} > ^{206}\text{Pb}/^{204}\text{Pb} > ^{208}\text{Pb}$, a sequence typical of many sets of discordant Pb isochrons (Stieff and Stern, 1961). Davis and Grew (1978) also obtained a similar pattern of Pb isochron age discordancy on a zircon concentrate from a Kilbourne Hole paragneiss. $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{208}\text{Pb}$ isochron diagrams are shown in Figures 1-5 and 1-6. Between samples, relative isochron ages decrease in the order: sample 1975 > 1976 > 1977 (cf. Figure 1-8) and yield a maximum age of 1.9 (± 0.7) Ga ($^{235}\text{U}/^{207}\text{Pb}$, sample 1975). Layers from sample 1977 form a virtual cloud on all of the Pb isochron diagrams. The degree of discordancy between samples for Pb isochrons is similar to that for Nd isochrons suggesting that the effective rate of Nd and Pb equilibration may be rather similar.

$^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$ layer-layer isochrons are approximately concordant between samples; all layers taken together yield an age of 2.1 Ga (+0.7/-0.9) (Figure 1-7). Although high, this age is easily within error of the Rb-Sr age determined for sample 1977 and the whole rock ages. In addition, although the error on the Pb-Pb isochron is also high, the fact that a Precambrian age is preserved suggests that the samples cannot have undergone extensive Pb isotopic reequilibration until recently, and particularly not during the Precambrian. A 1.6 Ga Pb-Pb isochron which contains 1.6 Ga initial Pb isotope characteristics as defined by the terrestrial lead curve of Stacey and Kramers (1975) can be fit to the data. This suggests that the paragneisses cannot have had a significant prehistory in a upper crustal reservoir with high $\mu$. This aspect is discussed further elsewhere (Chapter 3).
Figure 1-5

$^{206}\text{Pb}/^{204}\text{Pb}-^{238}\text{U}/^{204}\text{Pb}$ isochron diagrams for Kilbourne Hole pelitic paragneisses. Reference isochron through initial ratios of 1.6 Ga conformable lead array given by Stacey and Kramers (1975). Topology and symbols analogous to Figure 1-3. Also shown in figures b and c are isotopic compositions and estimated $^{238}\text{U}/^{204}\text{Pb}$ for layers not analyzed for the latter but used in calculating whole rock characteristics shown in figure d. U and Pb concentrations estimated from correlations to trend in other trace element variations (see also Chapter 4).
Figure 1-6

$^{208}\text{Pb} / ^{204}\text{Pb} - ^{232}\text{Th} / ^{204}\text{Pb}$ isochron diagrams for Kilbourne Hole pelitic paragneisses. Topology and symbols analogous to Figure 1-3.
Figure 1-7

$^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$. Symbols as in summary diagram of Figure 1-3. Reference isochron is best fit to the data. Inset shows field of paragneisses relative to terrestrial Pb isotopic growth curve of Stacey and Kramers (1975). Whole rocks and a layer from an additional paragneiss (diamond) are also shown.
DISCUSSION

Nd equilibrium - Sr disequilibrium: isotopic response to reequilibration

Conventional wisdom holds that Nd isotopes are the most robust of the isotopic systems discussed in this paper, due largely to the more sluggish diffusion rate of Nd, which has a higher charge to radius ratio than Sr or Pb, and to the selective responsiveness of its parent-daughter ratio to only magmatic processes. In addition, in this study Nd would be expected to diffuse slowly because, unlike Sr or Pb, it is should be concentrated in garnet for which diffusion coefficients are extremely low. Figure 1-2 illustrates the likelihood that closure temperatures for Nd equilibration are higher than for Sr equilibration. The temperature dependence of Nd diffusion in garnet and Sr diffusion in the feldspars is also such that the diffusion rates of the two species apparently do not cross over at higher temperatures. Consequently, the results for the Kilbourne Hole xenoliths may at first seem surprising.

The principal factors underlying the rate of isotopic equilibration are the effective diffusion rate integrated over the thermal history of the rocks and the physical scale at which isotopic heterogeneity occurs: that is, the characteristic diffusion distance. Potentially the most significant effect here is the absolute scale of isotopic heterogeneity, a factor which is difficult to adequately constrain in the case of xenoliths. As can be discerned from Figure 1-3, $^{87}\text{Sr}/^{86}\text{Sr}$ varies monotonically across the xenoliths. While this is also generally true of Nd (Figure 1-4), much less compositional variation is observed between most of the layers of samples 1977 and
1975, the two which appear to be equilibrated the most. Thus, the appropriate characteristic diffusion distance of Nd isotopic equilibration may only be that from, for example, layers 1977A4 to 1977A7, or less than 6 cm. In contrast, the appropriate characteristic diffusion distance for Sr equilibration may be much larger than that exhibited by the xenoliths. The absence of apparent "edge effects" (preferential partial equilibration due to proximity to the end of a Rb/Sr gradient) is consistent with this suggestion.

There is an additional consideration which may have profoundly affected the relative rates of Sr and Nd equilibration. In a strictly phenomenological sense, it is reasonable to assume that volume diffusion may exceed grain boundary diffusion for those minerals into which an element partitions in significant amounts, while grain boundary diffusion may be more significant for those minerals in which an element is largely absent. Thus, we would assume that most of the Nd resides in garnet and therefore, that the diffusion of Nd is rate-limited by garnet locally, but by grain boundary diffusion everywhere else. Since Nd diffusion along grain boundaries is presumably slower than Sr because the former has a higher charge to radius ratio, we would expect Sr to equilibrate faster than Nd. However, our mineral analyses indicate that the lion's share of the Nd does not reside in the garnet, but rather in plagioclase where it coexists with garnet (Chapter 2). Nd also occurs in sanidine in amounts subequal to that of garnet. The diffusion rates of cations in the feldspars plagioclase and sanidine typically exceed those of garnet by at least an order of magnitude at temperatures of 600-1000°C (see, for example, the diffusion data compilation of Freer,
The principal layering in the xenoliths is garnet-rich bands adjacent to garnet-poor, felsic bands. Thus, one interpretation of our results is that the feldspars are providing relatively fast, interconnected diffusion paths for Nd through the felsic layers while the garnet-rich layers are inhibiting Sr diffusion. The analyzed layers (comprised of paired garnet-rich and garnet-poor bands) everywhere contain >40% garnet and feldspars combined while many layers are comprised of <25% feldspars. Possibly a critical change from dominantly volume diffusion to dominantly grain boundary diffusion occurs between these two modal abundance levels. In light of this, the fact that 79K6 appears to retain a Paleozoic age Sm-Nd isochron may reflect the relatively low abundance of the feldspars in this sample (particularly layers 1 and 2) and consequently, the lack of fast diffusion paths for Nd.

Quantifying this scenario is hampered by a paucity of appropriate diffusion coefficients for grain boundary diffusion and for volume diffusion at the appropriate temperatures and compositions. The success of such a model is critically dependent on barrier phases acting as sufficiently slow diffusion paths for Sr such that they retard Sr equilibration dramatically with respect to Nd. A detailed analysis of phase distributions and the relative extent of grain boundary/volume diffusion paths could potentially illuminate this proposition. Nevertheless, applying reported diffusion data for Sm in grossularite and pyrope (Harrison and Wood, 1980 as reported by Freer, 1981), Nd isotopes in the 2 mm garnets will effectively exchange with their surroundings in 0.02 - 0.04 million years at temperatures of 900°C.
(approximately the temperature of sample 1977). A 10 cm xenolith composed entirely of garnet requires 32-62 Ma to equilibrate by volume diffusion. However, if the feldspars act as an interconnected diffusion path between garnets and have a diffusion rate for Nd two orders of magnitude larger than garnet, that xenolith will equilibrate in about 5 million years. Thus, a thermal pulse of relatively short duration (even compared to the ~30 Ma life span of the rift) may be sufficient to equilibrate Nd isotopes.

Pb is concentrated in the feldspars and zircon which are localized in occurrence. Thus, the kinematics of Pb isotopic equilibration would be expected to be like that of Sr. In fact, the results for Pb are much more like those for Nd. In part, this may reflect a shorter characteristic diffusion distance for Pb; in part, the effective diffusion rate of Pb must be somewhat higher. Reported diffusion coefficients for Pb in potassium feldspar are $10^{-10^3}$ higher than Sr (Rosenqvist, 1949). If this disparity in diffusion rates is also true of grain boundary diffusion, the disparity in extent of equilibration may be understood.

Given our present understanding of the xenoliths, we discount the following factors in explaining the disparity in scales of Nd and Sr isotopic equilibria:

1) Equilibration in presence of fluid phase. While the presence of CO$_2$, H$_2$O, or other fluids might facilitate equilibration, it is difficult to reconcile with the lack of Sr equilibration under such conditions. That is, we can discount it unless fluid flow was strictly layer parallel or unless the solubility of Sr relative to Nd in that
fluid was negligible. However, in the absence of geologic observations indicating the likelihood of such conditions, we discount the role of fluids.

2) Nd isotopic equilibration during mineral reactions. If reheating of the lower crust resulted in changes in mineralogy, these reactions may facilitate isotopic equilibration, at least on an intralayer scale. However, as discussed below, we do not believe such mineral changes occurred. Moreover, many mineral reactions involving garnet involve the feldspars as well and therefore, it is not apparent how this could explain the discrepancy in scales of equilibria between the two isotopic systems.

3) That the Sr isochrons are simply diffusion gradients between larger isotopic reservoirs. Accordingly, this would require a fortuitous correlation in the behavior of Sr and Rb such that isochronous relationships are maintained. Even if this were possible, edge-effects (defined above) might be expected, particularly at the low Rb/Sr ends of the isochrons which have to be near the end of the gradient.

Summary of the geochronology

Ages retained by the various isochrons are summarized in Figure 1-8 where they are organized according to the physical scale integrated by the data. The oldest plausible isochron for the Kilbourne Hole paragneisses is that obtained from Rb-Sr in sample 1977 and yields an age of approximately 1.6 Ga. This age is consistent with a Sr isochron for the whole rock data and, at least to a first order, with a
Figure 1-8

Summary diagram showing spectra in isochron ages versus scale of analysis. Generalized on the right-hand side are ages of significant tectonothermal events in the region of Kilbourne Hole. Numbers on layer isochron ages refer to samples: 7=1977; 5=1975; 6=79K6.
Explanation

- Rb-Sr
- Sm-Nd
- $^{235}\text{U-Pb}$
- $^{238}\text{U-Pb}$
- Th-Pb

South New Mexico/W. Texas Chronology

- Orogeny
- Anorogenic Magmatism
- Llano Terrane (Grenville)
- Ancestral Rocky Mtns. (Alleghanian)
- Laramide/R.G. Rifting

Age (Ga) ± 6

Whole Rocks  Layers  Minerals

Decreasing Scale →
$^{207}\text{Pb}/^{204}\text{Pb}-^{206}\text{Pb}/^{204}\text{Pb}$ isochron through the paired ratios of all of the data for the layers; it probably records the last pervasive episode of metamorphism in the lower crust beneath Kilbourne Hole. A similar age has been obtained for basement rocks in this area, as discussed below. Our success at obtaining these isochrons derives from the large physical scale of Rb-Sr heterogeneity which prohibited significant equilibration and from the large spread in measured Sr isotope ratios which swamp out small-scale sampling or equilibration effects on Rb/Sr or $^{87}\text{Sr}/^{86}\text{Sr}$, as well as small differences in initial ratios.

Apparent isochrons from the other isotopic systems yield ages mostly $\leq 1.6$ Ga (Table 1-2; Figure 1-8). Between the different isotopic systems, the relative degree of divergence from this age is generally coherent, suggesting that the results are largely artifacts of the effective scale of isotopic heterogeneity and/or rate of diffusion. Possible exceptions to this are the Sm-Nd isochrons for the whole rocks and for the layers of sample 79K6, which yield roughly concordant ages of approximately 270 Ma. Although the slope of the whole rock isochron is largely determined by the summed whole rock of 79K6, the other whole rocks fall on or near the intralayer isochron of sample 79K6. Therefore, it is also possible that the similarity between the isochron of 79K6 and the whole rocks is not entirely the result of recent partial equilibration but rather, may reflect a Paleozoic thermal event. The fact that 79K6 retains a Paleozoic isochron may result from its general lack of fast Nd diffusion paths (i.e. plagioclase and sanidine), and its more strongly pronounced garnet-feldspar banding than the other samples, which together may retard Nd diffusion.
Possible evidence for lack of xenolith-scale equilibration from the Precambrian to the Tertiary

Recognition of a discrete phase of isotopic equilibration intermediate in age to crustal stabilization and recent isotopic equilibration in the Kilbourne Hole xenoliths is clouded by the effects of the latter. The U-Th-Pb isochrons clearly show substantial reequilibration of the Pb isotopes, presumably recently, which indicates their mobility during thermal activation of the lower crust. Extensive equilibration since ~1 Ga is not permitted by error limits on the Pb-Pb isochrons (Figure 1-7; Table 1-2). Partial reequilibration of the Pb isotopic systematics other than fairly recently, would have resulted in some shallowing of the α-β array (Figure 1-7) and a younging of the apparent age. Relatively recent thermal disruptions cannot be constrained by the data due to the large error in $^{207}\text{Pb}/^{204}\text{Pb}$ with respect to the spread in $^{206}\text{Pb}/^{204}\text{Pb}$.

Another way to consider the U-Pb systematics is on a modified concordia diagram wherein the slopes of the U-Pb isochrons in each of the xenoliths are plotted (Figure 1-9). The age significance of these slopes can be derived from their equivalence to $(e^{\lambda t} - 1)$ and those ages are illustrated on the concordia array. The denominators on both axes are the range in appropriate parent-daughter U-Pb ratios on the isochron diagrams and differ by a constant equal to the difference in U isotopic abundance ($^{238}\text{U}/^{235}\text{U} = 137.88$). Thus, the diagram is effectively a mixing diagram and changes in U/Pb ratios will produce a linear array which, for recent changes in $\mu$, passes through the origin. By analogy
Figure 1-9

Modified concordia diagram showing slopes of $^{238}\text{U}/^{204}\text{Pb}$-$^{206}\text{Pb}/^{204}\text{Pb}$ isochrons (equivalent to $e^{\lambda^{238}t} - 1$) versus $^{235}\text{U}/^{204}\text{Pb}$-$^{207}\text{Pb}/^{204}\text{Pb}$ isochrons (equivalent to $e^{\lambda^{235}t} - 1$) defined by layers within individual samples. Age significance indicated on concordia. Errors on sample 1977 are extremely large but enclose the origin. See text for further discussion.
to an $\alpha$-$\beta$ isochron diagram, partial equilibration in $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ will retain the isochron slope, so long as equilibration is effectively mixing within a closed system. Similarly, in Figure 1-9, samples which have undergone partial equilibration must also plot along a line whose slope is equivalent to that of the $\alpha$-$\beta$ isochron. For recent isotopic equilibration, this line passes through the origin. Consequently, interpretation of this diagram is identical to that for discordant zircons and the approach bears many similarities to that for three or more zircons described by Stieff and coauthors (1961; 1963).

As evident from Figure 1-9, the paired slopes of the U-Pb isochrons fall on a chord from the origin through concordia at 1.6 Ga. Thus, the apparent U-Pb ages for the xenoliths are consistent as discordant ages produced by a two-stage (middle Proterozoic and recent) thermal history. Like zircons, limited, continuous diffusion occurring to variable degrees between xenoliths will result in curved arrays which may be difficult to distinguish from episodic diffusion. However, to the extent that this treatment adequately represents the response of U-Pb isochrons to equilibration, partial equilibration at a xenolith scale since 1.6 Ga ago, other than recently, is prohibited. The slopes of U-Pb isochrons for sample 79K6 fall to the right hand side of but within error of a chord through concordia at 1.6 Ga. An intermediate phase of equilibration of sufficient intensity to shallow the slopes of these isochrons would have displaced them to the left of this chord. Thus, thermal activation of the lower crust during the Paleozoic as well as during the late Proterozoic may be ruled out by these considerations. Partial equilibration in the last ~50 Ma is difficult to rule out but is
not required by the data. Also included in Figure 1-9 are the ages reported by Davis and Grew (1978) for a zircon concentrate from a Kilbourne Hole paragneiss. While also generally consistent with a two-stage thermal history, the coordinates of this point and their errors depend on the common Pb correction used by Davis and Grew and cannot be assessed from their paper. If the plotted location is approximately correct, the fact that it lies somewhat to the left of the 0-1.6 Ga equilibration chord may indicate failure of zircon to close completely or a previous phase of partial equilibration of insufficient intensity to be evident at a xenolith scale. From the existing data, the minimum age for such an event is not appreciably different from zero but further zircon studies could elaborate on this possibility.

IMPLICATIONS FOR THERMAL STATE AND EVOLUTION OF THE LOWER CRUST

State of the lower crust: intensive properties ($P$, $T$, $pH_2O$)

Padovani and Carter (1977a) obtained pressure and temperature estimates for the lower crust from phase equilibria in the Kilbourne Hole paragneisses. These estimates are consistent with geothermal gradients based on observed heat flow in the southern Rio Grande Rift (Figure 1-2). Their results are based on the temperature and pressure dependence of Ca exchange equilibria between garnet and plagioclase (Ghent, 1976) and of K, Na and Ca between potassium feldspar and plagioclase (Stormer, 1975). Implicit in the application of these geothermometers and geobarometers is the assumption that equilibrium obtains on a mineral-mineral scale. Our isotopic results support the
validity of this assumption and show that equilibration at these pressure and temperature conditions was attained recently and not in the Precambrian. Virtual isotopic equilibrium of Sr between plagioclase and sanidine and of Nd between plagioclase and garnet is observed on a mineral scale. Moreover, as our discussion above indicates, Nd equilibration times are probably on the order of tens of millions of years, too long to be satisfied only by magmatic effects related to production of the maar. Therefore, relatively high temperatures (700-1000°C) in the lower crust of the Rio Grande Rift are confirmed, at least to the extent that the temperature and pressure dependence of the exchange coefficients are known.

Together, the apparent high temperatures in the lower crust and the preservation of ~1.6 Ga age layer-layer Sr isochrons imply that the paragneisses have probably been relatively anhydrous since the Precambrian. Had water or hydrous minerals been present during recent reheating, they would be expected to facilitate reequilibration and possibly to induce partial melting. Liquidus temperatures for vapor-absent muscovite granite range from about 725°C at 7.5 kb to 750°C at 10 kb, even in the presence of a significant CO₂ partial pressure (Huang and Wyllie, 1981). For hydrous granite, melting temperatures are even lower. Only the unlikely occurrence of melting in extremely localized pockets with no magma migration could preserve the observed isochronous relationships. Further, the lack of melting is supported by consideration of the geochemistry and petrology of the pelitic paragneisses (Chapters 2 and 4). Thus, the absence of water in the lower crust since the Precambrian means that retrograde mineral
reactions, save sillimanite to kyanite, probably could not occur.

Tectonothermal evolution of the lower crust since the Precambrian

Tectonic events are also thermal events in so far as compression and extension may be accompanied by higher than normal geothermal gradients. As previously discussed, the lower crust is closer to the activation temperature for isotopic reequilibration and for ductile deformation than is the upper crust and therefore, may be more readily affected by penetrative tectonism. Figure 1-8 summarizes tectonothermal events which have occurred in the proximity of Kilbourne Hole since 1.6 b.y. ago. In the following section, we speculate on the thermal responsiveness of the lower crust of southern New Mexico to these events in light of the geochronologic data. Since the effects of later events may compound the record of earlier ones, we consider them individually in order of their increasing age.

1) Rio Grande Rifting: On an intralayer scale, most minerals analyzed are approximately in isotopic equilibrium. As discussed in the introduction, it is unlikely that this is the result of heating during transport since equilibration times on the order of years to millions of years are required. Instead, high heat flow in the Rio Grande Rift may be interpreted as having enhanced temperatures in the lower crust by a factor of ~2 (Figure 1-2; Cook et al., 1978; Decker and Smithson, 1975) as confirmed by mineralogically determined temperatures. As a result, equilibration times on a layer scale (<1.5 cm) have been reduced to less than 3 million years, a fraction of the duration of Rio Grande Rifting (Chapin, 1979). Thus it is not surprising that on a mineralogical
scale, many of the isotopic characteristics of the Kilbourne Hole xenoliths have been equilibrated.

2) Ancestral Rocky Mountains (Ouachita-Marathon orogeny; ~Alleghenian equivalent): When considered together, Sm-Nd isochrons for whole rocks and for the layers of sample 79K6 suggest an ~270 Ma age, broadly contemporaneous with Pennsylvanian to early Permian age amagmatic intracratonic uplifts, loosely referred to as the Ancestral Rocky Mountains. Tectonic activity was focused in Colorado and immediately adjacent regions but extended into southern New Mexico by late in the Middle Pennsylvanian (Pray, 1961; Bachman, 1975). Treating this apparent isochron as a true isochron is questionable in view of the pervasiveness of recent Nd isotopic reequilibration; rather, it may indicate incomplete attainment of isotopic equilibration during recent reheating. This interpretation is consistent with inferences based on the U-Pb isochrons (next section). On the other hand, it is noteworthy that Rb-Sr scatterchrons for whole rocks and layers from middle crustal xenoliths from Portrillo Maar, just south of Kilbourne Hole, yield ages of 359 ±146 Ma (Chapter 3). Moreover, pyroxenes separated from mantle xenoliths erupted at Kilbourne Hole suggest possible Nd isotopic equilibration at ~400 Ma but are permissive of a younger age of equilibration (Roden, in prep. 1986). It seems reasonable to assume that thermal activation in the mantle would be linked to that of the lower (and middle?) crust and therefore, that the Pennsylvanian age derived from the Kilbourne Hole xenoliths may indicate a Paleozoic event which was deeply rooted, at least thermally.

In a synthesis of Pennsylvanian-Permian tectonics of the central
U.S., Kluth and Coney (1981) extended on the work of previous authors in linking the Ancestral Rocky Mountain uplifts to the Ouachita-Marathon orogenic belt and, on a larger scale, to closure of the proto-Atlantic ocean. The Marathon orogen occurs ~400 km to the southeast of Kilbourne Hole (Figure 1-1) and has been linked to deformation in southern New Mexico (Ross, 1979). Deformation was characterized by large-scale fault-bounded uplifts of large structural, and possible topographic relief (Kluth and Coney, 1981 and references therein). We know of no topographic expression of such deformation in the immediate vicinity of Kilbourne Hole but note that Kilbourne Hole lies along strike of the axis of the Florida Island (aka Burro Mountain) Uplift, which may extend for 200 km and was strongly active in the late Pennsylvanian (Bachman, 1975). The Florida Mountains are ~60 km to the northwest (Figure 1-1).

3) **Llano Orogeny** (~Grenville equivalent): Igneous and metamorphic rocks of approximately 1 Ga age (Wasserburg et al., 1962; Muehlberger et al., 1966) occur in the Franklin Mountains of west Texas, 45 km. to the east of Kilbourne Hole. They are considered part of the Llano terrane of central Texas (Muehlberger et al., 1966) which may represent accretion of juvenile crust (Condie, 1982; Nelson and DePaolo, 1985; Garrison, 1981) and which may extend considerably farther north along the New Mexico-Texas border than illustrated in Figure 1-1 (Muehlberger et al., 1966). The proximity of Kilbourne Hole to orogenic activity of the Llano Terrane suggests its nearness to the leading edge of a continental margin during the middle-late Proterozoic.

We invoke no specific mechanism for emplacement of the Llano terrane but simply note here the absence of any isotopic evidence
suggestive of a tectonic event involving crustal thickening in southern
New Mexico during the Llano orogeny. This result was anticipated by the
lack of geologic evidence for significant uplift in this area since
crust formation. In a modern analogy, deformation is also notably
lacking in the Indian plate in spite of the Asia-Indian continental
collision. Our results may indicate analogous crustal rigidity in
southern New Mexico during Grenville time due to thermal stabilization
of the crust (Molnar and Tapponnier, 1981). This is altogether
consistent with previously suggested time constants of 200-300 Ma for
thermal relaxation of continental crust based on isotopic and heat flow
considerations (Sclater et al., 1980; Hamilton et al., 1979).

4) Anorogenic magmatism: Rather extensive middle to upper
Proterozoic anorogenic granitic rocks and anorthosites were emplaced in
a broad band from the southwestern U.S. across the central U.S. to
Labrador and beyond. In New Mexico, intrusive ages for these granites
range from 1.38 to 1.44 Ga (Condie and Budding, 1979). Relatively
unradiogenic Nd initial ratios (Nelson and DePaolo, 1985) and
unradiogenic to radiogenic Sr initial ratios (summarized by Anderson,
1983 and Condie and Budding, 1979) may indicate an origin which was
predominantly intracrustal including the lower crust. The nearest
occurrences of anorogenic granites are plutons of the Florida Mountains
(Figure 1-1) and plutons of the Organ Mountains, 60 km to the northeast
of Kilbourne Hole. The lower crust beneath Kilbourne Hole, at least as
represented by the paragneisses, was not affected by crustal melting
during this event (as stabilization of compositional heterogeneities by
1.6 Ga indicates) nor does it appear to have been thermally affected by
it to any detectable extent.

5) **1.6-1.9 crust-forming event:** Our best estimate for the metamorphic age of the lower crust beneath Kilbourne Hole is 1.6 Ga based on the concurrence of the "whole-rock" Sr isochron and the layer-layer Sr isochron of sample 1977. This age is younger than the oldest ages for the southwestern U.S. (1.82 Ga, see Condie and Budding, 1979, for a compilation of radiometric ages) but only somewhat younger than a maximum in plutonic activity at about 1.67 Ga. Initial ratios so constrained \( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} = 0.7080-0.7110 \) are higher than those of associated basalts (0.7033-0.7040; Chapter 3) and are consistent with some period of crustal residence prior to metamorphism as expected from their sedimentary heritage \( \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \) greater than 2). We address the significance of their crustal residence history in Chapter 3.

The Rb-Sr systematics of the xenoliths are dominated by the feldspars. While it is tempting to assume that Proterozoic ages recorded by two of the samples represent the time at which the lower crust previously cooled through the feldspar closure temperature (400-600°C; Hart, 1981), the negligible effect of recent 750-950°C temperatures on these isochrons cautions against such a conclusion. It is clear that the robustness of Sr isochrons at these high temperatures means that the Precambrian closure temperatures were significantly above that considered typical of the feldspars. Moreover, in the absence of a comprehensive analysis of the effective rate of Sr diffusion, using the scale of Sr isotopic heterogeneity to constrain temperatures at the base of the crust is also precluded. On the other hand, because Pb isotopic equilibration reflects zircon-feldspar equilibration, the lack of
complete Pb isotopic equilibration in zircon (Davis and Grew, 1978) and the apparent two-stage U-Pb evolution of the xenoliths indicate that pre-rifting temperatures there were at least below the closure temperature of zircon. Unfortunately, as Mattinson (1985) summarizes, the closure temperature of zircon is not easily constrained due to a plethora of factors which affect its ability to retain Pb.

CONCLUSIONS

The extraction of xenoliths from the lower crust beneath Kilbourne Hole has provided an opportunity to test the response of Sr, Nd, and Pb isotopes to reequilibration during a fairly well-constrained metamorphic history. As the results of this study show, Rb-Sr isotopic heterogeneities at the decimeter scale can withstand temperatures of \(-900^\circ\text{C}\) for \(\leq 30\) Ma. Thus, layer-layer Sr isochrons may be very useful for "seeing through" regional metamorphism. The robustness of these isochrons indicates that the effective closure temperature for this system is very high; hence layer-layer Sr isochrons may be useful for constraining the early cooling history of metamorphic rocks. Layer-layer Sr isochrons of \(-1.6\) Ga in the Kilbourne Hole paragneisses are consistent with metamorphic ages of basement rocks exposed in this region as indicated in Figure 1-1. Because the lower crust is largely anhydrous in this area, a critical factor which remains to be tested is the effect of metamorphic fluids on these isochrons.

In marked contrast to the Rb-Sr results, Sm-Nd isochrons are largely equilibrated both at the centimeter and decimeter scales. The most dramatic example is sample 1977 which retains the best layer-layer
Rb-Sr isochron but which has layers in virtual isotopic equilibrium with respect to Nd. This result contravenes conventional wisdom that considers Nd isochrons to be unresponsive to metamorphism. As for the other isotope systems, it is important to the interpretation of Nd isotope data to sample the range in parent-daughter ratios of highly heterogeneous materials which may have been metamorphosed.

U-Pb and Th-Pb isochrons are partially equilibrated; for each xenolith, the extent of U-Pb equilibration is comparable to that of Sm-Nd. The relative discordancy of layer-layer $^{238}\text{U}-^{206}\text{Pb}$ and $^{235}\text{U}-^{207}\text{Pb}$ isochrons are consistent with a two-stage thermal history, initial metamorphism and recent reheating, and with equilibration in a closed system.

Based on our isotopic studies of the Kilbourne Hole xenoliths we envision the following tectonothermal evolution for the lower crust in southern New Mexico:

1) Crust formation at a convergent margin and cessation of orogenesis at least by 1.6 Ga.

2) Thermal decay and tectonothermal stability of the crust through the remainder of the Precambrian and much of the Phanerozoic, in spite of relative proximity to a convergent margin during the late Precambrian (~Grenville time). Although Nd isochrons defined by whole rocks and by an internal isochron for sample 79K6 are contemporaneous with Pennsylvanian-aged orogeny to the southeast of Kilbourne Hole and foreland deformation in southern New Mexico, this result is not corroborated by considerations based on discordant U-Pb isochrons. Thus, the lower crust may have been thermally stable from 1.6 Ga until
the inception of Rio Grande rifting, a result which seems remarkable in view of regional tectonic considerations but wholly unremarkable in view of the lack of surface expression of local tectonic activity.

3) Recent reheating of the lower crust related to Rio Grande Rifting. This has resulted in phase equilibria on a local (intralayer) scale and resetting of mineral-mineral isochrons.
REFERENCES


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Chapter 2

WHERE DO RARE EARTH ELEMENTS RESIDE IN THE LOWER CRUST?
An ion microprobe study of rare earth element (REE) concentrations in garnet, plagioclase, and sanidine in two granulite xenoliths from Kilbourne Hole was undertaken in order to investigate REE distributions in the lower crust. These common rock-forming silicates account for 40-70% of the light REE (LREE) and >90% of the heavy REE (HREE) and indicate the importance of major mineral phases as residence sites for the REE in the lower crust. Partitioning of Nd favored plagioclase over garnet, contrary to expectations based on mineral-melt and mineral-mineral equilibria. Furthermore, LREE concentrations in the KH plagioclase considerably exceed those of plagioclase in sialic volcanic and plutonic rocks. Consequently, the KH granulites may never have equilibrated with a melt. Since melting during high grade metamorphism is the most frequently invoked mechanism for dehydration of the lower crust and for creating compositional stratification in the crust ultimately leading to crustal stabilization, further study of the REE distributions in granulites may help constrain the efficacy of melt-related phenomena in the evolution of the crust.

The xenoliths discussed here probably had sedimentary protoliths and contain quartz and accessory apatite in addition to the phases discussed below. The chemistry of the xenoliths is permissive of melt segregation and of extraction of not greater than 10% melt (Chapter 4). Mineral assemblages in the Kilbourne Hole xenoliths equilibrated recently (<10 Ma) at pressures of 7-10 kbars and temperatures of 900-1000°C (Padovani and Carter, 1977; Chapter 1). On a xenolith scale, the xenoliths retain 1.6 Ga Sr isochrons, equivalent in age to those of
upper crustal basement rocks and suggesting that the lower crust was thermally quiescent from initial granulitization until fairly recently (Chapter 1).

The analyses were performed on a Cameca IMS 3f ion microprobe as described in Figure 2-1 and elsewhere (Shimizu et al., 1978; Shimizu and Richardson, in press; Shimizu and le Roex, 1986); the sputtered area was approximately 25-30 microns. Concentrations in garnet were determined using a pyrope from the Monastery Mine, South Africa as a standard (Shimizu, in prep.); those in feldspar were determined by internal reference to Sm and Nd concentrations determined by isotope dilution analyses of plagioclase concentrates from two of the xenoliths. The relative accuracy of the data between the REE's is likely to be better than 10% for garnet and, excepting Eu, 20% for the feldspars (Shimizu and Richardson, submitted 1986; Crozaz and Zinner, submitted 1986); the chief unknown for the latter arises from the variation in ionization yields across the lanthanide series. Work on silicates to date suggest that, if anything, the relative abundances of La and Ce could be higher than those measured (Crozaz and Zinner, submitted 1986; Reed 1983; Zinner and Crozaz 1986). Sm/Nd in the garnets agrees well with isotope dilution data of a garnet concentrate, but Sm and Nd concentrations are approximately 25% too high. This error exceeds that expected based on recent studies of pyrope-rich garnets (Shimizu and Richardson, submitted 1986) and may reflect a matrix effect on ionization. The calibration curve for Nd in plagioclase yielded a positive intercept; as a result, the data may also slightly underestimate the Nd concentrations of these feldspars.
Andesine and sanidine from each sample vary in composition by less than 20-25% and are LREE-enriched (Figure 2-la). LREE concentrations in plagioclase exceed those of coexisting sanidine by factors of 1-4 as expected from previously published data (Gromet and Silver, 1983; Fourcade and Allegre, 1981; Buma et al., 1971; Worner et al., 1983). The garnets are homogeneous at the 10-20% level; they are LREE-depleted and have significant negative Eu anomalies (Figure 2-lb). Chondrite-normalized concentrations from Ce to Yb in the garnets vary by more than two orders of magnitude in some samples. The LREE abundances are significantly lower where the garnet is in equilibrium with plagioclase. REE concentrations were found to be negligible in rutile and sillimanite. Analysis of a zircon inclusion from within garnet yielded a very steep REE pattern, enriched in the HREE as expected.

Plagioclase-garnet fractionation is in excess of 100 for La and ~3 for Nd. Pride and Muecke (1981) report a significantly lower maximum value of 6.4 for La in mafic granulites, while maxima expected from combining published mineral-melt partition coefficients are even lower: 2.3 and 0.4 for La and Nd respectively (Irving and Frey, 1978; Drake and Weill, 1975; Nagasawa and Schnetzler, 1971; Nash and Crecraft, 1985; Worner et al., 1983). Plagioclase-liquid REE partition coefficients appropriate to the xenoliths can be adequately predicted from existing constraints on their compositional and temperature dependence (Drake and Weill, 1975; Nagasawa and Schnetzler, 1971; Hildreth, 1977; Nash and Crecraft, 1985; Worner et al., 1983). In addition, the relative partitioning of Sm and Nd between plagioclase of similar composition and clinopyroxene in a mafic KH granulite (Chapter 3) is consistent with
that expected from combining mineral-melt partition coefficients. In contrast, both experimental and natural studies of almandine garnet-liquid partitioning indicate that both the absolute magnitude of REE partition coefficients (Nicholls and Harris, 1980; Irving and Frey, 1978) and the degree of La-Sm fractionation (compare data of Irving and Frey, 1978) correlate with the grossular content of garnet. Thus, the partitioning of the LREE in garnet may be highly dependent on composition, which may explain its anomalous partitioning relationship to the feldspars in the Kilbourne Hole xenoliths.

A significant fraction of the mass of rare earth elements (REE) in rhyolitic and granitic rocks resides in accessory phases such as apatite, zircon, allanite, and monazite (Fourcade and Allegre, 1980; Mittlefehldt and Miller, 1983; Gromet and Silver, 1983; Buma et al., 1971). Often less than 10% reside in major phases such as the feldspars and as a result, concentrations in plagioclase are often less than 20% of the whole rock concentrations (Fourcade and Allegre, 1981; Gromet and Silver, 1983; Buma et al., 1971; Worner et al., 1983). By analogy, if granulite grade silicic rocks equilibrate with melts during metamorphism, it is to be expected that the common rock-forming silicates should contain similarly low proportion of the REE and that feldspars should show similarly low concentration levels. Mass balance calculations for the REE in these xenoliths using mineral abundances determined by inversion of the major element data (Chapter 4), indicate that approximately 40-70% of the LREE and >90% of the HREE are contained in garnet and the feldspars. While this is not particularly surprising for the HREE, the results for the LREE reflect their unusually high
concentrations in the feldspars. The KH plagioclase are at least a factor of 2 richer in LREE than those of other crystalline rocks with similar and higher whole rock REE abundances (Figure 2-2). Pride and Muecke (1981) report a similar wealth of REE in major phases for mafic and silicic granulites from the Scourian complex which they attribute to a paucity of accessory phases.

If the protolith underwent partial melting and melt extraction, the high LREE content of the feldspars could be accounted for if a LREE-rich phase was stable during melting, but broke down subsequent to cooling below the solidus temperature. Only the accessory phases allanite and monazite are likely candidates for holding back the LREE and these phases are certainly stable in the lower crust (e.g. Leyreloup et al., 1982; DePaolo et al., 1982). In addition, although the precise solubility levels of allanite and monazite in silicate melts are unknown, they are likely to be exceeded over a large interval of melting considering their fairly early appearance during crystallization (Mittlefehldt and Miller, 1983; Gromet and Silver, 1983; Hildreth, 1979; Michael, 1984). By analogy to the feldspars presented in Figure 2-2, high LREE contents in plagioclase probably could not be maintained in the presence of a melt. Thus, if the LREE contents of the Kilbourne Hole plagioclase are similar to those which obtained during initial granulite metamorphism, it is unlikely that they equilibrated with a melt and dehydration of the lower crust was probably achieved by some other means, such as by decarbonization (e.g. Newton et al., 1980) or mineral dehydration in the solid-state. In the absence of a melt, the conditions required for nucleation of accessory phases may never be
attained and modal abundances of accessory phases in metamorphic rocks may largely reflect those of the protolith.


FIGURE 2-1

Chondrite-normalized partial (a) and full (b) rare earth element patterns for the feldspars and garnet respectively. Normalizing factors are 1.27 times chondrite abundances of Evensen et al. (1978); Eu anomaly constrained by extrapolating HREE from Sm to Dy. Samples discussed in text are squares (1977) and inverted triangles (7K3). Field of garnet (shaded) in these samples shown in (a). Also shown in (b) are analyses of garnets in other parts of sample 1977 which are compositionally distinct (circles and diamonds) and in samples 79K6 (crosses) and 2220 (plusses). With the exceptions of La and Ce, two masses of each element were monitored to assure elimination of isobaric interferences. Because of BaO interferences on the heavy-REE in the feldspars, only La through Eu (corrected for BaO) concentrations were determined. Counting statistics yield an error of <5% for Dy - Yb in garnet and La - Ce in the feldspars and <15% for the remainder. In most cases, each point represents 3 or more analyses.

FIGURE 2-2

Comparison of chondrite-normalized rare earth element concentration levels in the Kilbourne Hole feldspars to those of feldspars in granites, rhyolites, and other granulites. Normalization as in Figure 2-1. Also shown are Ce concentrations (ppm) in the whole rocks whose feldspars define the field boundaries labelled. Data sources: Fourcade and Allegre, 1981; Gromet and Silver, 1983; Hildreth, 1977; Leeman and Phelps, 1981; Mahood and Hildreth, 1983; Mittlefehlt and Miller, 1983; Nash and Crecraft, 1985; Pride and Muecke, 1981)
In Equilibrium
With Sanidine

Only

In Equilibrium with
Plagioclase and Sanidine

Feldspars

Garnets

Garnets

In Equilibrium with Sanidine Only

0.5

1

10

100

400

La Ce Nd Sm Eu Dy Er Yb

Chondrite Normalized

Chondrite Normalized

La Ce Nd Sm Eu Dy Er Yb

0.5

1

10

100

400
Chapter 3

AN ISOTOPIC PROFILE OF EARLY PROTEROZOIC CRUST:

PROGRESS REPORT ON CRUSTAL XENOLITHS FROM SOUTHERN NEW MEXICO
INTRODUCTION

Two explosive volcanic eruptions related to Rio Grande rifting in southern New Mexico have sampled different portions of the deep crust by transporting crustal xenoliths to the surface. At Kilbourne Hole maar, the suite of deep crustal xenoliths is comprised of fragments of the lower crust (6-10 kb; Padovani and Carter, 1977) which are anhydrous granulites. Xenolith lithologies include mafic and silicic meta-igneous granulites (orthogneisses) and meta-sedimentary granulites (paragneisses) which may be predominantly pelitic in origin. In contrast, the xenolith suite at Potrillo Maar was extracted from intermediate depths (~8-14 km; Padovani, pers. comm. 1986) and is comprised of mafic and silicic orthogneisses which are amphibolites. From isotopic analyses of these samples and existing data for temporally equivalent basement lithologies exposed at the surface we can ultimately construct a vertical geochemical profile and history of early Proterozoic crust.

Southern New Mexico lies in the southernmost and youngest of lower to middle Proterozoic crustal terranes of the North American midcontinent that were stabilized between approximately 1.6 and 1.9 Ga (Van Schmus and Bickford, 1981). Locally, U-Pb age determinations on zircons and Rb-Sr whole rock analyses yield crustal stabilization ages which cluster at ~1.75 Ga (Condie and Budding, 1979). Rb-Sr and Pb-Pb isochrons determined for the paragneiss xenoliths from Kilbourne Hole indicate that they were metamorphosed at approximately 1.6 Ga (Chapter 1). Thus, processes leading to the growth of this portion of the crust were largely complete by 1.6 billion years ago.
The tectonothermal history of southern New Mexico and vicinity following crustal stabilization is summarized in Chapter 1. Recent reheating of the lower crust has produced variable scales of reequilibration for the different isotopic systems with Pb and Nd isotopes being more equilibrated than Sr isotopes at a xenolith scale. Unfortunately, this has had the effect of obscuring most initial isotope ratios and their time-integrated record of the protolith history. In addition, reequilibration may have also averaged the isotopic characteristics of domains larger than that represented by the xenoliths. Consequently, the possibility that the domain represented by the xenoliths was an open system during recent reequilibration will be considered.

The Kilbourne Hole xenoliths have been previously described by Padovani and Carter (1977). Those discussed here are mafic and silicic orthogneiss granulites which contain feldspars and pyroxene ± quartz and pelitic paragneiss granulites which contain feldspar, garnet, sillimanite and quartz. The lineage of sample 7K3 from Kilbourne Hole is unknown: it does not contain sillimanite and has a low K/Na ratio. However, half of the sample contains garnet while the other half contains pyroxene. This suggests a protolith which was a graywacke, aluminous silicic orthogneiss, or hybrid of both. The Potrillo Maar amphibolites contain biotite, amphibole, and feldspars ± quartz and alternate between mafic and silicic bands on a xenolith scale. They are classified in Table 3-2 on the basis of our unpublished major element data.
REVIEW OF OXYGEN ISOTOPE DATA FOR KILBOURNE HOLE XENOLITHS

Many of the samples discussed here have also been analyzed for oxygen isotopes (James et al. 1980). The results of that study show that the granulites retain $\delta^{18}O$ values of likely protoliths. Internally, both orthogneisses and paragneisses are largely in isotopic equilibrium. A limited range in $\delta^{18}O$ values was measured in the layers of the pelitic paragneisses (10.12 to 11.84; samples 1975, 79K6, and K4), within the range of values measured in pelitic metasediments from high grade metamorphic terranes. Similarly, a limited range in $\delta^{18}O$ values was measured in the layers of a mafic and a silicic orthogneiss (6.14 to 6.57; samples K59 and 79K4), within the range of mantle-derived materials. Sample 7K3 has an intermediate $\delta^{18}O$ signature of approximately 8.8 consistent with either a graywacke protolith or a hybrid igneous-sedimentary one.

The oxygen isotope data of James and others (1980) indicate that large-scale oxygen isotope equilibration has not occurred and that isotopic equilibration between the different lithologies at a scale larger than that of the xenoliths was probably not appreciable. Thus, equilibrium with a pervasive fluid phase did not occur; notably, dehydration by mantle-derived CO$_2$ (Janardhan et al., 1982; Newton et al., 1980) is precluded. In general, the rate of oxygen isotope equilibration may be expected to be markedly faster than that of other isotopic systems. If the oxygen isotopes are not equilibrated, then other isotopic systems have probably resisted significant equilibration between the different lithologies in spite of recent partial Nd and Pb isotopic reequilibration at the xenolith scale.
RESULTS

Isotopic analyses for the orthogneisses from Kilbourne Hole and Potrillo maars are presented in Tables 3-1 and 3-2 respectively. Data for the pelitic paragneisses are presented in Chapter 1. These data are representative of a range in physical scale from minerals to centimeter-thick slabs to whole xenoliths. Our sampling approach is described in Chapter 1.

Rb-Sr

Kilbourne Hole Sr isotope analyses have been performed on a range of lithologies from both maars as shown in Figure 3-1. Although not shown in this figure, plagioclase and sanidine concentrates from within layers of samples 7K3 and 1977 from Kilbourne Hole are virtually in isotopic equilibrium (Table 3-1 and Chapter 1). In addition, in spite of a small variation in $^{87}\text{Rb}/^{86}\text{Sr}$, layers from within two xenoliths from Kilbourne Hole do not define isochrons and exhibit limited isotopic variation. These features probably reflect variable scales of isotopic equilibration resulting from reheating of the lower crust related to Rio Grande rifting as discussed in Chapter 1.

Both mafic and silicic orthogneisses from Kilbourne Hole have low to extremely low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios, from that of arc basalts to that of depleted mafic granulites. Since Rb generally increases relative to Sr with increasing silica content, it is evident that both groups of orthogneisses are depleted in $^{87}\text{Rb}/^{86}\text{Sr}$ to some extent with respect to likely protoliths. In the case of the mafic orthogneisses, Sr isotopic
### TABLE 3-1. Rb-Sr and Sm-Nd Isotope Data for Kilbourne Hole Xenoliths, New Mexico.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Rb</th>
<th>Sr</th>
<th>87Rb/86Sr</th>
<th>87Sr/86Sr</th>
<th>Sm</th>
<th>Nd</th>
<th>147Sm/144Nd</th>
<th>143Nd/144Nd</th>
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<td><strong>Mafic Orthogneisses</strong></td>
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<td>Plagioclase</td>
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<td>12.78</td>
<td>0.2400</td>
<td>0.51271</td>
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<td>79K2</td>
<td>0.00415</td>
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<td>79k4-1</td>
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<td>844.6</td>
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<td><strong>Arkosic Paragneiss (1)</strong></td>
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<td>14.60</td>
<td>421.4</td>
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<td>0.71415</td>
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<td>31.61</td>
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<td>-2</td>
<td>10.21</td>
<td>449.3</td>
<td>0.0642</td>
<td>0.71167</td>
<td>3.559</td>
<td>13.79</td>
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<td>9.64</td>
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<td>0.0192</td>
<td>0.71161</td>
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<td>0.0869</td>
<td>0.51204±2</td>
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<td>13.75</td>
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<td>2.281</td>
<td>8.990</td>
<td>0.1534</td>
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<td>Garnet</td>
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<td>482.8</td>
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<td>0.70795</td>
<td>1.725</td>
<td>6.051</td>
<td>0.1723</td>
<td>0.51200±5</td>
</tr>
<tr>
<td></td>
<td>4.053</td>
<td>573.1</td>
<td>0.0200</td>
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<td>3.055</td>
<td>16.05</td>
<td>0.1151</td>
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<td>0.0491</td>
<td>0.70664</td>
<td>3.307</td>
<td>15.29</td>
<td>0.1308</td>
<td>0.51201±2</td>
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<tr>
<td></td>
<td>8.922</td>
<td>500.5</td>
<td>0.0503</td>
<td>0.70877</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Analytical techniques as described in Chapter 1.

b) 87Sr/86Sr corrected for fractionation using 86Sr/86Sr = 0.1194 and normalized to 0.7080 for E&SA SrC03.

c) 147Nd/144Nd corrected for fractionation using 146Nd/144Nd = 0.7219 and normalized to 0.51284 for BCR-1. Sm/Nd ratios are reproducible to better than 1%.

1Rb-Sr data calculated from unweighted sum of the layers.
### Table 3-2 Rb-Sr data for Potrillo Maar xenoliths, New Mexico

<table>
<thead>
<tr>
<th></th>
<th>Mafic Orthogneisses (&lt;58% SiO₂)</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rb (µg)</td>
<td>Sr (µg)</td>
<td>⁸⁷Rb/⁸⁶Sr</td>
<td>⁸⁷Sr/⁸⁶Sr(a)</td>
</tr>
<tr>
<td>PMA1</td>
<td>83.21</td>
<td>844.6</td>
<td>0.278</td>
<td>0.70541</td>
</tr>
<tr>
<td>PMA6</td>
<td>45.34</td>
<td>954.8</td>
<td>0.134</td>
<td>0.70492</td>
</tr>
<tr>
<td>PMA8</td>
<td>76.47</td>
<td>728.4</td>
<td>0.296</td>
<td>0.70504</td>
</tr>
<tr>
<td>PMA3</td>
<td>36.53</td>
<td>782.3</td>
<td>0.132</td>
<td>0.70559</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Silicic Orthogneisses (&gt;58% SiO₂)</th>
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<th></th>
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<tbody>
<tr>
<td></td>
<td>PMA M1</td>
<td>132.9</td>
<td>491.9</td>
<td>0.762</td>
</tr>
<tr>
<td>PMA M3A</td>
<td>107.6</td>
<td>413.6</td>
<td>0.734</td>
<td>0.70732</td>
</tr>
<tr>
<td>-B</td>
<td>105.1</td>
<td>506.5</td>
<td>0.585</td>
<td>0.70666</td>
</tr>
<tr>
<td>-C</td>
<td>104.0</td>
<td>445.9</td>
<td>0.658</td>
<td>0.70669</td>
</tr>
<tr>
<td>WR</td>
<td></td>
<td>0.654</td>
<td></td>
<td>0.70685†</td>
</tr>
</tbody>
</table>

(a) Analytical techniques as described in Chapter 1. ⁸⁷Sr/⁸⁶Sr corrected for fractionation using ⁸⁶Sr/⁸⁸Sr = 0.1194 and normalized to 0.7080 for E&A SrCO₃. Analytical precision <0.005%.

†Calculated from unweighted sum of the layers.
Rb-Sr isochron diagrams for a) orthogneisses from Kilbourne Hole and Potrillo Maar and b) pelitic paragneisses and sample 7K3 from Kilbourne Hole. Fields around two samples indicate range in variation between layers. Approximate trend of data for 1.68-1.78 Ga greenstones of the mid-continent (Nelson and DePaolo, 1984) shown in (a); greenstone data is bracketed by 1.6 Ga reference isochrons in (b) except for Tijeras greenstones indicated by +'s.
OR

EARLY PROTEROZOIC GREENSTONES
NEW MEXICO - WYOMING
Tijeras Greenstones

T ~ 300 Ma

KILBOURNE HOLE
MAFIC
SILICIC

POTRILLO MAAR
WHOLE ROCKS
LAYERS

PARAGNEISSES

T ~ 1.6 Ga

EARLY PROTEROZOIC GREENSTONES
7K3

KILBOURNE HOLE
PELITIC WHOLE ROCKS
PELITIC LAYERS
7K3
signatures are also correspondingly unradiogenic. Sr isotopic
signatures in the silicic orthogneisses are considerably higher and
distinct from those of the mafic orthogneisses. Nevertheless, apparent
initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of both lithologies are equal to or greater
than that of a plausible ~1.7 Ga depleted mantle (~0.7018; Ben Othman et
al., 1984; Nelson and DePaolo, 1984) as discernable from Figure 3-la,
indicative of interaction with or residence in an $^{87}\text{Rb}/^{86}\text{Sr}$-enriched
crustal reservoir at some time during their evolution.

Precambrian-aged isotope systematics in the Kilbourne Hole pelitic
paragneisses have survived reequilibration on a layer-layer scale during
recent granulite grade metamorphism. The paragneisses exhibit a
significant range in $^{87}\text{Rb}/^{86}\text{Sr}$ (0.7 to 3.4: whole rocks), ratios which
are high and similar to those of shales. On a Sr isochron diagram
(Figure 3-1b), layers and whole rocks cluster about a 1.6 Ga isochron
and yield an initial ratio of ~0.7092 ± 6 (Chapter 1). As for the
silicic orthogneisses, this ratio is significantly greater than that of
an early to middle Proterozoic mantle and is consistent with a crustal
prehistory in a time-integrated Rb/Sr-enriched reservoir. Further, both
initial isotopic ratios and present-day isotopic ratios are greater than
those of the orthogneisses. Thus, as for O isotopes, the Sr isotopic
signatures of the different rock types are distinctive and prohibitive
of extensive equilibration between them.

Sample 7K3, which may have had a silicic igneous rock or graywacke
protolith, shows a considerably larger range in internal isotopic
variation than that of the orthogneisses. $^{87}\text{Sr}/^{86}\text{Sr}$ ranges from that of
the silicic orthogneisses in layers lacking garnet to that of the least
radiogenic pelitic paragneiss in layers containing garnet. Those layers in which garnet is absent are virtually in isotopic equilibrium while those containing garnet yield a fictitious isochron age of \( -5 \text{ Ga} \). Overall, the initial Sr isotope signature of sample 7K3 falls within that of the silicic orthogneisses permissive of a juvenile sedimentary protolith (i.e. graywacke) derived from sources like those of the silicic orthogneisses, or of a composite xenolith of graywacke and silicic orthogneiss as previously noted for oxygen isotopes.

**Potrillo Maar** Sr isotope signatures of the orthogneisses from Potrillo Maar fall between those of the mafic and silicic orthogneisses from Kilbourne Hole. However, \( \frac{\text{Rb}}{\text{Sr}} \) ratios range to much higher values, \( -0.8 \), and together with \( \frac{\text{Sr}}{\text{Sr}} \) define a trend of \( -300 \text{ Ma} \) age significance. The data trend may have temporal significance (cf. Chapter 1) or may represent partial equilibration in response to crustal reheating related to the Rio Grande Rift. The latter has been suggested for many of the internal variations in the Kilbourne Hole paragneisses discussed in Chapter 1.

**Sm-Nd**

Nd isotope data for the Kilbourne Hole paragneisses, an orthogneiss, and sample 7K3 are shown in Figure 3-2. As for Sr isotopes, mineral separates (plagioclase-clinopyroxene or plagioclase-garnet in this case) are in Nd isotopic equilibrium on a layer scale. Sample K59, a mafic orthogneiss, is LREE depleted and has the highest \( \frac{\text{Nd}}{\text{Nd}} \) measured in the xenoliths. As shown in Figure 3-3, its Nd evolution curve does not intersect that of the depleted mantle. While
Figure 3-2

Sm-Nd isochron diagram for orthogneiss K59, sample 7K3, and pelitic paragneisses from Kilbourne Hole. Shaded fields are Precambrian rocks from the Colorado Front Range (DePaolo, 1981). Other supracrustal rocks of New Mexico to Wyoming from Nelson and DePaolo (1984) and Nelson and DePaolo (1985). Average $^{147}$Sm/$^{144}$Nd of shales and 2σ limits (dashed vertical lines) compiled from data of O'Nions et al. (1983); Miller and O'Nions (1984); Nance and Taylor (1976); Nance and Taylor (1977); Michard et al. (1985); Patchett et al., (1984).
Figure 3-3

Nd isotope evolution diagram for whole rock samples shown in Figure 3-2; symbols are same. The hatched horizontal line indicates probable upper limit to depleted mantle if that identified by Nelson and DePaolo (1984) existed in the earliest Proterozoic.
this could be interpreted as the result of contamination by less radiogenic crust during its emplacement, crustal assimilation would probably also have resulted in a significantly lower Sm/Nd ratio. Instead, the Sm/Nd ratio measured is probably not representative of its time-integrated one. The xenolith may have had a two-stage history involving an increase in its Sm/Nd ratio or may be a high Sm/Nd subsystem of a more felsic, lower Sm/Nd domain or both. Additional data for a range in mafic orthogneiss compositions should elucidate this problem.

The pelitic paragneiss xenoliths have been partially reequilibrated internally with respect to Nd isotopes, in contrast to the Precambrian-aged Sr isochrons preserved at this scale. Individual layers in the pelitic paragneisses scatter about a 270 Ma isochron and summed whole rocks fall close to this isochron (Figure 3-2). Layers show a wide range in Sm/Nd ratios, some being extremely enriched (to upwards of 0.4). This spread in Sm/Nd largely reflects the relative abundance of garnet to feldspar (Chapter 4). Few of the layers analyzed have $^{147}\text{Sm}/^{144}\text{Nd}$ ratios equivalent to that of post Archean shales and clays, which is virtually constant at $0.117 \pm 0.007$ ($2\sigma$, $N=115$; see Figure 3 for references); most layers are enriched in Sm/Nd. For isotopic evolution in a reservoir with Sm/Nd equal to that of shales, a model extraction age from a depleted mantle ($\epsilon_{\text{Nd}} = -4.9$; mean of mafic tholeiites, Nelson and DePaolo, 1984) of $-1.5$ Ga can be calculated, younger than their metamorphic age. Evolution in a reservoir with higher Sm/Nd than that of shales and/or a more complex equilibration history can produce older model ages (discussed below).
Paragneiss/charnockite 7K3 is lowest in $^{143}\text{Nd}/^{144}\text{Nd}$ of the samples analyzed. Like the pelitic paragneisses, sample 7K3 has been partially equilibrated on a xenolith scale and the data define an array subparallel to that of the pelitic paragneisses. Similarly, its bulk composition is also higher in Sm/Nd than typical crust. As for both sample K59 and most of the layers of the pelitic paragneisses, this could represent sampling bias relative to the domain with which it equilibrated, in this case towards more garnet-rich compositions. Using the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the whole rock, a model extraction age from a depleted mantle is $\sim 2.2$ Ga.

**U-Pb**

Pb isotope data have only been obtained for the pelitic paragneisses and one layer from sample 7K3 from Kilbourne Hole. As for Nd isotopes, the Pb isotopes have been partially reequilibrated resulting in variable and younger than middle Proterozoic apparent U-Pb and Th-Pb isochron ages (Chapter 1). As discussed in Chapter 1, the relative isochron ages are consistent with a thermal history involving complete equilibration in the Proterozoic and recent partial equilibration. Thus, although recent equilibration has disrupted isotopic relations on U-Pb isochron diagrams, an $\alpha-\beta$ isochron array is preserved (Inset, Figure 3-4a).

Like many granulite terranes, the Pb isotope characteristics of the paragneisses fall to the left of the geochron indicating a time-integrated depletion in U/Pb relative to bulk earth and mantle. Measured $\mu$'s between individual xenolith layers of the Kilbourne Hole
Figure 3-4

Pb-Pb isotope diagrams comparing fields of pelitic paragneisses from Kilbourne Hole (KH) to whole rock and ore data of Stacey and Hedlund (1983) and Ewing (1979) and to conformable lead array of Stacey and Kramers (1975). Tic marks indicate 0.25 Ga. Insets show Kilbourne Hole data: closed symbols are whole rocks, open symbols are layers. a) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$; b) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$. 
paragneisses show a limited range, generally decreasing with increasing
U concentration and not exceeding 3 with only one exception (Chapter 1).
The contribution of this exceptional layer (79K6-1) to the sum of both \( \mu \)
and \( ^{206}\text{Pb}/^{204}\text{Pb} \) in the sample is negligible. Thus, summed whole rock
\( \mu \)'s are likely to be representative (\( \mu = 1.5 \pm 2 \)) and are lower than any
likely protolith. In comparable pelitic sediments, \( \mu \) averages 7.8
(White et al., 1985; Church, 1973; Sinha and Hart, 1972), indicating
that the pelitic paragneisses are depleted in \( \mu \) by a factor of at least
3.

In general, each xenolith exhibits a small and distinctive range
in \( ^{206}\text{Pb}/^{204}\text{Pb} \) and \( ^{207}\text{Pb}/^{204}\text{Pb} \). The one layer of sample 7K3 which has
been analyzed has lower ratios than the pelitic paragneisses. As shown
in Figure 3-4, these paired characteristics fall below the conformable
lead array of Stacey and Kramers (1975). Whole rock Pb isotope ratios
in the pelitic paragneisses do not exhibit any simple correlation with \( \mu \)
on U-Pb isochron diagrams (Chapter 1), and therefore there exists a
small range in calculated initial Pb isotope ratios.

\textbf{Th-Pb}

Unlike U/Pb, Th/Pb is more highly variable between layers of the
xenoliths. Th/Pb ratios of the layers exhibit a strong correlation with
Th concentrations (Chapter 4) and layers 1975-1 and 79K6-4 have
dramatically higher Th concentrations than their adjacent layers. These
facets, together with the relatively higher Nd contents and lower Sm/Nd
of these layers in the absence of a major element discontinuity (Chapter
4), implicate the role of an accessory phase, e.g. monazite. In spite
of this, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ correlate between xenoliths (Figure 3-5), suggesting that a representative Th/Pb ratio for the pelitic paragneisses must lie along this array.

For a given $^{206}\text{Pb}/^{204}\text{Pb}$, the Kilbourne Hole pelitic paragneisses are enriched in $^{208}\text{Pb}/^{204}\text{Pb}$ with respect to the conformable Pb array (Figure 3-4b). Model Th/U ratios calculated relative to this array for a 1.6 Ga history are 17 to 20. As previously discussed, U is probably depleted with respect to Pb by a factor of at least 3 or more; thus, the Th/U ratio implied for the protolith was lower (<7), similar to that of likely protoliths including mature sediments (Bhatia and Taylor, 1981; McLennan and Taylor, 1980).

**DISCUSSION AND INTERPRETATION**

*Review of Isotopic Data for Supracrustal Rocks and Ores of New Mexico*

Nelson and DePaolo (1984) report Sr and Nd isotopic analyses for 1.68-1.78 Ga greenstones from the southern Rocky Mountains from Wyoming to New Mexico. These are predominantly mafic, presumably island arc, volcanic rocks and therefore are likely candidates for the material from which early Proterozoic crust was constructed. As shown on an isochron diagram (Figure 3-1), except for the Tijeras greenstones of central New Mexico, the Rb-Sr isotopic characteristics of this greenstone belt define an array of the appropriate age significance. Amongst tholeiites other than those of the Tijeras greenstones, $^{87}\text{Rb}/^{86}\text{Sr}$ are greater than 0.01 and range to upwards of 0.4. Unlike the other greenstone localities analyzed by Nelson and DePaolo (1984), $^{87}\text{Rb}/^{86}\text{Sr}$ in the Tijeras greenstones range to almost 0.7 and together with $^{87}\text{Sr}/^{86}\text{Sr}$. 
Figure 3-5

Th-Pb isochron diagram for pelitic paragneisses from Kilbourne Hole. Symbols as in Figure 3-4. Initial ratios for reference isochrons from evolution curves shown in inset. Inset is a $^{208}\text{Pb}/^{204}\text{Pb}$ evolution diagram and shows two possible $^{208}\text{Pb}/^{204}\text{Pb}$ evolutions paths which satisfy correlated $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ characteristics of the whole rocks as described in text: extraction at 1.6 Ga from a reservoir with initial ratios of 1.6 Ga conformable leads (Stacey and Kramers, 1975) and extraction from 2.25 Ga depleted mantle and crustal prehistory in a reservoir with $\mu=14.5$ and Th/U=4.3. Depleted mantle curve as described in Figure 3-6.
define an array whose age significance is approximately 0.5 Ga age significance as shown in Figure 3-1a, in spite of the fact that the rocks are 1.68 Ga old.

The trend of Nd isotopes for these greenstones is shown in Figure 3-2. $\epsilon_{Nd}$ averages $\sim 4.9$, indicative of derivation from a mantle more depleted than predicted by the depleted mantle evolution curves of DePaolo (1981) and Ben Othman and others (1984). Additional Nd isotopic analyses (DePaolo, 1981; Nelson and DePaolo, 1985) of other lower to middle Proterozoic supracrustal lithologies from the mid-continent plot along or near the trend of the greenstone data (Figure 3-2), consistent with ultimate extraction from the mantle within a few hundred million years of $\sim 1.7$ Ga. This includes plutonic rocks presumed to be derived largely by anatexis of subjacent crust (Nelson and DePaolo, 1985). These results are consistent with earlier interpretations of zircon chronologies which suggested that this portion of the crust was constructed between $\sim 1.7$ and $\sim 2.0$ Ga.

Pb isotope data exist for a few Precambrian igneous rocks and for Cenozoic ore deposits whose sources were probably in the crust (Stacey and Hedlund, 1983; Ewing, 1979). These are shown in Figure 3-4. Both igneous rocks and ores show a considerable range in $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ which are internally well-correlated and define a Pb-Pb isochron of $\sim 1.5$ Ga in the $\alpha-\beta$ diagram. The low $^{206}\text{Pb}/^{204}\text{Pb}$ end of the $\alpha-\beta$ array extends below the conformable Pb array of Stacey and Kramers (1975). This suggests that the initial Pb isotopes ratios for crust in this area were relatively unradiogenic and therefore that the crust does not contain a significant quantity of
recycled, older, and more radiogenic material (Stacey and Hedlund, 1983). Thus, this result also corroborates previously cited interpretations of a relatively juvenile origin for crust in this region.

Representative Characteristics, Crustal Prehistories, and the Effects of Granulite Metamorphism

From isotopic and geochemical data on crustal xenoliths, it is possible to construct a geochemical and temporal profile of the crust including: 1) the range of chemical characteristics in the middle and lower crust, 2) the nature of changes which occur during metamorphic stabilization of the crust, and 3) the time required to amass a vertical section of the crust. As illustrated below, this information requires constraints on representative parent-daughter and initial ratios. The major difficulty with extrapolating from decimeter-sized xenoliths to larger reservoirs in the crust is a problem of representativeness: the extent to which the lithologies we have analyzed are representative of the crust as a whole, a problem which may have to be assessed by geologic, geophysical, and geothermal considerations. Unfortunately, an additional question regarding representativeness has been introduced by recent isotopic reequilibration of Nd, Pb and in some cases Sr: the extent to which the parent-daughter ratios of the xenoliths represent those of the domain over which equilibration occurred. Because of this, where evidence exists for a disparity between the isotopic characteristics of the xenoliths and that expected of closed system since extraction from the mantle, the question arises as to whether we
are seeing a subset of a larger isotopic domain. The Nd isotope characteristics of the pelitic paragneisses best exemplify this problem: it is evident from Figures 3-2 and 3-3 that there exists a range of correlated isotope and parent-daughter characteristics permissive of a range in conclusions regarding their chemical and temporal evolution.

For the present, we make two conservative assumptions regarding those lithologies which exhibit a large range in parent-daughter ratios. First, we assume that the internal systematics of the isotopic data are at least representative of their respective lithologies. This is supported by the internal consistency of the data and the distinctive isotopic signatures exhibited by different lithologies for most isotopic systems. Second, we assume that the parent-daughter and isotopic ratios have not been decoupled from each other in some spurious fashion by recent isotopic reequilibration such as, for example, by the development of diffusion gradients. In other words, we assume that a composition representative of the lithologic domain exists in or on an extension of the data array. This is supported by the internal consistency of the apparent isochrons, where available, between layer-layer and xenolith-xenolith scales.

**Orthogneisses**

The initial Sr isotopic signatures of the mafic orthogneisses are more radiogenic than predicted for an early Proterozoic mantle (Figure 3-1). By analogy to ~1.7 Ga supracrustal basalts, this feature does not necessarily require special pleading such as a protracted period of crustal residence. However, the anomalously low $^{87}\text{Rb} / ^{86}\text{Sr}$ ratios of two
of the mafic orthogneisses appear to require Rb loss at some point in their evolution, probably during granulite metamorphism. The Kilbourne Hole silicic orthogneisses have clearly have higher $^{87}\text{Sr}/^{86}\text{Sr}$ for a given $^{87}\text{Rb}/^{86}\text{Sr}$ ratio than ~1.7 Ga supracrustal equivalents and therefore have evolved in a reservoir with a time-integrated $^{87}\text{Rb}/^{86}\text{Sr}$ ratio higher than that measured in the rocks today. Like the mafic orthogneisses, the silicic orthogneisses have lost Rb, presumably during granulite metamorphism. Accordingly, if the protolith had a $^{87}\text{Rb}/^{86}\text{Sr}$ ratio equal to that of an average granodiorite, i.e. ~1, a crustal residence time of ~350 Ma prior to granulite metamorphism is required.

The relatively unradiogenic Sr isotope signatures of the Potrillo Maar orthogneisses are difficult to reconcile with their high Rb/Sr ratios. Notably, the Rb-Sr isochron array for the Precambrian Tijeras greenstones is roughly coincidental with that of the Potrillo Maar xenoliths (Figure 3-1). If, like the Tijeras greenstones, the Potrillo Maar orthogneisses are really early to middle Proterozoic in age and their apparent isochron indicates reequilibration in a closed system, their relatively unradiogenic isotopic signatures require a time-integrated $^{87}\text{Rb}/^{86}\text{Sr}$ ratio less than that of most xenoliths from Potrillo Maar (i.e. less than or equal to that indicated by the intersection of the Potrillo Maar array with the depleted mantle reference array). Thus, the xenoliths may be unrepresentative and more Rb-enriched than the reservoir with which they equilibrated or they may have been enriched in Rb with respect to Sr fairly recently. The latter could have occurred in the Paleozoic if the data array has temporal significance. Alternatively, the Potrillo Maar xenoliths may not be
Precambrian in origin, but may represent a magmatic event of Pennsylvanian-Permian age in southern New Mexico for which there is no known magmatic expression at the surface. Tectonism of late Pennsylvanian to early Permian age related to the Ancestral Rocky Mountains extended into New Mexico but was amagmatic (cf. Chapter 1).

Paragneisses

The evolution of the pelitic paragneisses is of particular interest since they represent the stabilization in the lower crust of materials which were once at the surface. They were clearly involved in the major crust building process vis-a-vis the orthogneisses, which could plausibly have been intruded later. In light of the previously cited evidence for a fairly restricted range in crustal extraction ages for this portion of the crust, we are interested in delimiting the crustal extraction ages of the paragneisses in order to understand their relationship to the restricted range in Nd model ages determined in rocks at the surface. In addition, limits on the duration of crustal prehistory can constrain representative parent-daughter ratios for those isotopic systems which have partially equilibrated.

Likely Duration of Crustal Prehistory An initial $^{87}$Sr/$^{86}$Sr ratio for the pelitic paragneisses constrained by a Sr isochron is significantly higher than that of early Proterozoic mantle (Figure 3-1). Shales do not appear to equilibrate with seawater (Dasch 1969), and therefore the moderately high $^{87}$Sr/$^{86}$Sr of early Proterozoic seawater (~0.705: Veizer and Compston, 1976) was probably not a contributing factor. Since the evolution from igneous to sedimentary rocks is
accompanied by an increase in Rb/Sr (Dasch, 1969), it is reasonable to use the Rb/Sr ratios of shales as a representative upper limit for that operative during supracrustal evolution, thereby constraining a minimum age of extraction. Unfortunately, Rb/Sr ratios in shales are variable, typically ranging to values as high as 6. Based on geochemical considerations discussed in Chapter 4, granulite metamorphism does not appear to have significantly affected the Rb/Sr ratios of the pelitic paragneisses. Thus, if we use a typical $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of the pelitic paragneisses of 1.5, the minimum duration of crustal prehistory of the rocks is approximately 300 Ma.

As previously discussed, the pelitic paragneisses are depleted in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ with respect to the geochron, i.e. they are B-type Pb's. As shown in Figure 3-4, they are also depleted relative to putative crustal Pbs of New Mexico. Thus the lower crust, at least as exemplified by the pelitic paragneisses is significantly depleted in U with respect to Pb. In addition, the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ isotope characteristics of the paragneisses fall on the Pb-Pb array for the upper crust suggesting a consanguinous origin. Moreover, if these isotope characteristics exemplify crust which has been interpreted to have a short prehistory prior to crustal stabilization, this correlation may indicate that the paragneisses had a relatively short crustal prehistory.

Initial Pb isotope ratios calculated from measured $\mu$'s for 1.6 Ga metamorphic histories are greater in $^{206}\text{Pb}/^{204}\text{Pb}$ and similar to greater in $^{207}\text{Pb}/^{204}\text{Pb}$ than the conformable lead isotope array of Stacey and Kramers (1975). One interpretation of this is that loss of U during the
recent episode of granulite metamorphism or by subaerial weathering has resulted in undercorrection for radiogenic Pb. However, we regard recent U-loss as minimal given the probable absence of a fluid/vapor phase in the lower crust and the goodness of fit of the layers to interlayer isochrons (Chapter 1). Moreover, the relative position of the initial ratios to conformable leads is qualitatively similar to that observed between conformable leads and oceanic sediments today, the latter having somewhat negative model ages (to -200 Ma).

As shown in Figure 3-6, the initial $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ characteristics of the pelitic paragneisses can be modelled as the result of a second-stage evolution in a crustal reservoir following extraction from a model depleted mantle. A best-fit line to the initial Pb isotope characteristics of the pelitic paragneisses and a model depleted mantle at 1.6 Ga yields an age of extraction of $-2.25\text{ Ga}$. The intervening period of Pb isotopic evolution in a crustal reservoir can be satisfied by a $\mu$ of 13-16. Thus, the data is permissive of a crustal prehistory of $-0.65\text{ Ga}$ in a reservoir with a $\mu$ which is reasonable for rocks at the surface. Extraction from a more radiogenic mantle - analogous to many modern arcs - requires shorter crustal prehistories ± a lower $\mu$. Thus, this interpretation of the data is likely to yield an upper estimate for the duration of crustal prehistory.

The foregoing Sr and Pb isotope models of single-stage crustal evolution oversimplify the permutations in parent-daughter ratios possible during the igneous to sedimentary histories of the paragneisses. In particular, evolution in a crustal reservoir with
Figure 3-6

$^{207}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb diagram showing model Pb evolution of pelitic paragneisses from Kilbourne Hole. Depleted mantle calculated by fitting an evolution curve of constant $\mu$ to lead isotope characteristics of modern intraoceanic island arcs and Proterozoic (circled stars) and Phanerozoic komatiites (Brevart et al., 1985; Manhes et al., 1980; Tilton, 1983). Resulting Pb evolution curve has a $\mu$ of 9.4, like that estimated for MORB mantle by Zindler and Hart (1986), and fits the Pb-Pb ages of the Proterozoic komatiites. The temporal evolution of the depleted mantle curve is approximately consistent with the crustal evolution curve as indicated by coincidence to second stage isochrons derived from model of Stacey and Kramers (1975).
mantle-like parent-daughter ratios prior to an increase in $\mu$ cannot be precluded by the isotope data alone. However, in the case of U-Pb, the progression from crystalline to sedimentary lithologies is generally accompanied by a decrease in $\mu$. So long as the igneous protolith had a $\mu$ significantly higher than that of the mantle, as suggested by the radiogenic lead data from New Mexico (Figure 3-4), this single-stage crustal evolution for Pb will tend to overestimate the duration of crustal prehistory. This can be understood by considering that the generation of $^{207}$Pb has been diminishing at a rapid rate and therefore higher $\mu$'s are more effective earlier on. Therefore, if crust at or near the surface has appreciably higher parent-daughter ratios than the mantle, these models are realistic. In particular they show that long crustal prehistories are not required but rather that the materials from which the paragneisses were derived may have been assembled from the mantle during the early Proterozoic.

Representative Sm/Nd and Th/Pb characteristics of the Pelitic Paragneisses. The ranges in Sm/Nd and Th/Pb ratios of typical crustal rocks are more conservative and therefore model ages based on Nd and $^{208}\text{Pb}/^{204}\text{Pb}$ isotope characteristics are likely to be less equivocal. Unfortunately, in the Kilbourne Hole pelitic paragneisses both of these systems do not retain Precambrian isochrons, and therefore the isotopic ratios at 1.6 Ga are relatively unconstrained. In addition, both of these systems exhibit correlated parent-daughter isotopic variations between xenoliths. Accordingly, calculated model ages are critically dependent on the identification of representative isotopic and parent-daughter ratios. In these cases, it may be more instructive to turn the
tables and utilize constraints on likely crustal prehistories in order to estimate reasonable parent-daughter ratios of the pelitic paragneisses. These may then be compared to likely crustal protoliths in order to estimate the effects of granulite metamorphism on these elements and in order to assess the ultimate contribution of pelitic paragneisses to the crustal budgets of these elements (Chapter 4).

**Sm-Nd** Other than basalts the Nd isotope signatures of the pelitic paragneisses are more radiogenic than most supracrustal rocks from New Mexico and Colorado for which Nd isotopes are known. If Nd data of anorogenic granitoids from New Mexico (Nelson and DePaolo, 1985) are representative of average crust in this area, then the pelitic paragneisses have evolved in reservoir whose time-integrated Sm/Nd ratio is greater than average. This interpretation is only strengthened if the anorogenic granitoids also contain a mantle, and therefore more radiogenic than the average crust, component.

Each point along the pelitic paragneiss array in Figure 3-2 yields a different age of extraction from the mantle. This is demonstrated by the different Nd model ages of the whole rocks (Figure 3-3). Representative Sm/Nd ratios for the pelitic paragneisses can be calculated from the intersection of the data array with depleted mantle reference isochrons of the appropriate model age. These points of intersection are illustrated in Figure 3-2. For example, the intersection of the ~1.7 Ga greenstone data array with the pelitic paragneiss array defines a representative bulk composition for the pelitic paragneisses if they were extracted from the mantle at ~1.7 Ga. In other words, the intersection defines a center of rotation for isotopic equilibration of
a closed system extracted from a depleted mantle ~1.7 Ga ago.

For model ages of 1.6 Ga and greater, the time-integrated Sm/Nd ratio of the pelitic paragneisses is greater than that of typical shales as well as average crust in New Mexico as shown in Figure 3-2. Increasing the duration of crustal prehistory increases the time-integrated Sm/Nd ratio as does ultimate extraction from a less depleted mantle. Possible interpretations of this result are that the protolith was more juvenile and hence higher in Sm/Nd than typical shales or that the paragneisses have undergone REE modification during high grade metamorphism. Immature arc detritus is a likely example of more Sm/Nd enriched sediments. However, the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the pelitic paragneisses as well as their high K/Na ratios (Chapter 4) are difficult to reconcile with such an origin. Therefore, it more likely that Sm/Nd was fractionated somewhat during granulite metamorphism.

For a crustal extraction age of ~2.0 Ga, a representative time-integrated Sm/Nd ratio of the pelitic paragneisses is 0.145 similar to that of two of the pelitic paragneisses and many of the layers. If Sm/Nd was lower prior to granulite metamorphism, the time-integrated ratio slightly underestimates that of the granulite. For example, if the protolith had a Sm/Nd ratio equivalent to that of shales, the Sm/Nd of the granulite must be ~0.005 higher for each 100 Ma of crustal prehistory in order yield the effective time-integrated ratio.

$Th-Pb$ Time-integrated $^{232}\text{Th}/^{204}\text{Pb}$ ratios for the pelitic paragneisses are conservatively less than 40 (Figure 3-5) based on the intersection of a 1.6 Ga reference isochron through conformable lead (Stacey and Kramers, 1975) and the data array defined by the whole
rocks. If the Th/Pb ratio was unchanged by granulite metamorphism and \( \mu \) was that predicted from the modelling of the U-Pb data (13-16), the Th/U ratio implied for the protolith is less than \( \sim 3 \), lower than that of likely crustal equivalents. This proposition differs from our previous suggestion that it may be unchanged because of evidence that U may have been depleted by much more than a factor of 3. One explanation for this is that the Th/Pb ratio in the paragneisses was higher prior to granulite metamorphism than that measured today and that Th may have been depleted by this event.

If the protoliths had a Th/U ratio of 4.3 (McLennan and Taylor, 1980), a crustal prehistory of 0.65 Ga (from U-Pb model) and consequently, a \( \text{\\^{232}Th}/\text{\\^{204}Pb} \) ratio of 62, the intersection of the resulting reference isochron and the Th-Pb data of the pelitic paragneisses defines a lower limit for \( \text{\\^{232}Th}/\text{\\^{204}Pb} \) in the paragneisses of 15 as shown in Figure 3-5. For a crustal extraction age of 2.0 Ga, \( \text{\\^{232}Th}/\text{\\^{204}Pb} \) predicted for the paragneisses is 20, lower than that of most sediments (White et al., 1985; Church, 1973; Sinha and Hart, 1972). According to our model of the crustal prehistory of the paragneisses, Th has probably been depleted somewhat from its precursors.

7K3

The Nd isotopes of sample 7K3 are isotopically similar to the lower to middle Proterozoic crust delimited by the data of Nelson and DePaolo (Nelson and DePaolo, 1985, DePaolo, 1981) shown in Figure 3-2. Moreover, the trend of the Sm-Nd data of 7K3 crosses that of the greenstones at ratios similar to that of typical shales and crust.
Therefore, the isotopic compositions of 7K3 is consistent with a Nd model age of \(-1.7-1.8\) Ga and with a Sm/Nd ratio indistinct from that of average crust. If this is true, the xenolith itself is somewhat enriched in garnet relative to its source. On the other hand, the relatively high initial ratio of 7K3 may require a more protracted period of crustal prehistory (e.g. 0.6 Ga if \(^{87}\text{Rb}/^{86}\text{Sr}=0.5\)). Longer periods of crustal prehistory would implicate a higher representative Sm/Nd. In any case, its extremely low \(^{87}\text{Rb}/^{86}\text{Sr}\) ratio today probably requires Rb loss during granulite metamorphism.

**COMPARISON TO OTHER GRANULITE LOCALITIES**

The isotopic characteristics of the Kilbourne Hole xenoliths (principally the pelitic paragneisses) are compared to those of other granulites in Figures 3-7 and 3-8. Included in these figures is our best estimate of the isotopic characteristics of a representative pelitic paragneiss reservoir (Chapter 4). Relative to the bulk earth, the paragneisses are enriched in \(^{87}\text{Sr}/^{86}\text{Sr}\) and depleted in \(^{143}\text{Nd}/^{144}\text{Nd}\) as shown in Figure 3-7. They fall to the right of average upper crust indicating that, at least in terms of Nd and Sr isotopes, the paragneisses are indistinguishable to more enriched in \(^{87}\text{Sr}/^{86}\text{Sr}\) that the upper crust. This is contrary to models of a chemically stratified crust in which the lower crust becomes increasingly unradiogenic in \(^{87}\text{Sr}/^{86}\text{Sr}\) with time. In this regard, the pelitic paragneisses are similar to more radiogenic in Sr than most granulites studied by Ben Othman and others (1984). The pelitic paragneisses and modern sediments have roughly similar crustal residence times resulting in roughly
Figure 3-7

$^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for Kilbourne Hole xenoliths. Symbols as in Figure 3-1. Circled star indicates our estimate of the representative isotope characteristics of the pelitic paragneisses. Right hand axis shows Nd model ages ($T_{DM}$) assuming $^{147}\text{Sm}/^{144}\text{Nd} = 0.117$ (average crust) and extraction from a depleted mantle (evolution curve taken from Ben Othman et al., 1984). Also shown are fields of Proterozoic and younger granulites (Ben Othman et al., 1984) and pelagic and accretionary sediments (White et al., 1985). Representative lower, total, and upper crustal characteristics are calculated from parent-daughter ratios from Taylor and McLennan (1985) for a continuum of ages assuming extraction from a depleted mantle.
similar $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. In spite of this, by virtue of their residence in a closed system with higher Rb/Sr than that of the average crust, the paragneisses are even more enriched in $^{87}\text{Sr}/^{86}\text{Sr}$ than modern pelagic and some arguably atypical accretionary sediments (Figure 3-7).

Figure 3-8 compares the Pb isotopic characteristics of the Kilbourne Hole paragneisses to those of other granulites. With the exception of the Bournac xenoliths which were metamorphosed in the Phanerozoic, the granulites fall to the left of the geochron indicating evolution in an environment which had a time-integrated $\mu$ less than that of the bulk earth. Moreover, the Pb model ages for the least radiogenic members of each suite are very similar to the metamorphic ages for these granulites, indicating the extreme nature of U-depletion during granulite metamorphism. Unlike most of the other granulites, the Kilbourne Hole paragneisses and Lewisian orthogneisses fall below the conformable lead data array. As for the Lewisian orthogneisses, which had a short crustal residence time prior to granulite metamorphism (Moorbath et al., 1969), and in contrast to the Fyfe Hills granulites which were metamorphosed well after crustal extraction (DePaolo et al., 1982), the relatively unradiogenic $^{207}\text{Pb}/^{204}\text{Pb}$ of the pelitic paragneisses supports our interpretation that the pelitic paragneisses had a fairly short crustal residence time prior to metamorphism.
Figure 3-8

$^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram for field of Kilbourne Hole pelitic paragneisses and one layer from sample 7K3 (KH) and fields of other granulite localities (DePaolo et al., 1982; Tilton and Barreiro, 1980; Gray and Oversby, 1972; Moorbath et al., 1969; Michard Vitrac et al., 1981). Circled star is estimate of the representative Pb isotope characteristics of the pelitic paragneisses. Conformable lead array from Stacey and Kramers (1975); tic marks indicate 0.5 Ga.
SUMMARY AND CONCLUSIONS

Compositional Stratification and the Effect of Granulite Metamorphism

Orthogneisses from both the lower and middle crust are relatively unradiogenic in \( \frac{87\text{Sr}}{86\text{Sr}} \). In the case of the lower crust, this probably indicates a depletion in Rb with respect to Sr as indicated by low to extremely low Rb/Sr ratios. In the case of the middle crust, relatively unradiogenic \( \frac{87\text{Sr}}{86\text{Sr}} \) may indicate that it is relatively mafic since appropriately low Rb/Sr ratios correlate with SiO\(_2\) contents of ~50%. Thus, there is no evidence for an appreciable Precambrian enrichment in Rb in the middle crust as might be expected if this element was expelled from the lower crust during crustal stabilization. The intriguing possibility that Rb-enrichment may have occurred in the last ~300 Ma remains to be explored.

The pelitic paragneisses from Kilbourne Hole are not depleted in Rb/Sr and are amongst the most radiogenic in \( \frac{87\text{Sr}}{86\text{Sr}} \) of granulites analyzed to date. In addition, they retain the \( \delta^{18}\text{O} \) signatures of their protolith. At the other extreme, the pelitic paragneisses are significantly depleted in U with respect to Pb resulting in unradiogenic \( \frac{206\text{Pb}}{204\text{Pb}} \) and \( \frac{207\text{Pb}}{204\text{Pb}} \) isotope signatures approaching those of their model ages. The pelitic paragneisses are slightly more radiogenic in \( \frac{143\text{Nd}}{144\text{Nd}} \) than expected from their age, possible evidence for a small depletion in Nd with respect to Sm. In addition, they may be somewhat depleted in Th with respect to Pb. On the whole however, with the exception of uranogenic Pb, the pelitic paragneisses are indistinguishable to more radiogenic and heavier in \( \delta^{18}\text{O} \) than comparable
lithologies of the upper crust. Estimates for Sr concentrations in the lower crust (Taylor and McLennan, 1985) are subequal to that of the paragneisses. As can be discerned from Figure 3-7, volumetrically insignificant quantities of pelitic materials in the lower crust (e.g. 10%) can have a significant effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ budget of the crust. Therefore, estimates of the trace element and isotopic budget of the lower crust are critically dependent on accurately assessing the relative abundance of pelitic paragneisses and comparable lithologies in that reservoir.

*Duration of crustal prehistory and role of tectonics in evolution of the lower crust*

The southward younging of metamorphic terranes in Precambrian to Paleozoic basement rocks of the Central U.S. exemplifies the concept of crustal growth by lateral accretion. Accordingly, material newly extracted from the mantle in volcanic arcs as well as terranes of older, recycled material are accreted to the leading edges of continental masses. Cenozoic analogies to this process are evident in the amalgamation of allochthonous terranes in the circum-Pacific. If anorogenic granitoids analyzed by Nelson and DePaolo (1985) are indeed crustally derived, the fact that their Nd model ages cluster around 1.9 Ga indicates that a large tract of crust was extracted from the mantle within a relatively short period of time. Working on the assumption that significantly older crust has not gone undetected, Reymer and Schubert (1986) and Patchett and Arndt (1986) have shown that the rate of crustal extraction during the early Proterozoic markedly exceeded
that of modern volcanic arcs. Clearly, a consanguineous origin for the lower crust of southern New Mexico would lend support to this result.

Considered en toto the isotopic data for the Kilbourne Hole xenoliths are consistent with mantle extraction ages for their precursors of ~2 Ga. In the case of the pelitic paragneisses, the range in permissible ages is also consistent with a provenance of relatively young orogenic materials from the newly constructed crust. However, the fact that their sedimentary protolith may have been locally derived should not be taken as definitive evidence that early Proterozoic materials were in place in the lower crust during its construction. This is true only if the sediments were added by deposition rather than emplaced by tectonic means. Burial by overthrusting during crustal shortening provides a means of transporting appreciable quantities of sediment to the lower crust and keeping them there so long as the amount of crustal thickening is insufficient to produce uplift and erosion. In southern New Mexico, low to medium grade metamorphic Precambrian basement appears to prohibit the likelihood of significant uplift. Further, the lack of unequivocal evidence for partial melting during granulite metamorphism of the paragneisses (Chapter 4) also suggests a high P, moderate T trajectory during prograde metamorphism, consistent with limited crustal thickening. By analogy to modern environments, underplating of accretionary sediments at convergent margins would satisfy these constraints.

The existence of relatively siliceous lithologies such as the paragneisses and silicic orthogneisses from Kilbourne Hole in the lower crust contravenes conventional wisdom which holds that the lower crust
is a relatively mafic residuum of melt and LILE extraction. Isotopic data like those presented here and by Ben Othman and others (1984) as well as other geochemical and geophysical evidence (summarized by Weaver and Tarney, 1984 and Smithson and Brown, 1977) suggest that in many respects, the lower crust may not be dramatically different from the upper crust. Kay and Kay (1985) have proposed a relatively mafic lower crust for intraoceanic volcanic arcs. If such arcs are representative of the milieu from which new crust is ultimately shaped, tectonic transfer of upper crustal materials to the lower crust seems the only viable means of effectively rehomogenizing the crust. As a consequence of this process, geochemically significant quantities of sediments may be emplaced in the lower crust. With regard to the radiogenic isotopes, the relative durations of crustal prehistory and granulite history will especially determine the degree of \( \frac{^{207}\text{Pb}}{^{204}\text{Pb}} \) and \( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \) and to lesser extent, \( \frac{^{208}\text{Pb}}{^{204}\text{Pb}} \), \( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \), and \( \frac{^{143}\text{Nd}}{^{144}\text{Nd}} \) differentiation between the lower and upper crust.
REFERENCES


Chapter 4

GEOCHEMICAL CONSTRAINTS ON THE CONTRIBUTION OF METASEDIMENTARY ROCKS TO THE LOWER CRUST: PARAGNEISS XENOLITHS FROM KILBOURNE HOLE, NEW MEXICO
INTRODUCTION

Recent geophysical surveys of the lower crust have recognized the preponderance of structural heterogeneities there (Oliver, 1978 and 1982 and references therein). Isotopic and geochemical studies of granulitic xenoliths and terranes have shown that the lower crust may be markedly more like the upper crust than previously thought (Ben Othman et al., 1984; Dupuy et al., 1979; Leyreloup et al., 1982; Barbey and Cuney, 1982; Gray, 1977; Sighinolfi et al., 1981; Iyer et al., 1984). When considered in light of increasing evidence for the importance of crustal recycling in the evolution of the crust since the Archean (Armstrong, 1981; Allegre and Ben Othman, 1980; O’Nions and Hamilton, 1981; Veizer and Jansen, 1979; Allegre and Rousseau, 1984), these data may ultimately be interpretable in terms of tectonic reprocessing of an initially igneous crustal milieu.

Amongst the suite of lower crustal xenoliths at Kilbourne Hole are lithologies which had sedimentary protoliths. These paragneisses, as well as evidence for supracrustal precursors in many granulite terranes, exemplify the importance of tectonic and sedimentary processes in shaping the composition of the lower crust. Certainly, some granulite-grade terranes reflect relics of a cycle of crustal thickening which are returned to the surface by erosion. However, other occurrences clearly indicate that paragneisses can be stabilized in the lower crust (e.g. Bournac pipe xenoliths, Leyreloup et al., 1977; granulite terranes summarized by Fountain and Salisbury, 1981). As such, the lower crust may provide a repository for convergent margin sediments which are neither added to accretionary prisms nor subducted into the mantle.
When considered in the framework of tectonic processes, it is easy to envision significant sediment incorporation into the lower crust during crustal growth by underplating at convergent margins. This could occur both on a continuous basis during subduction of oceanic crust and catastrophically by amalgamation of arc terranes through plate collision.

Previous workers have often paired the concepts of LILE-depletion during granulite metamorphism and low radiogenic heat production in the lower crust. Accordingly, it is argued that U, Th and possibly K are transported to higher levels of the crust during granulite metamorphism (Heier, 1973; Lambert and Heier, 1967; Fyfe, 1973; Moorbath, 1975) resulting in an enriched upper crust-depleted lower crust dichotomy; partial melting, dehydration and decarbonization reactions, and hydrothermal circulation have all been invoked to account for this (Lachenbruch, 1970; Newton et al., 1980; Albarede, 1975; Jaupart et al., 1981). Increasingly, attention is being focussed on the importance of bulk composition in determining the ultimate extent to which this depletion occurs (Tarney and Windley, 1977; Rollinson and Windley, 1980; Rudnick et al., 1985). Because of their fertility both as sources of minimum melt and radiogenic heat production, the geochemical response of sedimentary lithologies to high grade metamorphism is therefore important in understanding the efficacy of metamorphic processes leading to compositional stratification in the crust.

The Kilbourne Hole paragneisses were extracted from a range of depths (20-30 km) (Padovani and Carter, 1977) and thus are likely to represent more than local occurrences. In this paper, we focus on those
granulites which were probably once shales, i.e. the pelitic paragneisses. The paragneisses have attained their chemical characteristics by a procession of igneous, sedimentary, and metamorphic reconstitutions. In addition, like many unmetamorphosed sedimentary equivalents, the paragneisses are compositionally stratified. Thus, the xenoliths reflect a mere fraction of a reservoir which is heterogeneous in both time and space. By a twist of kinematic fate, the Nd but not Sr isotope systematics have been partially reequilibrated within the last 30 Ma (Chapter 1). We have used these isotopic features to our advantage both in Chapter 1 to establish the metamorphic age of the lower crust and in Chapter 3 to realize a representative time-integrated Sm/Nd ratio for the paragneisses as a whole.

Although our sample population is small, the samples exhibit a considerable range of systematic internal variation. Our principal interest is in understanding the origins of these variations and the implications of these variations for the residence sites and behavior of the trace elements during high grade metamorphism. In particular, since pelitic sediments are hydrous and rich in minimum melt components, we consider the efficacy of partial melting in their dehydration and metamorphism. As will become evident in this paper, much of the compositional variation in the paragneisses can be reduced to two-component arrays, prompting us to reconstruct the composition of a representative pelitic paragneiss reservoir (RPP) using the time-integrated Sm/Nd as one point of reference. In parallel fashion, we estimate likely supracrustal equivalents in order to constrain the extent of differentiation during metamorphism. Finally, we evaluate our
estimate for the composition of the RPP in terms of their contribution to the lower crust and as an analog to subducted sediments.

The geologic setting of the Kilbourne Hole maar is reviewed in Chapter 1. As also discussed there, the thermal effects of transport in the magma were evidently minimal due to the short ascent times. Therefore, the chemical characteristics of the paragneissess are those extant in the lower crust at the time the paragneisses were transported to the surface. As demonstrated by mineral equilibria at temperatures of 750-950°C (Padovani and Carter, 1977) and by mineral-scale isotopic equilibration (Chapter 1), the distribution of elements between minerals probably reflects relatively recent (<30 Ma) equilibration to a high geothermal gradient as a result of Rio Grande rifting.

SAMPLE DESCRIPTIONS

The spectrum of crustal xenoliths at Kilbourne Hole and their depth of origin are described by Padovani and Carter (1977) and Padovani et al. (in prep.). The general constitution and physiognomy of the samples discussed in this paper are largely covered in Chapter 1. All samples contain sillimanite, garnet, plagioclase, sanidine, and quartz, with accessory apatite, rutile, and zircon. Other accessory mineral(s?) are probably present as discussed below. The samples are visibly zoned. This feature is evident in the virtually monotonic variations in the Sr isotope data presented in Chapter 1. This extent of internal variation in the xenoliths was documented by analyses of individual layers cut from each sample as described in Chapter 1.
ANALYTICAL TECHNIQUES

Geochemical data for the paragneiss layers are given in Table 4-1. The means of isotopic and companion trace element determination are described in Chapter 1. In addition, Cs, K, and Ba were determined by isotope dilution as described by Hart and Brooks (1977). Major elements were determined by XRF at the University of Massachusetts at Amherst. In some instances, Na$_2$O was determined by INAA as indicated in Table 4-1.

MAJOR ELEMENTS

Evidence for a Shale Protolith

Because we want to use the characteristics of pelitic sediments as a reference frame, it is essential to establish that the compositions of the paragneisses most closely approximate those of shales. The average shale line in Figure 4-1 illustrates the major evolutionary change which occurs as igneous rocks become shales: the initial dissolution of Na followed by the development of clay minerals (e.g. illite) with an increase in $K_2O/Al_2O_3$ and $K_2O/Na_2O$. Thus, the sedimentary nature of the xenoliths is evident from their relatively high $K_2O$ and $Al_2O_3$ contents and high $K_2O/Na_2O$ and $Al_2O_3/SiO_2$ ratios; the mineralogical expression of this is the presence of an aluminosilicate, in this case, sillimanite. Some of the xenolith layers fall outside of the fields of sediments although the only bulk composition outside of the circumscribed region is that of sample 79K6. As also shown in Figure 4-1, partial melting trends for sedimentary compositions are transverse to that of average shale and drives the residua towards the compositions of many of the
<table>
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<th>Table 4-1 Major and Trace Element Geochemistry of the Kibuline Hole Pelitic Paragneisses</th>
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<td>Year</td>
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<tr>
<td>Suma</td>
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<tr>
<td>Sto2</td>
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<td>TiO2</td>
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<td>Na2O</td>
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<td>P2O5</td>
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**Note:**
- Suma = Sto2 + TiO2 + Al2O3 + FeO + MnO + MgO + CaO + Na2O + K2O + P2O5

**Normative Mineralogy (weight %):**
- Plagioclase = 27.0 | 20.7 | 7.2 |
- Sillimanite = 2.1 | 1.6 | 1.5 |
- Quartz = 19.8 | 28.5 | 27.3 |

**Mineral Abundances:**
- K feldspar: 3.33 | 2.32 | 2.48 |
- Rb: 13.1 | 14.2 | 14.8 |
- Ca: 0.06 | 0.06 | 0.03 |
- Sr: 396.3 | 279.8 | 184.9 |
- Ba: 1049 | 994 | 1146 |
- Nd: 29.48 | 28.61 | 25.45 |
- Sm: 4.40 | 3.62 | 6.62 |
- U: 0.24 | 0.38 | 0.31 |
- Th: 1.37 | 1.15 | 1.56 |
- Pb: 17.57 | 13.43 | 13.86 |

**Other Elements:**
- Sm/Nd: 0.14 | 0.19 | 0.26 |
- Nd/Th: 21.52 | 24.88 | 9.94 |
- Th/U: 5.68 | 2.99 | 7.51 |
- K/Nd: 1130 | 809 | 976 |
- K/Rb: 345 | 286 | 262 |
- K/U (10^3): 1382.6 | 602 | 72.9 |
- K/Ce (10^3): 546 | 502 | 657 |
- Ba/Sr: 84.1 | 82.8 | 147.1 |
- Ba/Pb: 10.6 | 10.6 | 11.1 |

**Notes:**
- All abundances determined in ppm.
- Abundances recalculated to weight percent.
- *Sum of composition of layers weighted according to relative layer thickness.*

"Abundances of the major phases determined by inversion of the oxides in molar proportions using the following compositions: Garnet=(Na,Fe)O, Ga=Ca+Mg, Al=Si=O2; Plagioclase=CaO.64SiO3; Sillimanite=(Al2Si3O8); and Quartz=SiO2. Molar abundances recalculated to weight percent."
Figure 4-1

Na$_2$O/Al$_2$O$_3$ versus K$_2$O/Al$_2$O$_3$ (wt. ratios) for sample layers which comprise the Kilbourne Hole paragneisses. Average shale line and lower limit for igneous rocks from Garrels and Mackenzie (1971, p.229). Also shown are fields of shales (including 90% contour line) and Archean and post-Archean sandstones as defined by data of Nance and Taylor (1976, 1977) and Maynard et al. (1982). Diagonal lines labelled with sample numbers illustrate effect of addition of a minimum melt component (White and Chappell, 1977) to bulk xenolith compositions indicated by open symbols. Tic marks indicate increments of 10% melt addition.
ARCHEAN SANDSTONES

IGNEOUS ROCKS

MINIMUM MELTS

SANDSTONES (except Archean)

SHALEs

AVERAGE SHALE LINE

K2O/Al2O3

Na2O/Al2O3

1977

79K6

1975

ILLITE

90%
Figure 4-2

SiO$_2$/Al$_2$O$_3$ versus CaO+Na$_2$O/K$_2$O for Kilbourne Hole paragneisses compared to sandstones and shales. Only summed whole xenoliths are shown for each sample; symbols as in Figure 4-1. Igneous trend taken from Garrels and Mackenzie (1971). Sources for sandstone and shale data and for minimum melt compositions same as for Figure 4-1.
sandstones
shales

\[ \text{minimum melts} \]

\[ \text{igneous trend} \]
paragneiss layers.

On a diagram of $\text{SiO}_2/\text{Al}_2\text{O}_3$ versus $(\text{CaO} + \text{Na}_2\text{O})/\text{K}_2\text{O}$ (Figure 4-2), the general compositional difference between sandstones and shales is seen. Relative to the trend of igneous rocks, sandstones fall to higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{CaO}+\text{Na}_2\text{O}/\text{K}_2\text{O}$ while shales fall to lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{CaO}+\text{Na}_2\text{O}/\text{K}_2\text{O}$. Igneous rocks are effectively partitioned into sandstone and shale components upon weathering. The ordinate in this diagram is essentially an expression of the quartz to clay abundance ratio, while the abscissa is an expression of the plagioclase feldspar to potassium feldspar or clay abundance ratio. The Kilbourne Hole paragneisses fall below the igneous trend and, as can be seen from the diagram, even if we factor in the effect of melt extraction, cannot have originated in the sandstone field.

Internal compositional variation - possible origins and implications

The Kilbourne Hole paragneisses have arrived at their compositions at the hands of igneous, sedimentary and metamorphic processes. These processes act in kind on both mineralogical and major element domains. In this section, we explore what constraints the internal compositional heterogeneity of the paragneisses imposes on the evolution of the paragneisses. Specifically, in light of the Nd isotope evidence for a possible disparity between the time-integrated $\text{Sm/Nd}$ ratio of the RPP and the $\text{Sm/Nd}$ ratio of typical shales as well as Pb isotope evidence for $\text{U/Pb}$ and possible Th/Pb fractionation (Chapter 3), we are particularly interested in the role of partial melting in creating and/or modifying this compositional spectrum.
The Kilbourne Hole paragneiss layers exhibit an extremely large range in major element variation (Table 4-1). In order to consider all of the major elements simultaneously we have inverted them into ideal or nonideal endmembers, analogous to normative mineralogy calculations. Figure 4-3 is a modified A'KF diagram. The data are normalized in terms of the ideal endmembers corundum (Al=AlO$_{1.5}$) and FeO+MgO+MnO (Fmo) and a nonideal feldspar-like endmember (Fsp=(K,Na)AlO$_2$-Ca$_{0.5}$AlO$_2$), and projected through SiO$_2$. The feldspar component is essentially the ideal endmember KAlO$_2$: the low concentrations of CaO and Na$_2$O in these samples probably do not significantly affect the stability of any of the minerals represented in this composition space (Thompson and Thompson, 1976).

As seen in Figure 4-3a, the projected compositions of layers from the pelitic paragneisses fall in the field of sillimanite-feldspar-garnet, consistent with their mineral constituents. Although not shown in Figure 4-3, the projection scheme successfully discriminates between those Kilbourne Hole garnet granulites which are pelitic in origin and those which are not, the latter falling below the feldspar-garnet join. Many of the layers fall within the field of projected shale compositions; only sample 79K6 considered as a whole falls outside (Figure 4-3b). The discrepancy between this sample and typical shales may be accounted for by sampling bias if adjacent, more felsic layers are capriciously absent. On the whole, those pelitic paragneiss layers within the shale field are indistinguishable to somewhat more Al-, Fe-, and Ti-rich and Si- and Mg-poor than most shales.

The most striking feature to emerge from this projection scheme is
Figure 4-3

Modified AK'F [Corundum (Cor)-Feldspar (Fsp)-FeO+MgO+MnO (Fmo)] ternary projection of the Kilbourne Hole paragneisses and of reference sedimentary and paragneiss data. Compositions are projected from SiO₂ as discussed in text and are in mole %. a) Kilbourne Hole paragneiss layers. Symbols as in Figure 4-1. Garnet projection is of analysis of garnet from sample 1977 (Reid, unpublished data). b) Representative sediment analyses (numbered) and fields of Kilbourne Hole paragneisses, Archean/Proterozoic boundary sediments (dashed; McClennan et al., 1979; Taylor and McLennan, 1983), and sandstones and shales (data sources in Figure 4-1). Numbered analyses and their sources are (ss:-sandstones; sh:-shales): Immature sediments: 1-4: (sh) Sugisaki, 1980; 4-6: (ss) Barbey et al., 1982; Mature sediments: 7-8: (ss,sh) Calvert 1976; 9-10: (ss,sh) Van de Kamp et al., 1976; 11: (sh) Pettijohn, 1969; 12: (ave.) Calvert, 1976; Pelagic: 13-15: (ss,sh,sh) El Wakeel and Riley, 1961; 16-17: (ave.) Goldberg and Arrhenius, 1958; El Wakeel and Riley, 1961. c) Paragneiss xenoliths from Le Bournac pipe (circles) and paragneiss granulites from Fennoscandia compared to fields of Kilbourne Hole paragneisses and of representative sediment analyses (from b)). Data sources: Fennoscandia [Barbey et al. (1982); Merilainen (1976); Eskola (1952)]; Le Bournac [Leyerloup et al. (1977); Dupuy et al. (1979)].
c.

- COR
- SILL

BOURNAC

KILBOURNE HOLE

MIN. MELT

FSP

GARNET

FENNOSCANDIA

REPRESENTATIVE SEDIMENTS
the adherence of the data array to a linear trend. The data array projects towards feldspar at one end and towards an approximately 2:1 mix of garnet and sillimanite at the other (Figure 4-3a). Of particular note is the fact that the variations across each xenolith are monotonic: no reversals in compositional trend occur. We obtained Rb-Sr isochrons of middle Proterozoic age (Chapter 1) by taking advantage of this feature. The fact that meaningful isochronous relationships are retained by the paragneisses indicates the likelihood that composition zonation was not created or modified during recent rifting-related reactivation of the lower crust. Two possible explanations of this trend are original sedimentary layering and partial melting associated with original metamorphism of these samples. It is reasonable, perhaps even likely, that both of these processes have occurred to varying degrees and their effects are superimposed. As the following discussion is intended to illustrate, it is inherently difficult to distinguish arrays produced by sedimentary processes from those produced by partial melting.

The trends in the major elements across the xenoliths may reflect initial sedimentary compositional variations. Compositional variations within sedimentary units are most easily envisaged in terms of graded beds which effectively reflect mixtures of clays and more clastic materials. Unfortunately, we know of no comparably detailed geochemical studies of centimeter scale variations in turbidites. The range in clay compositions alone span the compositional space represented in the projection scheme. Accordingly it would appear unlikely that clastic materials containing abundant feldspar (or clay equivalents) would be
mixed with pelitic materials composed of fixed relative abundances of chlorite and kaolinite. Therefore, it is somewhat surprising that over a dozen averages of various sedimentary lithologies define a linear array in our projection scheme. While this array, as well as the compositional field of shales in general, intersects the Fsp-Fmo join at more Fmo-enriched compositions than expected of minimum melt, it parallels our paragneiss data array. Limited data for fine-grained and shaly sediments from the Archean-Proterozoic boundary are more corundum-normative than these averages and form an array which coincides with that of the paragneisses. Thus, it is at least conceivable that the data array of the paragneisses could have been generated by sedimentary processes; this interpretation only requires that some of the layers become extremely clay-rich.

Recent work on the granulite grade paragneisses of Fennoscandia by Barbey and others (1982) favor just such an interpretation albeit their sampling reflects a much larger scale. The trend of data for the Fennoscandia paragneisses (Figure 4-3c) diverges from ours and may be more properly considered to be a mixing array between the sedimentary equivalents of feldspar and garnet. Paragneiss xenoliths from the Bournac pipe exhibit a compositional trend subparallel to our own but displaced to lower normative corundum, coincidental with that of modern sediments.

A geologically compelling explanation for the linear data array involves partial melting in some fashion. The compositions of the Kilbourne Hole paragneisses fall within the stability fields of biotite and/or muscovite. Abundant field, theoretical and experimental evidence
exists for the production of a partial melt during the dehydration of biotite and muscovite at high pressures in the crust (Thompson, 1982) which may explain the absence of these phases in the rocks today. Thompson (1982) also presents arguments that minimum melt compositions should fall within both the muscovite-biotite-ksp and ksp-cordierite-garnet fields while the loci of putative minimum melt compositions (White and Chappell, 1977) are virtually coincident with the feldspar apex (Figure 4-3). Thus, partial melting will drive shale compositions away from this apex and the trend of the Kilbourne Hole paragneiss data could be viewed as a melting array.

It is worth considering the kinematics of producing the observed compositional heterogeneity by partial melting at the same time we consider the combined effects of initial compositional heterogeneity and partial melting. While the observed compositional trends suggest that variable amounts of partial melt have been removed from a relatively homogeneous metasediment, this was almost certainly not the case. Such a process would require thermal gradients or kinetically controlled processes to be established on a decimeter scale. On the other hand, extraction of a melt from a heterogeneous metasediment whose compositional trend is coincident to that of a melting trend would probably diminish the extent of compositional variation by driving the more feldspar-normative and therefore more fertile end of the array for partial melting towards the more refractory end.

It may also be kinematically reasonable to consider a process of melt extraction which is variable in extent across the xenoliths. If this occurred as melts coalesced into conduits to be volumetrically
extracted or simply "floated" into sills, the observed compositional trends would reflect two-component mixing arrays of melt and residuum. Possible analogs for such phenomena can be found in layered intrusions (Raedke and McCallum, 1980). Depending on the amount of melt which is physically removed from the system, some of the resulting layers could potentially be more enriched in feldspar components (i.e. frozen melt) than the protolith (e.g. layer 1 of sample 1977). Metamorphic overprinting would have largely erased any solid solution (e.g. FeO/MgO, CaO+Na₂O/K₂O) or trace element record of such a process within xenoliths themselves by mineralogical reequilibration at this scale. However, if individual xenoliths represent discrete domains of different degrees of melt extraction, it might ultimately be possible to elucidate the role of such a process by intercomparison of the xenoliths, but then only if the sedimentary starting material was approximately homogeneous with respect to major and trace element ratios. Our data base is insufficient for such an exercise at this time.

Partial melting trends in Figure 4-1 are at a high angle to the trend of most of the data and may be evidence against partial melting. However, the actual composition of melt in equilibrium with the paragneisses will depend on the relative abundance of plagioclase to potassium feldspar in the rocks. The minimum melts used in Figure 4-1 are probably in equilibrium with plagioclase. Samples 1975 and 79K6 are relatively poor in plagioclase components and therefore, a melt in equilibrium with these rocks may be more orthoclase-normative, i.e. have a lower Na/K ratio. Additionally, once plagioclase is effectively removed from the rock, reequilibration of the rock following melting
will produce a uniform Na/K just as observed in these two samples.

On the basis of compositional variations alone, we cannot distinguish the extent of initial compositional variation from that which resulted from partial melting in some fashion. Kinematic considerations preclude any simple process of melt extraction but, as suggested, somewhat ad hoc scenarios can be envisioned which could produce the observed compositional trends. Perhaps the only substantive argument that can be brought to bear against partial melting/partial extraction as a means of producing the compositional spread, at least as envisioned here, is the extent of melting required to produce the most depleted layer, 79K6-1. Depletion of this layer by partial melting of the feldspar-poor end of the shale composition field would require at least 40% extraction of a minimum melt composition (cf. Figure 4-1). Melting to this extent must occur at temperatures well above the water-saturated solidus and therefore requires extremely high temperature metamorphic conditions.

**Correlation with Sm-Nd: major element composition of the representative pelitic paragneiss (RPP)**

Implicit in the identity between the trend of the major element array of the pelitic paragneisses and a melt extraction curve is the fact that samples fortuitously biased in composition towards one end of the array will critically affect our ability to constrain the likelihood and extent to which melt extraction is required. In attempting to construct a representative composition for the pelitic paragneisses, the RPP, we acknowledge that the compositions of the individual xenoliths
may not be representative given the high degree of internal heterogeneity in the samples. Rather, we treat the range in observed composition as representative of a pelitic paragneiss domain in the lower crust and assume that metamorphic processes have acted homogeneously on this domain. The roughly linear array of data from a paragneiss terrane which is exposed at the surface (Fennoscandia, Figure 4-3c) and the fact that the data for the Kilbourne Hole paragneisses conform to a simple array (Figure 4-3a) suggest that a working composition for the RPP is a viable endeavor.

In a companion paper (Chapter 3), we delimited a probable Sm/Nd ratio for a representative pelitic paragneiss (RPP) on the basis of Nd isotope systematics. We concluded that the time-integrated Sm/Nd ratios of the paragneisses may be -0.24 (assuming a crustal prehistory of ~2 Ga) or ~20% higher than that of typical shales, possible evidence that the protoliths underwent partial melt extraction. On the other hand, equilibration with a melt may be precluded by the high REE abundances of the major phases in the KH xenoliths (Chapter 2) and the similarity between the REE abundances of the paragneisses and typical shales (Wandless and Padovani, 1985). Therefore, unless REE were modified in the paragneisses by some other means, a reasonable lower estimate for Sm/Nd in the RPP is that limit for most shales, i.e. ~0.18. In either case, most of the layers analyzed have equal or higher Sm/Nd ratios than these, indicative of sampling bias.

The compositional dependence of the Sm/Nd ratio is illustrated in Figure 4-4. In this diagram, the horizontal axis is a projection of the data array in Figure 4-3 onto the feldspar-garnet join (or FeO+MgO+MnO/
Figure 4-4

Correlation of Sm/Nd to the ratio of garnet:garnet+feldspar in the Kilbourne Hole paragneisses. Circled star indicates composition suggested to be representative of the paragneisses (RPP); other symbols as in Figure 4-1. Range in gar:gar+fsp in shales from Figure 4-3; range in Sm/Nd is 2σ of mean of isotope dilution or spark source mass spectrometry data from: O’Nions et al. (1983); Miller and O’Nions (1984); Nance and Taylor (1976); Nance and Taylor (1977); Michard et al. (1985); Patchett et al. (1984). Small stars indicate samples thought to contain an accessory phase (see text).
FeO+MgO+MnO+.5CaO+K0 .5+Na0 .5 in molar abundances). Most of the layers conform to a single curve, indicating that the Sm/Nd ratio of any layer is largely governed by the relative abundance of garnet and feldspar. Fractionation of Sm/Nd between these phases is generally that expected from considerations of mineral/liquid and mineral/mineral distribution coefficients for these phases (Hanson, 1980; Pride and Muecke, 1981).

Two, and possibly three, layers fall to the low Sm/Nd side of the array and are precisely those layers we have elsewhere (Chapter 3) inferred to contain an unknown accessory mineral. From the correlation of Sm/Nd to the gar:fsp ratio in this diagram, it is evident that our sampling is biased towards garnet-rich xenoliths and that the RPP is more enriched in feldspar components than our xenolith analyses. For Sm/Nd = 0.21 ±0.03 and gar:fsp = 0.28-0.34, we can reconstruct the major element composition of the RPP from the arrays of individual elements with respect to the gar:fsp ratio. This is given in Table 4-2.

Summary of the major element characteristics

Variations in major elements across the xenoliths are largely controlled by the relative proportions of feldspars to garnet plus sillimanite. The resultant compositional trend mimics both that amongst Proterozoic sediments and that expected of melt extraction from a relatively homogeneous shale. The absence of detailed sediment data on the one hand and of constraints on the kinematics of partial melting on the other hinders establishing the relative roles of these processes in producing the observed compositional variations. Based on likely Sm/Nd ratios for the RPP constrained by the isotope data and by typical shales
and the correlation between Sm/Nd and the major element array, we have estimated a range in possible major element composition for the RPP (Table 4-2). This composition falls within the compositional field of shale. Most of the analyzed layers are biased towards garnet and sillimanite and consequently are depleted in feldspar components relative to the RPP.

TRACE ELEMENT SYSTEMATICS

The presence of internal compositional variation in the xenoliths both complicates assessing how representative the xenoliths are of a metasedimentary reservoir in the lower crust and yet provides clues as to the mineralogical dependence of the various trace elements. In our view, the trace elements are passive during metamorphism, being merely reshuffled between minerals in which they are compatible as the phase assemblage changes with variations in pressure and temperature. In order to effectively use the isotopic signatures as absolute tracers of trace element behavior in the paragneisses, we need to recognize and look through the filter imposed by major elements and phase equilibria.

Our purpose in this section is principally twofold: first, to estimate the trace element characteristics of the paragneisses from the spectra of observed compositional variation and second, to compare them to likely sedimentary protoliths in order to establish how shale compositions may be modified during high grade metamorphism. While isotopic systematics can constrain time-integrated relative enrichments or depletions between parent-daughter pairs (Chapter 3), they cannot discriminate relative changes between the different isotope systems nor
constrain absolute trace element abundances. This latter aspect is particularly important for the heat-producing elements; sample bias could both overestimate or underestimate trace element concentrations, just as partial melting could have both enriched or depleted the various trace elements. Constraining considerations such as these will ultimately lead to an understanding of compositional stratification in the crust.

In the sections to follow we use the isotopic framework as a means of comparing the behavior of parent and daughter elements to each other and to elements of similar chemical affinities. Following a strategy already established in this paper, wherever possible, we reduce compositional variations in the Kilbourne Hole paragneisses to single arrays. These arrays must pass through the bulk composition of the system spanned by these arrays. Consequently, isotopic or intraelement ratio constraints can delimit possible ranges in trace element concentrations. In addition, where possible, we use known or inferred trace element abundances or their ratios in constitutive phases to delimit the effects of sample bias on measured concentration levels. In like fashion, we attempt to reconstruct possible characteristics of the shale protolith from what is currently known about their relative abundances in shales and the behavior of these elements during weathering and diagenesis. Although some of the systematics of trace element behavior in shales with respect to provenance and geologic time have been investigated (see recent summary by Taylor and McLennan, 1985), considerable latitude may still remain.
Sm and Nd

It is for the REE in particular that our goal of estimating a representative composition for the pelitic paragneisses and for likely protoliths merge. The REE behave as a relatively coherent group geochemically; thus, the systematics of relative and absolute abundances in fine-grained sediments are at least generally known. While subject to some speculation, the behavior of the REE during granulite metamorphism can also be predicted to a first degree. Moreover, in the case of the Kilbourne Hole paragneisses, Nd isotopes may provide an additional constraint. Therefore, these constraints are considered simultaneously in arriving at a set of possible solutions to the composition of the RPP and its protolith.

Paragneisses As shown by Figure 4-5, Nd concentrations in the paragneisses generally exhibit a limited and smooth variation with Sm/Nd and are generally higher in those layers containing the most feldspar (those with lower Sm/Nd). This result is consistent with ion probe analyses of garnet and the feldspars (Chapter 2). As previously discussed, reasonable estimates for the Sm/Nd ratio of the RPP are between 0.18 and 0.24. Using this range in Sm/Nd, the Nd content of the RPP can be estimated from Figure 4-5: reasonable Nd concentrations are 23 (extension of 79K6 array, excluding layer 4) to 36 ppm. Corresponding Sm concentrations are 4.1 to 8.6 ppm.

Protolith As seen in Figure 4-5, the proposed range in Nd concentrations for the RPP is well within that of most shales and clays (and particularly post-Archean shales which dominate the data field). Accordingly, it is reasonable to assume that the REE concentrations of
Comparison of Nd contents (ppm) and Sm/Nd concentration ratios of Kilbourne Hole pelitic paragneisses and shales and clays. Symbols same as in Figure 4-4 including circled star (RPP). Lines drawn through data suggest possible envelope of composition in the paragneisses. Data sources for sediments as in Figure 4-4. 70% of the data fall within a restricted portion of that field as shown. Plagioclase and sanidine fields drawn from preliminary ion probe data discussed in Chapter 2 and isotope dilution data summarized in Chapter 3. Line with tic marks labelled 4 and 10 is trend of possible parent compositions for various degrees of partial melting (increments of 4% and 10% melt extraction labelled) if the paragneisses are residues of partial melting. This trend was calculated from partition coefficients and mineralogy given in Table 4-2 and assumes that melt was in equilibrium with the mineral assemblage observed in the rocks today. Star indicates composition of paragneiss xenolith from lower crust in Chihuahua, Mexico (Nimz et al., 1986).
the protolith may have been similar to that of the paragneisses and that the REE were conserved during granulite metamorphism. On the other hand, if the Sm/Nd ratio of RPP is higher than that of typical shales, it may have been attained by extraction of a partial melt or some other LREE-enriched phase. The effect of partial melting may be considered by calculating the REE characteristics of melts in equilibrium with the modal mineralogy of the RPP at various degrees of partial melting and reconstituting the protolith. A limiting trace for the reconstitution of the protoliths is shown in Figure 4-5 and assumes that LREE-concentrating accessory phases were largely absent during partial melting (cf. Chapter 2). Consequently, these calculations probably underestimate somewhat the degree of partial melting required since LREE-enriched accessory phases generally have low Sm/Nd and therefore will buffer the effect of melting in changing Sm/Nd. At Sm/Nd ratios like that of typical sediments, Nd concentrations in the reconstituted protolith may be as high as 60 ppm. Although this Nd concentration is high, of 115 samples compiled for Figure 4-5, ~10% of these had Nd contents >50 ppm. Thus, the data is permissive of 10-15% partial melting and permissable Nd contents of the protolith could be as high as 60 ppm.

**U and Th**

*Paragneisses* As opposed to Nd, the Th systematics of the paragneisses are decoupled from the major elements and appear to be governed by the behavior of an accessory phase(s). Judging from locally high concentrations of Th, this mineral appears to occur sporadically.
Those layers with anomalously high Th also have higher than average Nd and are more LREE-enriched (Figure 4-6b). By analogy to other paragneisses, the accessory phase is probably monazite.

As seen in Figure 4-7a, the ratio of Th to Pb is wholly dependent on Th concentrations due to the fact that Pb concentrations are constant between the layers. From the intersection of likely reference isochrons and the trend of isotopic variation between the paragneisses, a reasonable range in Th/Pb ratios of 0.37 to 0.64 can be obtained for the RPP (Chapter 3). The $^{208}\text{Pb}/^{204}\text{Pb}$ characteristics of the different xenoliths overlap at Th/Pb ratios less than 0.2 suggesting that the lower end this range in Th/Pb may be more representative. From this we can estimate a representative Th concentration of 8 ppm in the RPP (ranging to 10 ppm as an upper limit).

U concentrations seem to be only minimally correlated to the major element variations. They are also significantly less dependent than Th on the abundance of the mystery accessory phase as shown by their lack of a pronounced change with Nd (Figure 4-6b). The variation in U between layers is amongst the most modest of any trace element. As result, the range in U/Pb ratios is small. Additionally, U/Pb ratios do not correlate between the xenoliths (Chapter 1), probably the result of variations in initial uranogenic Pb. Therefore, we cannot apply Pb isotope constraints as was done for Th. Instead, we propose that the concentrations measured are typical of the RPP and estimate a concentration of 0.4 ppm, drastically lower than that of any sediment (cf. Figure 4-6b).

Protolith The LREE and Th behave coherently in the sedimentary
Figure 4-6

Concentrations of heat-producing elements (Th, U, and K) relative to Nd in the Kilbourne Hole paragneisses. Symbols as in Figure 4-4. Also shown are fields of shale data of Nance and Taylor (1976; 1977) and Cretaceous-Recent clayey sediments from the western Atlantic, probably derived in part from Archean shield of South America (White et al., 1985). a) Th versus Nd; b) U versus Nd; c) K (wt. %) versus Nd.
Figure 4-7

Th (ppm) versus Th/Pb concentration ratio for Kilbourne Hole pelitic paragneisses illustrating dependence of Th/Pb ratio on Th concentration. Th concentrations vary widely and sporadically between layers, probably due to the presence of an unknown accessory phase. Dashed vertical lines indicate likely lower and upper limits on Th/Pb in the RPP based on the $^{208}\text{Pb}/^{204}\text{Pb}$ characteristics of the paragneisses (Chapter 3). From these Th/Pb ratios, the range in permissible Th concentrations of the RPP can be estimated.
cycle (McLennan et al., 1980) and therefore, Th abundances in the sedimentary protolith can be estimated by reference to Nd. Available data indicate a decrease in Nd/Th from 4 to 2 with increasing Nd concentration (Figure 4-6a) which probably correlates with increasing maturity of the source region (Bhatia and Taylor, 1981). For Nd concentrations like those of the RPP (29 ±6), the sedimentary protolith of the Kilbourne Hole paragneisses may have had 5.8 to 18 ppm Th. These values are inclusive of those of early to middle Proterozoic fine-grained sedimentary rocks (ave.=12.6 ±2.2 ppm) reported by McLennan and Taylor (1980). Our estimate for Th in the paragneisses is at the lower end of this range. As noted above, we prefer the low end of the range for RPP. Therefore, it appears likely that the RPP is depleted in Th relative to its sedimentary protolith. This is particularly true if the source of the sediments were fairly mature as their high K/Na ratios (cf. Figure 4-1) suggest.

U is a less conservative property of sediments owing to its solubility during weathering and diagenesis. Thus, its concentration is sensitive to both sediment maturity and source characteristics. Applying the Nd concentrations of the RPP yield likely U concentrations of 1.4 to 4.5 ppm in the sedimentary protolith. In any event, the drastic depletion of the paragneisses in U relative to sediments is evident (Figure 4-6b): the sedimentary protolith was depleted in U by a factor of at least three during metamorphism.
Sr and Pb

Paragneisses Both Sr and Pb are concentrated in the feldspars; hence, we consider them together. Isotope dilution analyses of plagioclase and sanidine separates somewhat diluted by quartz indicate Sr concentrations of at least 398 ppm and 655 ppm respectively (Chapter 1). The concentration of Sr in garnet measured by isotope dilution of a mineral separate from sample 79K6 is \( \leq 0.21 \) ppm (Reid, unpublished data). When plotted against Sm/Nd (Figure 4-8), the variation in Sr concentrations yields a smooth and strongly curved array consistent with the dominant control of feldspar on Sr behavior. The two layers shifted to the left of that array are those with anomalously low Sm/Nd for their bulk composition (cf. Figure 4-4). From the data array, we calculate a Sr concentration for the RPP of 225 ±100 ppm.

The Pb concentrations of all but one of the layers analyzed fall within a relatively restricted range of 10 - 20 ppm. Pb concentration in a sanidine separate from layer 2 of sample 79K6 on the order of 3 ppm (Chapter 1). If that layer has \(-6\) ppm (calculated from constant K/Pb of other layers), <5% of the Pb is contained in sanidine in this layer; the remainder is likely to be in zircon and therefore largely independent of Sm/Nd. Neglecting layers with extremely high Sm/Nd, the range in permissive Pb concentrations in the RPP is 12 - 20 ppm.

Protolith Like U, Sr is soluble during weathering and diagenesis giving rise to a range in Sr concentrations in shales although concentrations are typically less than 300 ppm (Dasch, 1969; Reimer, 1972; White et al., 1985; Turekian and Wedepohl, 1961) excluding metalliferous sediments. Therefore, assessing the extent of Sr
Figure 4-8

Sr versus Sm/Nd in the Kilbourne Hole paragneisses. Symbols as in Figure 4-4.
enrichment or depletion during granulite metamorphism on this basis alone is difficult. We estimate a distribution coefficient for nonmodal partial melting of the paragneisses equal to approximately 1. Therefore, unless Sr fractionated into a vapor phase at granulite-grade conditions, the similarity between Sr in the paragneisses and that of shales suggests that the Sr concentration estimated for the RPP may be subequal to that of their protolith.

Pb concentrations in terrigenous shales are often in the range of 10-20 ppm (average \(-18\) ppm; White et al., 1985; Church, 1973; Sun, 1980; Sinha and Hart, 1972), like those of our RPP. Since Pb can arrive in sediments by several pathways, it is not unreasonable to assume that concentrations in the protolith varied by this much and may be related to the fact that the initial isotopic signature of 79K6 is different from that of the other two samples (Chapter 3). Reconstituted \(\mu\)s based on estimated U loss are approximately 6-13, also reasonable for terrigeneous shales (average \(-8 \pm 6\)). Therefore, both Sr and Pb appear to be conservative properties of their protoliths during granulite metamorphism.

\textit{K, Rb, and Cs}

Potassium concentrations vary widely \((0.06 - 4.88\%)\) between layers of the Kilbourne Hole paragneisses. In a general way, K contents can be correlated with the relative abundance of garnet to feldspar but each xenolith forms a somewhat independent trend. The different trends probably result from the variable abundance of potassium feldspar and plagioclase between xenoliths. Consequently, when compared to Nd,
considerable scatter in K for Nd concentrations of 23 to 35 results. Some of this scatter may be the result of recent alkali addition to sample 1975 (Chapter 1). However, the bulk xenoliths define a roughly linear, but steep, array and yield possible K contents for the RPP of 2.0 to 3.7%. Similarly, the abundance of potassium in shales is variable owing to its tendency to both adsorb onto and be incorporated into clays during weathering and diagenesis. As seen from Figure 4-6c, the K contents of the Kilbourne Hole paragneisses range from lower to higher than many shales. Unless we discount sample 1975 on the basis that it may have undergone recent alkali enrichment (Chapter 1), it appears reasonable at this point to consider the K contents of the RPP subequal to that of shales.

K/Rb ratios in the paragneiss layers are remarkably constant and normal for crustal materials. Over all layers, K/Rb averages $262 \pm 26.9$ (1σ); only one layer has a K/Rb ratio greater than 300. Therefore we can estimate a Rb content for the RPP of 75 to 140 ppm. The K/Rb ratio of the RPP is somewhat higher than typical estimates for K/Rb ratios in shales of ~200 (Rudnick et al., 1985; Campbell and Williams, 1965) but similar to those estimates which suggest that Precambrian shales may have had higher K/Rb ratios (217-270: Leask, 1967 as reported in Heier and Billings, 1978; Reimer, 1972). Thus, Rb loss is not required by the data, although up to a factor of almost two loss of Rb during prograde metamorphism cannot be precluded (assuming that no depletion of potassium occurred as well). The K/Rb ratios of paragneisses are like granulite-grade paragneisses from Fennoscandia and the Adirondacks where K/Rb averages 272 (Barbey and Cuney, 1982; Whitney, 1969) and lower than
those of paragneisses from the Bournac pipe and the Valle Strona (K/Rb ~400; Dupuy et al., 1979; Dostal and Capedri, 1978).

The consistency of K/Rb between the paragneiss layers reflects the fact that sanidine is the major site for these elements in the paragneisses. It appears that the stability of K-feldspar throughout metamorphism and its appearance at the breakdown of biotite, another residence for K and Rb, probably contributes to the preservation of a generally crustal K/Rb ratios in felsic rocks (Rudnick et al., 1985). Evidence for a smooth increase in K/Rb ratios in metamorphosed shales with increasing metamorphic grade has been presented (Barbey and Cuney, 1982) and some depletion of Rb with respect to K would be predicted on the basis of equilibration of potassium feldspar with an aqueous fluid phase or a melt (Rudnick et al., 1985). Thus, Rb loss may occur prior to the onset of granulite facies metamorphism and may not require mobilization in a partial melt or other fluid at high grade metamorphism.

In contrast to Rb, Cs is dramatically depleted with respect to potassium. K/Cs ratios vary with K within xenoliths and range from 0.14x10^5 to 6.27x10^5, averaging 2.10x10^5. From this average, we calculate a RPP concentration of 0.10 to 0.18 ppm. These K/Cs ratios are amongst the highest reported for any rock type exclusive of other granulites (Heier and Brunfelt, 1970). For comparison, reported K/Cs ratios in marine sediments are on the order of 4x10^3 (Sinha and Hart, 1973; White et al., 1985) while that of the upper crust is about 7x10^3 (Taylor and McLennan, 1985). K and Cs contents in a plagioclase separate from sample 1977 (15600 ppm and 0.037 ppm respectively) yield a
K/Cs ratio of 4.2x10^5, like that of the whole rock. Assuming this is also approximately true of sanidine, it appears that potassium feldspar preferentially excludes Cs relative to K or Rb resulting in the selective depletion of Cs with respect to its fellow alkalis. Like U, Cs concentrations are relatively uniform within xenoliths and seem to be independent of bulk composition. Between xenoliths, U and Cs are positively correlated with one another. Because it is unlikely that any single mineral contains both of these elements, their abundances probably reflect an absolute level of depletion in the rocks rather than any sort of sampling bias.

Limited Ba data for the paragneisses indicate that although concentrations are high (~1000 ppm), they are well within the range of sediments. Like Pb and Rb, Ba exhibits a positive correlation with K; unlike these elements, K/Ba also correlates positively with Ba.

SUMMARY AND DISCUSSION OF THE TRACE ELEMENT DATA

On the basis of the foregoing discussion, we have delimited likely ranges in trace elements in the RPP. These are tabulated in Table 4-2 along with our best estimate for the composition of the RPP assuming a Sm/Nd ratio of 0.21 ±0.03 (also shown in Figure 4-9). A Sm/Nd for the RPP somewhat higher than that of typical shales is reinforced by additional considerations presented below. In Table 4-2, the data are organized to reflect the elemental hierarchy used in their determination as presented above. The least constrained concentrations are those of the alkalis and possibly Pb, features which are due in part to the general lack of correlation of potassium feldspar abundance with Sm/Nd,
<table>
<thead>
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<th>TABLE 4-2: Representative Petrologic Paragenetic Compositions, Comparators of Crustal Reservoirs, and Effect of Partial Melting</th>
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<tr>
<td><strong>RPP</strong></td>
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<tr>
<td>SiO2</td>
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<td>TiO2</td>
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<td>Al2O3</td>
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<td>FeO</td>
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<td>Na2O</td>
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<td>K2O</td>
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<td>Fe2O3</td>
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^a Characteristics of minimum melt added: Major elements from White and Chappell (1977); trace elements calculated for equilibrium with 23.6% garnet, 9.2% plagioclase, 29.3% andalusite, 0.001 zircon, and 0.012 apatite using partition coefficients given in the table. Distribution coefficients are assumed to be negligible for sillimanite, quartz, and rutile. Abundances of major phases calculated by inversion of major element data of RPP using algorithm described in Table 5-1; zircon and apatite abundances calculated from P2O5 and Zr (Wandless and Pawarli, unpub. data) assuming stoichiometry.

^b Shale compositions: 1) Major Elements (amphibolite facies) for average green schist, Wedepohl (1969); Trace elements for shale, Wedepohl (1968); 2) North American Shale Composite, Green et al. (1983); 3) Honer and Migdisov (1971); 4) Early Proterozoic Pecora Formation, Canada, Taylor and McLennan (1983).


^d Mineral residuum site.

^e Partition coefficients: Arch (1976), Hanson (1980), Hildreth (1977), Mahood and Hildreth (1983), McLennan (1979), Watson and Green, 1981: Chap. 6; Na and Mg in garnet assumed from garnet-plagioclase equilibration (Chap. 3) and normalized to apatite: liquid partition coefficients of Hanson (1980); U in apatite and Pb in zircon from concentration data and isotope considerations using data of Doe (1970), Tables 4 and 6.
our point of reference. In addition, the scatter in the concentrations of these elements may reflect original variability between the protoliths, the more erratic behavior of these elements during initial metamorphism, and/or subsequent reshuffling with recent metamorphism.

The lower limit to possible protolith composition shown in Figure 4-9 is derived from the foregoing discussion (except for Ba, discussed below). This estimate is based on the assumption that the Sm and Nd concentrations of the RPP are those of the protolith. With the exceptions of U, Cs, and possibly Th, most characteristics of the RPP are within the ranges exhibited by typical shales. However, if the high Sm/Nd ratio implied by Nd isotopic considerations is real, it could reflect modification of the REE characteristics during high grade metamorphism. If this in turn reflects loss of the LREE, the Sm and Nd contents of the paragneisses may be lower than those of the protolith by a factor of -2 as discussed above. Consequently, in the section to follow, we explore this possibility using additional constraints on the REE and its implications for an upper limit to the composition of the protolith.

The REE revisited: considerations and complications in characterizing the protolith composition and consequently, the efficacy of partial melting

The REE are amongst the most conservative elements during metamorphism (Weaver and Tarney, 1981; Hamilton et al., 1979; Green et al., 1972; Dupuy et al., 1979). Based on Nd isotope considerations, we
Figure 4-9

Comparison of trace element characteristics of RPP to likely ranges in protolith composition and to estimated composition of the crust (Taylor and McLennan, 1985). Normalizing values are from Zindler and Hart, 1986 (Sr, Nd, U, and Pb) and from K/Ks = 35,000; K/U = 10^4; Th/U = 3.8; Rb/Sr = 0.031; Sm/Nd 0.1967; Ba/Nd = 5.07.
have shown that the time-integrated Sm/Nd ratio of the RPP is at the compositional fringes of the range in Sm/Nd of shales and clays. Since our reference compositional range is dominated by Phanerozoic sediments, it is possible that it is too restrictive if Sm/Nd in early to middle Proterozoic sediments was slightly higher. Alternatively, the particular provenance of the sedimentary protolith may have had anomalous Sm/Nd characteristics. Thus, on this basis alone, it is possible that the REE characteristics of the paragneisses were not modified during granulite metamorphism. In terms of the REE, support for this interpretation comes from the similarity between Nd concentrations of the paragneisses and most shales (Figure 4-5).

As currently understood, the REE are also amongst the most conservative properties of shales and, therefore, a good reference frame for comparison of the RPP to their protoliths. Consequently, if the inferred deviation in Sm/Nd in the paragneisses from that of shales is significant, it may record the effects of REE modification during metamorphic differentiation. Complete REE patterns obtained by Wandless and Padovani (1985) for the samples discussed in this paper supplement the Nd and Sm data presented here. The Yb contents of these paragneisses are higher than those of representative shale composites by a factor of almost 2. Notably, this is true of samples 1975 and 1977 (Figure 4-10) which have Sm/Nd similar to that of the RPP. Resulting Yb/Nd ratios in these samples are ~0.19, compared to values of <0.12 in many post-Archean shales (Nance and Taylor, 1976; Taylor and McLennan, 1983; Thomson et al., 1984). Thus, the high abundance of the HREE relative to likely protoliths warrants further consideration.
Yb versus Sm/Nd for average of samples 1975 and 1977 (circle). One sigma and three sigma ranges of Yb and Sm/Nd for shales and clays are also shown. Kilbourne Hole paragneisses are apparently enriched in Yb and Sm/Nd with respect to most sediments; the effect of sampling bias and partial melting on these paired characteristics of the paragneisses is shown. Yb data for Kilbourne Hole paragneisses taken from Wandless and Padovani (1985). Sm/Nd data for sediments from sources in Figure 4; Yb data from Nance and Taylor (1976; 1977) and Cullers et al. (1974; 1975) and excludes one kaolinite with 16.5 ppm Yb.
By themselves, the high Yb contents and high Yb/Nd ratios of the paragneisses may reflect 1) the fractionation of Yb amongst the paragneisses such that our RPP is more garnet-rich than the true RPP (garnet concentrates Yb), 2) the fractionation of Yb between different lithologies (i.e. scavenging of Yb from other lithologies), or 3) may in fact be representative of the RPP. The first two of these explanations require discounting the constraint on Sm/Nd inferred from the Nd isotopes for the following reasons. In order for the RPP to have Yb contents similar to that of NASC, there must exist a dilutant with extremely low Yb contents. In order to dilute the Yb contents by a factor of 2, this "missing component" must constitute at least 50% of the reservoir over which the REE equilibrated. In order for that missing component to be continuous in composition with that observed and in order to maintain Nd contents similar to those of shales, that component must contain feldspar (Figure 4-5), thereby lowering Sm/Nd (Figure 4-10). One possible compositional trend which is internally consistent with compositional variation in the paragneisses is defined by an extension of a line through samples 1975 and 1977 to 79K6 (79K6 subtraction line, Figure 4-10). Thus, although some combination of quartzofeldspathic material and the paragneiss xenoliths analyzed could produce REE patterns similar to that of NASC, the resulting Sm/Nd ratio is too low to be consistent with considerations based on the Nd isotopic composition (Chapter 3). In this case, it could be argued that considerably greater scatter exists in the isotopic and trace element characteristics of the Kilbourne Hole paragneisses as a whole and that our data base is therefore unrepresentative.
Alternatively, the paragneisses may have scavenged Yb by equilibration with another lithology or with a HREE-enriched vapor or fluid. Transport of the HREE has been suggested to occur in granulites and in late-stage magmatic fluids in $\text{CO}_3^{2-}$-rich or $\text{F}^-$-rich vapor phases (Collerson and Fryer, 1978; Taylor et al., 1981), the significance of which has been disputed (Weaver and Tarney, 1981). In this case, the Sm/Nd as well as Yb content of the RPP will depend on the REE characteristics of the component with which the paragneisses equilibrated. However, our interpretation of the isotopic constraint on the REE characteristics of a representative pelitic paragneiss assumes that the Nd isotopes average a domain typical of pelitic paragneisses in the lower crust. To the extent that the Nd isotopes of the paragneisses equilibrate with an isotopically dissimilar component, their Nd isotopic composition will represent an hybrid, thereby prohibiting any simple interpretation of the isotopic data with regard to the Sm/Nd ratio of the RPP. Based on the existing data base (Chapter 3), the isotopic signatures of the different rock-types are distinct, most notably with respect to the O isotopes, and therefore this scenario is rendered ad hoc.

Finally, the Yb contents may be truly representative of the RPP and therefore atypical when compared to most shales. Accordingly, the Yb contents may be approximately that of the protolith or, if the process of granulitization was accompanied by a loss of mass (e.g. by partial melt extraction), they may have been passively enriched relative to the protolith. If the former case applies, the Nd contents must be on the order of 50 ppm to produce Yb/Nd ratios similar to that of
shales. Depletion of the LREE without affecting Yb could conceivably be achieved in a CO₂ or Cl⁻-rich vapor phase (Tarney and Windley, 1977; Taylor et al., 1981). If the latter case applies, somewhat lower Nd contents in the protolith are permitted, depending on the amount of mass lost during high grade metamorphism. Unfortunately, no Yb data are available for those samples with extremely high Nd contents used in constructing Figure 4-5. However, it is interesting that the Nd and Yb contents predicted for the protolith are similar to those reported for a temporally comparable pelitic paragneiss extracted from the lower crust in Chihuahua, Mexico (Nimz et al., 1986), ~500 km south of Kilbourne Hole. In either case, Nd and Sm and consequently, Th, U, and possibly other trace elements are depleted in the paragneisses relative to possible protoliths.

An upper limit to the incompatible trace element composition of the protolith was calculated on the assumption that Yb has not been significantly modified and is shown in Figure 4-9. Nd and Sm concentrations are constrained by the Yb data; Th, U, and K concentrations were calculated from Nd/Th=2.5, Nd/U=12, and Nd/K=18x10⁻⁵ (cf. Figure 4-6). Finally, K/Rb and K/Cs were set at 220 and 3000 respectively. Changes in Sr, Ba, and Pb were not required for internal consistency of the data. With the principal exceptions of Nd, Sm, Th, and Rb, this protolith does not differ significantly from that determined in our earlier discussion of the trace element data.
Amount of partial melting permitted by the trace element data

We have elsewhere inferred (Chapter 2) that the paragneisses may never have experienced partial melting. Nevertheless, partial melting is a tractable process to model and in light of evidence for trace element depletions it is useful to evaluate its efficacy. Melt in equilibrium with the RPP for various degrees of partial melting can be added to the RPP in order to estimate likely protolith compositions (Table 4-2). For the major elements, the composition of a possible minimum melt is added (White and Chappell, 1977). For the trace elements, their abundances in the melt are constrained by bulk partition coefficients for the mineralogy of the residue (i.e. the RPP). The mineralogy of the RPP were determined by inversion of its major element data using the inversion described in Table 4-1, assuming that the melt was in equilibrium with the mineralogy observed in the rocks today. Partition coefficients applied to this calculation are given in Table 4-2.

One of the principal problems with estimating the maximum amount of partial melting that the paragneisses may have undergone is the accuracy with which partition coefficients can be estimated, particularly because of the degree of latitude permitted for many elements by the possibility of accessory phases. Of the trace elements, Rb is particularly useful since its partitioning will be governed solely by major phases, the partition coefficients for which are available. In addition, as indicated in our discussion of Rb above, some Rb may be preferentially lost before granulite metamorphism; therefore, if anything, this calculation will overestimate the degree of partial
melting required to remove Rb. From the K content determined as described for the major elements, the K/Rb of the reconstituted rock can be estimated and compared to likely sedimentary protoliths. This calculation yields a fit to a possible K/Rb of shales of 159 at 10% partial melting (Table 4-2). Even when the partition coefficients for Rb in sanidine is increased to 0.95 (Long, 1978), a likely lower limit to K/Rb in the protolith (150) is reached at 30% partial melting.

As modelled in Figure 4-5, if the paragneisses have undergone ~10% partial melting, the Sm/Nd of the protolith may have been equivalent to that of shales. Moreover, as modelled, partial melting has little effect on Yb (Figure 4-10) and therefore, the effect of ~10% melting is to require a Yb/Nd ratio in the protolith (0.1) which is similar to that of shales. As noted in our earlier discussion of Nd and Sm, this calculation does not include any accessory minerals other than apatite and zircon and therefore yields an upper limit to the LREE characteristics of the protolith. However, if accessory minerals in which Nd is compatible such as monazite or allanite were present, not only would they have the effect of buffering the Nd content of the melt, but they would tend to reduce the effectiveness of garnet in modifying the Sm/Nd and Yb/Nd ratios. Consequently, correspondingly higher degrees of partial melting would be required to change Sm/Nd from that of shales to that inferred from the Nd isotopes with the net effect of requiring similarly high Nd contents in the protolith.

As evident from Table 4-2 and from our discussion of the trace element characteristics of sediments above, reconstituted protolith compositions at levels of melt extraction of less than 10% yield trace
element concentrations and ratios consistent with those of sediments
with the exceptions of Cs, U, and possibly Th. Cs and U contents in the
reconstituted protolith are too low for shales and can be increased in
the model only if the bulk distribution coefficients are <0.001 for Cs
and <0.02 for U. These possibilities seem unlikely in view of the
presence of sanidine and zircon in the rocks. Thus, the depletion in U
and Cs may evidence the role of a metasomatic process in addition to or
instead of partial melting at granulite conditions. Alternatively,
these elements may have been depleted prior to granulite metamorphism as
previously suggested by Dostal and Capedri (1978) for U and by analogy
to Rb (discussed above) for Cs.

IMPLICATIONS FOR EVOLUTION AND STATE OF THE LOWER CRUST

For dehydration and trace element modification of the lower crust

The trace element data is permissive of a small degree of actual
melt extraction (~10%) in the presence of the mineral assemblage
observed in the rocks today. Consequently, as a means of dehydration,
partial melting seems untenable. At such low degrees of partial
melting, the melt would probably be fairly water-rich and therefore,
hydrous minerals would probably remain stable. Although higher degrees
of actual melting resulting in internal unmixing of melt and residue is
permitted by the major element data and is one interpretation of the
source of the major element variations, hydrous minerals would simply
recrystallize upon cooling. Some additional means of dehydrating the
rocks is therefore required. Further, melting in the presence of
biotite and/or muscovite rather than garnet would also require higher
degrees of partial melt extraction and concomittantly larger magnitudes of REE depletion because of their lower distribution coefficients and smaller fractionation of the REE (e.g. D(Nd) = 0.3, D(Yb) = 0.4 in biotite; Arth, 1976). This does not seem likely in view of the high REE contents which would be required of the protolith.

We regard partial melting leading to melt extraction from the paragneisses as unlikely. Rather, dehydration in the presence of a carbonate or halide-rich fluids or vapors which can mobilize the less volatile elements and which mimic the effect of partial melting is required. Th and the LREE were probably depleted by this phase; U and Cs may also have been extracted in this phase or may have been depleted prior to high grade metamorphism.

For composition of the lower crust.

Table 4-2 compares our model RPP to estimates of both upper and lower crustal compositions. Figure 4-9 compares the trace element characteristics of the RPP to that of likely protoliths and the average crust. With the exceptions of Cs, U, and Sr, the relative abundances of the trace elements in the RPP are not appreciably different from the crust as a whole. However, save for these three elements, trace element concentrations are even higher than those of the average crust, typically by factors of 2-3. This feature of the paragneisses is a direct reflection of the high concentration levels of their protolith and of sediments in general. Thus, even if the Kilbourne Hole paragneisses have undergone some small degree of LILE-depletion, their high trace element concentrations exemplify the importance of protolith
lithology in determining the composition of the lower crust.

In a similar vein, recent work on high grade metamorphic terranes and xenoliths has emphasized the importance of bulk composition in determining the extent of elemental depletions during granulite metamorphism by governing the stability of different minerals in which these elements reside (Rudnick et al., 1985; Rollinson and Windley, 1980; Tarney and Windley, 1977; Barbey and Cuney, 1982). We have used the compositional dependence of trace element variations or the lack thereof to infer mineralogical controls on the behavior of these elements in the lower crust. This is also summarized in Table 4-2.

It is evident from Table 4-2 and the foregoing discussion of the trace element data that potassium feldspar is an hospitable site for many elements which have elsewhere been considered to be depleted in the lower crust (Heier, 1973; Tarney and Windley, 1977; Collerson and Fryer, 1978; Heier and Thoresen, 1971). Consequently, the abundances of these elements in the lower crust may be critically dependent on the extent to which it is orthoclase-normative enough to stabilize potassium feldspar. The ramifications of this observation are particularly important for Pb isotopic systematics since potassium feldspar efficiently concentrates Pb over U. As a result, all else being equal, stabilization of potassium feldspar in the lower crust will decrease its $\mu$ thereby producing unradiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ signatures with time. The lower crust is one of the principal candidates for an unradiogenic Pb isotope reservoir required to balance the radiogenic Pb isotopic signatures of the upper crust and mantle (e.g. O'Nions et al., 1979).
For radiogenic heat production

The characteristics of the lower crust are assailable to surface observations by deconvolution of heat flow and seismic velocity studies. From their chemical characteristics, we can consider the contribution of the paragneisses to these aspects of the state of the lower crust. Calculated physical properties for the paragneisses are summarized in Table 4-3 and discussed below. The density of the paragneiss component of the lower crust at Kilbourne Hole was calculated from reasonable estimates of mineral densities and from modal mineralogies based on inversion of the major element data as described above and in Table 4-2. Errors were estimated from those for the composition of the RPP.

Heat production in the lower crust is generally inferred to be lower than that of the upper crust (e.g. Lachenbruch, 1970; Smithson and Decker, 1974; Heier, 1973) in order to balance the difference between mantle heat flux and surface heat flux with levels of radioactivity at the surface too high to be maintained throughout the whole of the crust. Nevertheless, just how depleted the lower crust must be is model dependent. Figure 4-11 is a plot of U versus K+Th for the paragneisses, shales and crustal averages. This diagram is contoured in terms of heat production for two representative K/Th ratios (.25%/ppm and 1%/ppm). Because of similarity in heat production for K at the percent level and Th at the ppm level, the effect of changing this ratio is small. As this figure illustrates, the major contributors to radioactive heat production in the paragneisses are K and Th. This is in contrast to sources of radioactive heat production at the surface which are
TABLE 4-3. Summary of Calculated Physical Properties

Pressures: 6-10 Kbars
Temperatures: 750°-950°C
$P_{H_2O}$: Anhydrous

Density: $3.05\pm0.07$ gm/cm$^3$
Heat Production: $2.2\pm0.7$ HPU
$V_p = 7.32\pm0.21$ km/sec
Figure 4-11

K + Th versus U for Kilbourne Hole paragneisses, shales and estimated compositions of upper and lower crust. K in percent; Th and U in ppm. Symbols as in Figure 4-4. Diagram is contoured for heat production (HPU = $10^{-13}$ cal cm$^{-3}$ s$^{-1}$) using algorithm of Birch et al. (1968) and illustrates the greater dependence of heat production on U concentration. Heat production in the paragneisses is dominated by K and Th and in most samples is less than 2 HPU. Estimated upper crustal composition labelled A and lower crustal composition from Taylor and McLennan (1985); upper crustal composition labelled B is for Canadian Shield (Eade and Fahrig, 1968). Shale data as in Figure 4-7.
K/Th = 0.25 (%/ppm)  

K/Th = 1

U

HPU = 2

UPPER CRUST

SHALES

LOWER CRUST
dominated by U decay. Consequently, errors associated with our estimate of the efficacy of U loss only contribute to a 3% error in the calculated heat production estimates.

Radioactive heat production in the paragneisses is equal to or greater than the upper limit (1.5 HPU) of values typically quoted for the lower crust (e.g. Smithson and Decker, 1974; Sclater et al., 1980). However, it is easily within the range reported for paragneissic xenoliths from the Bournac pipe (1.51 - 4.95 HPU; Dupuy et al., 1979). The predominance of K and Th activity on radioactive heat production in the paragneisses is in accord with the inverse modelling results of Jaupart et al. (1981) who showed a greater depth scale for K and possibly Th than for U. The K and Th contents of sediments are amongst the highest of typical crustal lithologies. Thus, if the observations of Jaupart and others can be generalized to the lower crust as a whole, paragneisses provide a representative upper limit to lower crustal heat production.

Heat production in the paragneisses is greater than the reduced heat flow; if the paragneisses constitute a significant component of the lower crust, the heat flow required of the mantle is considerably reduced. The abundance of paragneisses in the lower crust might ultimately be constrained from seismic velocity data for the lower crust. Unfortunately, like heat flow constraints, interpretations of seismic velocities are model-dependent and in the particular case at hand, this kind of data does not exist for the crust underlying Kilbourne Hole. The range of seismic velocities reported for the lower crust in general is 6.4-7.4 km/sec (Smithson and Brown, 1977) with most
estimates falling between 6.5-7.0 km/sec (Christiansen and Fountain, 1975). Toppozada and Sanford (1976) report a value of 6.5 km/sec for the lower crust beneath a more northerly segment of the rift while Cook and others (1979) report a seismic velocity of 6.2 km/sec for crust between 7.2 and 26.8 km depths in the rift ~100 km north of Kilbourne Hole. Few crystalline rocks have seismic velocities of <6.5 km/sec (e.g. Christiansen and Fountain, 1975) indicating that the effect of high temperatures and/or partial melting in the lower crust there must be a contributing factor. Using the approximate linear variation of seismic velocity with density determined by Christiansen and Fountain (1975), we calculate a seismic velocity of $V_p = 7.3 \pm 0.2$ km/sec for the RPP component of the lower crust (Table 4-3). If $V_p = 7.0$ km/sec represents a reasonable upper limit for average lower crust and other granulites (charnokites, gabbros) have seismic velocities greater than or equal to 6.5, the abundance of paragneisses in the lower crust in general is only limited to a generous 65%. Nevertheless, if the orthogneisses and nonpelitic paragneisses contribute less than 0.25 HPU (our estimate based on unpublished compositional data for the Kilbourne Hole xenoliths), total heat production in the lower crust is constrained to be less than or equal to 1.5 HPU from this limit.

As analog to subducted sediments

One compositional feature of island arcs which distinguishes them from likely mantle sources is their enrichment in Cs relative to the other alkaline earths and alkalis (Morris and Hart, 1983; Stern and Ito, 1983). Although attributed to a subducted sediment component in the
source regions of island arcs, prima facie evidence for significant
decoupling of Cs from the other LILE in metasedimentary rocks has not
been heretofore demonstrated. The dramatic depletion of Cs in the
Kilbourne Hole paragneisses illustrates the likelihood that the behavior
of Cs can be uncoupled from that of the other LILE elements during high
grade metamorphism of sediments and subducted sediments may provide a
source for selective Cs enrichment. However, if the Kilbourne Hole
paragneisses were emplaced by subduction as suggested in Chapter 3, the
fact that Cs was depleted at crustal conditions rather than at the depth
of volcanic arc sources may be significant. Alternatively, the driving
force for Cs depletion may be increased temperature and the paragneisses
could have been depleted in Cs after subduction ceased as a result of
prograde metamorphism accompanying thermal reequilibration of the crust.

We have also shown U to be depleted with respect to Th in the
paragneisses. U enrichment with respect to Th in volcanic arc lavas has
been demonstrated in the Marianas, Aleutians and Costa Rica by U-series
disequilibrium analyses (Newman et al., 1984; Allegre and Condomines,
1976), a feature which may be generalizable to oceanic arcs (Newman et
al., 1986; Allegre and Condomines, 1982). If derived from the subducted
slab, both U and Cs appear to be highly crustally reactive, that is,
they exhibit strong tendencies to be concentrated in the crust.
Alternatively, the possibility that high U/Th is associated with oceanic
arcs but not continental ones (Newman et al., 1986) may indicate that an
on-going process of crustal refinement in juvenile crust is occurring
such that labile U (and Cs?) is progressively depleted in the lower
crust and enriched above.
SUMMARY AND CONCLUSIONS

From the ultimate correlation of major and trace element compositional variations to representative Sm/Nd ratios constrained by Nd isotope considerations, we have determined a representative composition for a pelitic paragneiss reservoir in the lower crust beneath Kilbourne Hole. The composition of that reservoir is similar to that of likely protoliths with the salient exceptions of Cs, U, and to a lesser extent, Th. Some depletion in the LREE may be required by the data but their concentration levels are still comparable to those of shales. Thus the potential geochemical contribution of pelitic sediments to the lower crust can be estimated by reference to the range in shale compositions observed at the surface. As suggested elsewhere (Chapter 3), tectonic processes may stabilize geochemically significant quantities (i.e. ≥10%) of metasedimentary rocks. Proper accounting for the abundance of pelitic paragneisses in the lower crust may lead to compositions which are more siliceous and higher in LILE abundances (except U and Cs), the REE, δ¹⁸O, and ⁸⁷Sr/⁸⁶Sr.

A distinguishing feature of the pelitic paragneisses as well as the lower crust in general is the depletion in U with respect to Pb. Time-integrated ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb approach those of conformable Pbs which are temporally equivalent to the age of granulite metamorphism (cf Chapter 3). However, Pb is not depleted in the paragneisses and thus the paragneisses provide a suitable lower crustal reservoir for the Pb budget of the earth, vis-a-vis the core or lower mantle. Further, although the loss of U is nearly complete, the robustness of K and Th yields heat production rates only half that of
the upper crust. Thus, the abundance of paragneisses in the lower crust critically affects accurate estimation of heat production of lower crust and therefore of heat flow from the mantle.

In spite of compelling evidence that pelitic compositions should melt during high grade metamorphism, there is little reason to consider partial melting a contributing factor in the evolution of the Kilbourne Hole paragneisses. On the other hand, large-scale equilibration with fluid and/or vapor phases is precluded by the distinctive oxygen isotope signatures between the different crustal lithologies sampled at Kilbourne Hole. Consequently, the depletion in Cs, U, Th, and possibly the LREE must have occurred by fluids derived from the paragneisses themselves.
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identifying gneisses of metasedimentary origin. J. Geol. 84, 195-212.


Chapter 5

NEAR-TRENCH CALCALKALINE AND THOLEIITIC MAGMATISM,

KODIAK ISLAND, ALASKA:

Nd ISOTOPE AND TRACE ELEMENT EVIDENCE FOR ORIGIN BY

EARLY TERTIARY RIDGE-TRENCH ENCOUNTER
INTRODUCTION

Closure of ocean basins results in subduction of an active or fossil spreading center. However, an active ridge may also be subducted without necessarily eliminating an ocean (e.g., Atwater 1970). Northward-directed motion of the Pacific ocean plates throughout the Tertiary has resulted in the consumption of much of the now fossil Kula-Pacific and Kula-Farallon spreading centers of the northeast Pacific (Figure 5-1); (Engebretson et al., 1984; Byrne, 1979). In this paper, I present geologic and geochemical evidence for subduction of an active spreading ridge in the northeast Pacific during the Paleocene as the ultimate source of the Ghost Rocks volcanics of the Kodiak Islands, Alaska. Besides creating anomalous near-trench tholeiitic and calcalkaline magmatism, including intrusion of voluminous silicic plutons, ridge subduction bears on the problem of terrane trajectories and accretion in the North Pacific.

The Ghost Rocks volcanics are submarine basalts and andesites which were erupted into part of a Late Cretaceous to early Tertiary accretionary wedge, the Ghost Rocks Formation of the Kodiak Islands, Alaska. Geochemical analyses of somewhat younger submarine basalts from trench sediments along strike in the Kenai Peninsula area of the Gulf of Alaska indicate that they have oceanic affinities (Tysdal et al., 1977), possibly products of the Kula-Farallon ridge. Geochemical modelling of plutons that are temporally and compositionally equivalent to plutons which intrude the Ghost Rocks Formation has shown that a mafic component, possibly MORB, may have been involved in their origin (Hill et al., 1981) although the involvement of a basalt magma has been disputed.
Figure 5-1

Paleocene position of the now-fossil Kula-Pacific-Farallon triple junction (Engebretson et al., 1984) and present location in northeast Pacific (dashed). Also shown is latitude of formation of Ghost Rocks volcanics as constrained by paleomagnetic results (Plumley et al., 1983). Possible paleoposition of Kodiak Island (in black) is one of three discussed by Moore et al. (1983) from which this diagram is modified.
(Hudson et al., 1979). Geologically equivalent plutonism extends for 2000 km from Sanak to Baranof Islands and manifests the intensity of early Tertiary near-trench magmatism. Thus, a geochemical study of the Ghost Rocks volcanics was undertaken to determine whether they represent *prima facie* evidence for ridge interaction with an accretionary prism and to elucidate the origin of near-trench andesitic volcanism.

**GEOLOGIC SETTING**

The Kodiak Islands of southwest Alaska comprise an uplifted accretionary complex which youngs progressively in age from Jurassic to Oligocene to the southeast. The Ghost Rocks Formation is the Paleocene member of this complex and together with the Eocene to early Oligocene Sitkalidak Formation constitute part of the Prince William Terrane of Jones et al. (1981); (Figure 5-2, inset). The Paleogene formations have been the subject of structural, sedimentological, paleomagnetic, and geochemical studies; the reader is referred to Moore et al. (1983) and references therein for a comprehensive overview.

Although the Kodiak Islands currently occupy a fore-arc position between the Alaska Peninsula volcanic arc and the Aleutian trench, this volcanic arc and the Kodiak accretionary complex may not have been completely coupled during the Late Cretaceous-early Tertiary. Paleomagnetic data for the Ghost Rocks Volcanics indicate that they erupted ca. 17 degrees south of their current location and ca. 25 degrees south of their expected paleolatitude had they been coupled to North America during Paleocene time (Plumley et al., 1983; Figure 5-1).
Figure 5-2

Generalized geologic map of the Ghost Rock Formation showing locations of the landward (andesitic) and seaward (basaltic) belts of the Ghost Rocks volcanics of Paleocene plutons in the Ghost Rocks and Kodiak Formations. Sample locations are indicated according to the sample prefixes. Inset shows simplified tectonostratigraphic map after Jones et al. (1981); terranes indicated by P: Peninsula; C: Chugach; PW: Prince William.
In contrast, paleomagnetic data for volcanic rocks of the Alaska Peninsula conservatively suggest that less than 20 degrees of northward displacement of that portion of the Peninsular terrane has occurred since the early Paleocene (Thrupp and Coe, 1986). Regardless of location, geologic considerations indicate that the Kodiak Islands have been the site of subduction-related accretion throughout their history. Evidence includes: structural imbrication and isoclinal folding of oceanic sediments with seaward structural vergence, tectonic melange formation soon after deposition, and metamorphism at low geothermal gradients in several units (Connelly, 1978; Nilsen and Zuffa, 1982; Moore and Wheeler, 1978; Byrne, 1984; Sample and Fisher, 1986; Moore and Allwardt, 1980; Moore et al., 1983; Roeske, 1986).

The Ghost Rocks Formation is composed principally of melange and turbidite sequences with subordinate (<10%) pillow lavas and their hypabyssal equivalents. In general, the igneous rocks conform to two linear belts subparallel to the structural grain of both the Ghost Rocks Formation and the Kodiak accretionary complex as a whole (Figure 5-2). The seaward (hereinafter referred to as basaltic) volcanic belt is composed entirely of basalts and submarine (basaltic?) tuff and is associated with a more argillite-rich portion of the formation. Pelagic limestones in depositional contact with these lavas have yielded Late Cretaceous-early Tertiary foraminifera. The landward (hereinafter referred to as andesitic) volcanic belt is composed dominantly of andesites and is associated with a more sandstone-rich portion of the Ghost Rocks Formation. Basalts and dacites occur locally in this belt, as illustrated by the stratigraphic section measured at Shearwater Bay.
(Figure 5-3). Note that at Shearwater Bay, basalts overlie the andesites and a thin rhyolite tuff and are separated from them by less than 0.5 meters of argillite. The two belts are most widely separated at Kiliuda Bay, where the most extensive stratigraphic section of basalt occurs. The volcanic belts gradually approach each other to the southwest until they are nearly superimposed in the Jap Bay area of the Aliulik Peninsula. At the southwestern terminus of the island, a major exception to these restricted linear outcroppings occurs: on the northwest side of the Aliulik Peninsula the most extensive stratigraphic section of andesites is exposed. This area is also unusual in that a granodioritic satellite pluton of the Kodiak batholith intrudes the Ghost Rocks Formation. This pluton is along strike with the andesite occurrence.

In spite of nearly pervasive stratal disruption which obscures many original contacts, definitive evidence for depositional or intrusive igneous and sedimentary relationships remains. Basalts and andesites conformably overlie and are overlain by argillite and sandstones; dikes of both composition crosscut stratigraphy. Moreover, dikes and sills of both compositions have chilled margins where they intrude massive sandstone beds. In the Aliulik area, pebble conglomerates fill the interstices of andesitic pillow lavas. Thus, magmatism occurred in a region of substantial terrigeneous clastic deposition and the volcanic rocks do not simply represent fragments of layer 2 oceanic crust scraped off at the trench.

The volcanic rocks also erupted into an area of active structural deformation. The Ghost Rocks Formation has been interpreted as
Figure 5-3

Stratigraphic section through the seaward (andesite) belt at Shearwater Bay (see Figure 5-2 for location). Shaded portion is basaltic in composition. Numbers indicate paleomagnetic sites; results in Plumley et al. (1983).
BASALT -
PILLOW LAVAS AND
MASSIVE BASAL FLOWS

RHYOLITE TUFF

ANDESITE -
PILLOW LAVAS AND
MASSIVE BASAL FLOWS
dominantly trench sediments scraped-off the subducting slab (Byrne, 1982). Moreover, metamorphic conditions implied by studies of fluid inclusions in quartz veins suggest that rocks of the Ghost Rocks Formation were probably underplated (Vrolijk, pers. comm. 1986). The duration of deposition and deformation of the Ghost Rocks Formation is bracketed to probably less than 5 m.y. by the Late Cretaceous to Paleocene fossils and by post-deformational intrusion at 62 Ma (Moore et al., 1983). The igneous rocks are crosscut by and crosscut structural features associated with early deformation in the accretionary prism; hence, volcanism was syndeformational (Byrne, 1982). These considerations, taken together with intrusive contacts between the igneous rocks and massive sandstones, suggest that the volcanic rocks erupted in or very near an active Paleocene accretionary prism.

Plutonic rocks which locally intrude the Ghost Rocks Formation range in composition from gabbroic to granodioritic (Capps, 1937; Davies and Moore, 1984; Reid, unpub. data). The Jap Bay pluton on the Aliulik Peninsula is relatively undeformed indicating that deformation of the Ghost Rocks Formation had largely ceased by the time the pluton was intruded at 62 Ma (Moore et al., 1983). Moreover, this and other plutons of the Ghost Rocks and Kodiak Formations are petrographically and geochemically similar suggesting a similar heritage and the likelihood that the Chugach and Prince Williams terranes were coupled, at least locally, by early Paleocene time (Davies and Moore, 1984; Hill et al., 1981; Reid, unpub. data). Considered together with geologically equivalent early Tertiary plutons, early Tertiary plutonic activity was laterally extensive (Hudson, 1979), parallelling the continental margin
of southern Alaska for 2000 km.

MAJOR ELEMENT GEOCHEMISTRY OF THE GRV

Geochemical analyses of the Ghost Rocks Volcanics (GRV) have been performed in order to elucidate their origin and evolution; the analytical techniques are described in the footnotes to the appropriate tables. Because of both their age and their occurrence, the GRV have undergone alteration and metamorphism due to seawater interaction and subsequent burial. This has established zeolite to prehnite-pumpellyite facies mineral assemblages; chlorite, sphene, and epidote are present in addition to prehnite and pumpellyite. The presence of laumontite in the andesites at Kiliuda Bay indicates that the intensity of metamorphism may have been variable. Calcite (basalt belt) and quartz veins and amygdules (andesite belt) are also ubiquitous. Iddingsite is pseudomorphic for rare olivine; plagioclase is commonly sericitized in addition to being albitized. Glass has been replaced by chlorite, although crystallization textures are well-preserved. Sulphide mineralization occurs both in the lavas and locally in veins in nearby sediments. Only augite appears to have escaped unscathed.

Major and trace element analyses of the GRV are presented in Table 5-1. The sample numbers are annotated according to the type of igneous feature they represent. In addition, paleomagnetic site numbers are indicated for flows where such studies were undertaken (Plumley et al., 1983). Samples which are duplicates of the same flow or pillow lavas, or of other likely compositional equivalents, are tabulated in Figure 5-
### Table 5-1: Major and Trace Element Geochemical Analyses of the Ghost Rocks Volcanics, Kodiak Island, Alaska

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6. Major element analyses for the andesites on the Aliulik Peninsula are contained in Hill (1979); a few of his trace element analyses are reported here. In spite of efforts to sample the freshest material possible, loss on ignition invariably exceeded 2%.

Basalts sampled from both the seaward and landward volcanic belts are tholeiitic and show a limited range in SiO$_2$ (ca. 2%) (anhydrous basis). Comparable ranges in SiO$_2$ are observed between samples of the same flow. FeO*/MgO (wt.%) in the seaward belt ranges from 1.0 to 2.3. The range in TiO$_2$ concentration is large: from 1.3% to 2.3%. Basalts from the landward, andesite belt in Kiliuda Bay fall generally within the compositional ranges of those from the seaward, basalt belt (FeO*/MgO = 1.2 and 1.4; TiO$_2$ = 1.2 and 1.5%). TiO$_2$ roughly co-varies with Fe$_2$O$_3$ suggesting that, to a first order, chemical variability between most of the basalts may be interpreted as the result of fractionation.

Considering also the data of Hill (1979), the andesites are calcalkaline and range in SiO$_2$ from just under 55% to 59%. MgO decreases fairly smoothly with increasing SiO$_2$ and is rather high (5.1 to 7.8%) relative to typical andesites. TiO$_2$ contents are uniformly lower than those of the basalts and range from 0.8 to 1.2; FeO*/MgO is generally lower and less variable than in the basalts (0.9-1.3). Andesites from the Aliulik Peninsula tend to be somewhat more TiO$_2$-rich and SiO$_2$-poor but overlap the compositions of the andesites presented in Table 5-1.
ISOTOPE GEOCHEMISTRY OF THE GRV

Effects of Alteration

Isotopic ratios can be useful in discriminating the sources of magmatic rocks. However, these signatures may be modified by open system behavior following crystallization. In the geologic context of the GRV, the alteration effects of seawater and low grade metamorphic fluids are of concern. Because of the high Sr/Nd of seawater ($10^6$), $^{87}\text{Sr}/^{86}\text{Sr}$ will be significantly more sensitive to chemical exchange with seawater and precipitation of calcite, as illustrated by an hypothetical basalt-seawater mixing array in a paired Sr-Nd isotope diagram (Figure 5-4). The behavior of Sr and Nd in metamorphic fluids is more contentious. However, given the low degree of REE mobility during low grade metamorphism (Ludden and Thompson, 1979; Staudigel et al., 1979), alteration by metamorphic fluids may be expected to produce similar, albeit possibly less strongly curved, mixing arrays.

Sr and Nd isotope analyses of the GRV and sediments from the Kodiak Formation are presented in Table 5-2. For their Nd isotopic compositions, the samples from the basalt belt fall well to the high $^{87}\text{Sr}/^{86}\text{Sr}$ side of fields defined by magmatic rocks (Figure 5-4), consistent with the effect of seawater alteration and with the fact that these lavas are typically veined with calcite. Because their $^{87}\text{Sr}/^{86}\text{Sr}$ signatures are less than that of Late Cretaceous to Paleocene seawater (0.7077-0.7080: DePaolo and Ingram, 1985; Burke et al., 1982), isotopic equilibration of Sr with seawater was incomplete. Thus, it is likely that seawater alteration, at least as envisaged in Figure 5-4, did not
Figure 5-4

Sr-$\varepsilon_{Nd}$ isotopic diagram comparing correlated isotopic characteristics of the CRV basalts (circles) and andesites (diamonds) to basalts and andesites from elsewhere in the north Pacific. Squares indicate two Kodiak Formation sediments (Sr isotopes from Hill et al., 1981) and the approximate field of early Tertiary plutons (from Hill and Morris, 1982 and Hill et al., 1981). $\varepsilon_{Nd}$ deviations in parts per 10$^4$ from chondritic Nd at time of formation using present-day $^{143}Nd/^{144}Nd=0.512638$ and $^{147}Sm/^{144}Nd$ (Jacobsen and Wasserburg, 1984). Basalts from the basaltic belts have Nd isotopic compositions similar to MORB but fall to the high-$^{87}Sr/^{86}Sr$ side of other oceanic sources as a result of seawater alteration; a basalt and an andesite from the andesite belt fall near a possible assimilation curve between MORB and the Kodiak Formation sediments (derived from Hill and Morris, 1982). Late Cretaceous-Paleocene seawater from Burke et al. (1982); DePaolo and Ingram (1985); Piepgras et al. (1979). Other data sources: EPR/Small Seamounts: [MacDougall and Lugmair, 1986; Zindler et al., 1984]; Arcs: [McCulloch and Perfit, 1981; Morris and Hart, 1983; Nohda and Wasserburg, 1981; Nye and Reid, 1986; von Drach et al., 1986; White and Patchett, 1984]; Hawaii [Chen and Frey, 1985; M.F.Roden et al., 1984; Staudigel et al., 1984; Stille et al., 1983; White and Hofmann, 1982]; Boninites: [Cameron et al., 1983]; Altered oceanic basalts: [Jahn et al., 1980; McCulloch et al., 1980]; Tertiary No. Pacific sediments: [von Drach et al., 1986].
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<th>$^{87}\text{Sr}/^{86}\text{Sr}_0$</th>
<th>Sm</th>
<th>Nd</th>
<th>$^{147}\text{Sm}/^{144}\text{Nd}$</th>
<th>$^{143}\text{Nd}/^{144}\text{Nd}$</th>
<th>tNd(65)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chh unleached</td>
<td>2.8</td>
<td>7.6</td>
<td>0.70457(3)</td>
<td>0.70437</td>
<td>2.005</td>
<td>0.70409</td>
<td>0.703278(2)</td>
<td>0.703278(2)</td>
<td>12.3</td>
</tr>
<tr>
<td>leached residue</td>
<td>8.3</td>
<td>186</td>
<td>0.70469(2)</td>
<td>0.70487</td>
<td>0.623</td>
<td>1.200</td>
<td>0.703138(26)</td>
<td>0.703138(26)</td>
<td>10.0</td>
</tr>
<tr>
<td>Che</td>
<td>3.5</td>
<td>10.1</td>
<td>0.70549(4)</td>
<td>0.70549</td>
<td>3.513</td>
<td>10.01</td>
<td>0.703157(18)</td>
<td>0.703157(18)</td>
<td>10.0</td>
</tr>
<tr>
<td>BB5b</td>
<td>0.7</td>
<td>19.9</td>
<td>0.70546(4)</td>
<td>0.70546</td>
<td>5.851</td>
<td>19.99</td>
<td>0.703189(18)</td>
<td>0.703189(18)</td>
<td>10.8</td>
</tr>
<tr>
<td>Andesite Belt (Basalts)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>S45a</td>
<td>1.8</td>
<td>12.1</td>
<td>0.70487</td>
<td>0.70487</td>
<td>0.193</td>
<td></td>
<td>0.703143(17)</td>
<td>0.703143(17)</td>
<td>9.9</td>
</tr>
<tr>
<td>S47b unleached</td>
<td>1.6</td>
<td>15.6</td>
<td>0.70309(2)</td>
<td>0.70309</td>
<td>2.468</td>
<td>9.255</td>
<td>0.703135(16)</td>
<td>0.703135(16)</td>
<td>9.2</td>
</tr>
<tr>
<td>leached residue</td>
<td>1.0</td>
<td>39</td>
<td>0.70296</td>
<td>0.70296</td>
<td>0.377</td>
<td></td>
<td>0.703132(14)</td>
<td>0.703132(14)</td>
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<tr>
<td>leachate</td>
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<td></td>
</tr>
<tr>
<td>Kodiak Sediments</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Greywacke</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UI3a</td>
<td>3.5</td>
<td>17.6</td>
<td>0.70469(3)</td>
<td>0.70469</td>
<td>0.506</td>
<td>0.512592(31)</td>
<td>0.512592(31)</td>
<td>-0.9</td>
<td></td>
</tr>
<tr>
<td>B6a</td>
<td>3.4</td>
<td>16.5</td>
<td>0.70455(3)</td>
<td>0.70455</td>
<td>0.443</td>
<td>0.512535(17)</td>
<td>0.512535(17)</td>
<td>-1.4</td>
<td></td>
</tr>
<tr>
<td>Argillite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M5c</td>
<td>5.3</td>
<td>25.2</td>
<td>0.70486(3)</td>
<td>0.70486</td>
<td>0.502</td>
<td>0.512470(12)</td>
<td>0.512470(12)</td>
<td>-2.7</td>
<td></td>
</tr>
<tr>
<td>N4e</td>
<td>5.2</td>
<td>25.6</td>
<td>0.70488(3)</td>
<td>0.70488</td>
<td>0.499</td>
<td>0.512511(16)</td>
<td>0.512511(16)</td>
<td>-1.9</td>
<td></td>
</tr>
</tbody>
</table>

*a*) Nd and Sr isotopic ratios and trace element concentrations except those in parentheses determined at MIT following techniques of Hart and Brooks (1977); Richard et al. (1976), and Manhes et al. (1978) and summarized by Roden et al. (1984). Concentrations in parentheses from Table 1. Residues from HCl leaching as described in text; concentrations calculated relative to unleached sample weights.

*b*) $^{87}\text{Sr}/^{86}\text{Sr}$ corrected for fractionation using $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and normalized to 0.7080 for EAA SrCO3.

*c*) At t = 65 Ma.

*d*) $^{143}\text{Nd}/^{144}\text{Nd}$ corrected for fractionation using $^{146}\text{Nd}/^{144}\text{Nd} = 0.75193$ and normalized to 0.51264 for BCR-1. $^{147}\text{Sm}/^{144}\text{Nd}$ ratios are reproducible to better than 1%.

*e*) $^{153}\text{Nd}/^{144}\text{Nd}$: deviations in parts per 10^4 from chondritic Nd at 65 Ma using present-day $^{153}\text{Nd}/^{144}\text{Nd} = 0.512638$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$ (Jacobsen and Wasserburg, 1984).
affect the Nd isotopic compositions of the rocks at all. This is corroborated by the fact that samples BB5b and S45a have similar REE patterns, incompatible element ratios, and Nd isotopic signatures in spite of drastically different Sr isotope ratios. Although alteration by metamorphic fluids is more difficult to evaluate, no simple two-component mixing array can explain the observed variation amongst the samples. Moreover, in the case of samples S45a and PP33 from Kiluda Bay, their different Nd isotopic signatures would require alteration to have selectively affected the andesites to a much greater extent than the basalts less the 1-2 meters above. Given the isotopic characteristics of the sediments and seawater, a Sr/Nd ratio three orders of magnitude less than that of seawater would be required of a metamorphic fluid in order for the $^{143}\text{Nd}/^{144}\text{Nd}$ of the volcanic rocks to have been appreciably affected.

Acid leaching has proved an effective means of reducing seawater Sr isotope signatures from slightly altered samples. A few of the GRV were leached as powders in 6.2N HCl at 100°C overnight in covered teflon beakers. These leaching experiments are notable for their lack of success at reducing the effects of alteration: of the three acid-leached samples, two had higher $^{87}\text{Sr}/^{86}\text{Sr}$ than their unleached equivalents. However, in the case of andesite PP33, this may reflect the intrinsic Sr isotope ratio of the magma (see below). Only leaching of sample S47b, a virtually holocrystalline rock from the andesite belt, produced a somewhat lower $^{87}\text{Sr}/^{86}\text{Sr}$. In this case, the resultant ratio is less than that of the decay-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the unleached equivalent, consistent with the leaching having removed
secondary seawater Sr.

Acid leaching had a devastating effect on the light rare earth element concentrations of these samples, reducing them by a factor of approximately 80-85% and significantly increasing Sm/Nd. Sr concentrations in the andesites were similarly reduced by leaching. In contrast, Sr in the leached basalt and Rb concentrations overall were surprisingly somewhat less affected, decreasing by factors of only 34% and 35-45% respectively. By analogy to sericitized and fresh plagioclase analyzed from the early Tertiary plutons (Hill et al., 1981), sericitization may concentrate Sr and Rb, and, if formed in the presence of isotopically enriched fluids, may stabilize higher $^{87}\text{Sr}/^{86}\text{Sr}$. Thus, the high $^{87}\text{Sr}/^{86}\text{Sr}$ with respect to $^{143}\text{Nd}/^{144}\text{Nd}$ in both leached and unleached aliquots of sample C6b probably reflects the pervasiveness of sericitization in this sample. The decoupling of $^{87}\text{Sr}/^{86}\text{Sr}$ during acid leaching may indicate the preferential loss of Rb from phases such as sericitized plagioclase which will have higher time-integrated $^{87}\text{Sr}/^{86}\text{Sr}$.

**Probable sources of the GRV**

Figure 5-4 also compares the initial (65 m.y.) isotopic characteristics of the GRV to the range in isotopic compositions spanned in oceanic environments of the North Pacific. Only a very small error is introduced by the juxtaposition of this data of disparate ages: the difference in evolution in a depleted mantle reservoir (Ben Othman and Allegre, 1984) versus a bulk earth reservoir for 65 m.y. is only 0.2 and
0.00001 for $\epsilon_{\text{Nd}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ respectively, well within analytical error. The range in $\epsilon_{\text{Nd}}$ in the GRV is unlike that of volcanic from any other tectonic setting, spanning a range from that typical of MORB to that of more enriched ocean island basalts and calcalkaline arcs.

The Ghost Rocks basalts from both volcanic belts fall within a restricted range ($\epsilon_{\text{Nd}}(65\text{Ma}) = 9.4-11.9$). The only lavas which have $\epsilon_{\text{Nd}}$ as high as this are MORB and possibly small seamounts formed very near spreading centers (Figure 5-4; see von Drach et al., 1986 for a recent compilation). Thus, the high Nd isotopic signatures of the Ghost Rocks basalts alone indicate that they were derived at or very near an oceanic spreading center. In contrast, the andesites are isotopically similar to magmas from oceanic intraplate settings and from volcanic arcs. In view of geologic constraints on their origin, oceanic island basalts and possibly boninites are likely candidates for comparison.

Compared to the combined Nd isotopic signatures and light rare earth element (LREE) characteristics of basalts and andesites from other tectonic environments (Figure 5-5), the basalts are like MORB, as expected. On the other hand, the andesites fall within the compositional fringes of fields defined by lavas from oceanic intraplate and volcanic arc environments (see also Figure 5-4, Moore et al., 1983). They are less radiogenic than virtually all arc lavas from the Aleutians and Alaska Peninsula and sample PP33 is less radiogenic than any magmatic source characterized in the northeast Pacific, including the Bering Sea (cf. Figure 5-4). Thus, strictly on the basis of their isotopic and Sm/Nd characteristics, the andesites could represent somewhat atypical magmas derived from one or the other of these sources.
Figure 5-5

$\varepsilon_{Nd}$ versus Sm/Nd for the GRV and their correspondence to those of basalts and andesites from mid-ocean ridges, oceanic islands, and volcanic arcs. Also shown are Kodiak Formation sediments and the approximate fields of early Tertiary plutons (Hill and Morris, 1982; Hill et al., 1981). Symbols, $\varepsilon_{Nd}$ notation, and data sources as in Figure 5-4 with the additional data of O'Nions et al. (1977) and Hickey and Frey (1982).
Alternatively, the andesites and a basalt from the andesite belt fall on a linear array (Figure 5-5), suggesting that the andesites may have been derived from the basalts by contamination by a second component. Interpreting this array as an isochron yields an age of 1.3 Ga, an age which is geologically impossible except as an isochron inherited from their source. As shown below, the continuity in composition between the basalts, andesites, and sediments/plutons argues in favor of contamination.

Importantly, the data array for the andesite belt also passes through the compositional fields of the early Tertiary plutons and near that of the Kodiak Formation sediments. Returning briefly to Figure 5-4, andesite PP33 falls near a mixing curve predicted by Hill and Morris (1982) for evolution of the plutons. A better fit to the Sr-Nd data would be obtained if a bulk Sr partition coefficient more appropriate to basalts (<1) were chosen. Thus, a plausible origin for the andesites is by sediment assimilation into a MORB magma and/or mixing of MORB and the magma ultimately responsible for the plutons. As evident from Figure 5-5, the former possibility requires either bulk assimilation of the sediments or melting conditions such that the effective Sm/Nd ratio of the assimilant (allowing for simultaneous crystal fractionation) is not drastically different from that of the sediments as a whole. Although the sediments analyzed for Nd isotopes are from the slightly older (Maastrichtian age) Kodiak Formation, they were initially thought to be similar in composition to those of the Ghost Rocks Formation (Nilsen and Moore, 1979). Major (for all samples) and trace elements (for two) have been previously determined (Hill et al., 1981; Hill, 1979). Recent work
suggests, however, that the Ghost Rocks Formation may be somewhat richer in juvenile material than the samples analyzed (Sample and Reid, in prep. 1986) and therefore, may be somewhat higher (more arc-like) in $\varepsilon_{\text{Nd}}$ than the Kodiak Formation. In addition, by analogy to other Tertiary sediments from the north Pacific (Figure 5-5), they may be correspondingly higher in Sm/Nd.

TRACE ELEMENT GEOCHEMISTRY OF THE GRV

Effects of Alteration

The relative abundances of incompatible trace elements in igneous rocks are often diagnostic of the tectonic environment of their source and of processes operative during their evolution. On the basis of their Nd isotopes and Sm/Nd ratios, I have already shown that basalts from both volcanic belts were probably derived from an oceanic spreading center. In contrast, the andesites appear to have chemical affinities to calcalkaline arc volcanism. However, in view of the fact that they are overlain by basalts in the Kiliuda Bay area (Figure 5-3) and that, chemically, they may fall on a possible mixing trend between the basalts and plutons/sediments of the Kodiak Formation, a hybrid origin for the andesites warrants consideration.

The so-called incompatible trace elements are those elements which are concentrated in the melt during closed system magmatic processes and, as a result, do not experience dramatic changes in the interelement abundances. Fortunately, many of these elements are also fairly immobile under many metamorphic conditions (Wood et al., 1979a;
Staudigel et al., 1979; Ludden and Thompson, 1979). The correlation of Sm/Nd with $^{143}\text{Nd}/^{144}\text{Nd}$ in the GRV suggests that the REE are largely unaffected. In order to further test the reliability of the incompatible trace element characteristics, more and less altered portions of rocks which were probably otherwise compositionally equivalent were analyzed. The results are summarized in Figure 5-6a and the details of this comparison discussed there. Of the incompatible elements, Rb, K, Sr, and P show variations significantly greater than analytical error. The remaining elements vary by less than 25% and are typically within analytical error. Although this treatment does not rule out uniform enrichments or depletions of these elements during alteration/metamorphism (e.g. Hellman et al., 1979; Staudigel et al., 1979) or coherent changes in their abundances between more and less altered samples, the uniformity in the data overall for comparisons at vastly different physical scales and apparent degrees of alteration suggests that interelement abundances may be similar to their initial ones. All of these apparently immobile elements have been shown to be inert under some metamorphic conditions (Wood et al., 1979a; Staudigel et al., 1979; Ludden and Thompson, 1979).

Evidence for hybrid origin of the GRV andesites

Figure 5-6 also compares representative incompatible trace element characteristics of the basalts, andesites, sediments, and plutons of the Ghost Rocks and Kodiak Formations. Data for the sediments and plutons are bracketed from Hill et al. (1981). Those elements shown to be
**Figure 5-6**

a: Assessment of alteration in the GRV by normalization of incompatible trace element characteristics between "more" and "less" altered portions of otherwise equivalent geochemical domains in the GRV. Extent of alteration based on petrographic examination, water contents, and grade of metamorphism. Magnitude of vertical bar equals percent change in either direction. Symbols and physical scale of comparison are summarized below.

<table>
<thead>
<tr>
<th>More/Less Altered Samples</th>
<th>Volc. Belt</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 15-17c (core)/15-17a (rim)</td>
<td>AND</td>
<td>Intrapillow</td>
</tr>
<tr>
<td>O K8-2 &amp; -6 composition/SF-B3</td>
<td>BAS</td>
<td>Interpillow, 50 m.</td>
</tr>
<tr>
<td>△ BB6/BB5b and BB4 composite</td>
<td>BAS</td>
<td>Interpillow, base/top of flow, 200 m.</td>
</tr>
<tr>
<td>× S55/PP33</td>
<td>AND</td>
<td>Interpillow, 7 km.</td>
</tr>
</tbody>
</table>

b-d: Bulk earth normalized incompatible trace element characteristics of representative basalts, andesites, and plutons and sediments respectively. Normalizing factors from Pegram (1986). Note difference in scale between the b and c versus d. Except from Rb through P, elements are shown in order of increasing compatible behavior (greater bulk partition coefficients) from left to right.
More/Less Altered Samples

Basalts

[Graphs showing the distribution of elements such as Rb, K, Sr, P, Th, Ta, Nb, La, Ce, Nd, Hf, Zr, Sm, Eu, Ti, Yb, Lu, with different concentrations and bulk earth normalized values for altered samples.]
Andesites

Field of Basalts

Sediments/Plutons

Field of Basalts

Field of Andesites

Bulk Earth Normalized

Rb K Sr P Th Ta Nb La Ce Nd Hf Zr Sm Eu Ti Yb Lu

Bulk Earth Normalized

Rb K Sr P Th Ta Nb La Ce Nd Hf Zr Sm Eu Ti Yb Lu
unreliable in GRV are segregated to the left-hand side of the diagram. The others are plotted in order of increasingly compatible behavior during partial melting/fractional crystallization of ultramafic to intermediate materials. The basalts from both volcanic belts are weakly to strongly LREE-depleted (La/Yb = 0.6-1.7; Figure 5-6b), consistent with derivation at an oceanic spreading center. The trace element patterns are generally smooth with the exception of Nb and Ta in sample C6b, either due to analytical uncertainties in these elements whose levels are near detection limits or to some selective depletion in the LREE. Note especially that the trace element patterns overall, and particularly for the REE, are very similar between samples BB5b and SFB-3 from the basalt belt and sample S45a from the andesite belt, in accord with their similar Nd isotopic signatures, and again geochemically linking the source regions of these two belts.

The andesites are LREE-enriched (La/Yb = 2.6-10.1; Figure 5-6c). Relative to the basalts, they generally have greater LREE and Th contents and lower heavy REE contents, resulting in trace element patterns which cross those of the basalts in the middle REE. High field strength elements (HFSE) are similar in abundance to the basalts (Ta and Nb) or lower (Hf and particularly Ti). Thus, the HFSE are generally depleted with respect to the REE and Th resulting in negative HFSE anomalies. Like the REE, the HFSE become increasingly depleted with respect to the basalts towards the right-hand side of the diagram.

The sediments and plutons generally exhibit still more strongly fractionated incompatible element patterns than the andesites with greater abundances of Th and the LREE and similar to lower HREE
abundances. In particular, the sediments and plutons have pronounced negative Ti anomalies. Between the sediments and the plutons, the trace element characteristics are largely similar except that the plutons have greater negative Ti anomalies and are typically more enriched in Th (up to a factor of 4). In spite of the likelihood that they are somewhat mobile, the general trends from basalt to andesite to sediment/pluton are also mimicked by Sr and P (decreasing) and Rb and K (increasing). Thus, in a qualitative sense, the incompatible trace element characteristics of the sediments/plutons and the basalts bracket those of the andesites and provide reasonable end-members for assimilation/mixing in the evolution of the andesites.

Amongst those elements considered to be particularly immobile and therefore particularly useful as tectonic discriminants, the compositional trend from basalts to andesite to plutons/sediments is evident. Figure 5-7a is a Hf-Th-Ta tectonic discrimination diagram (Wood, 1980; Wood et al., 1979a). As previously discussed, relative HFSE abundances are not likely to be appreciably affected by crystal fractionation, a requisite for its usefulness in elucidating magmatic sources. The basalts and andesites exhibit a similar range in Hf/Ta but the andesites are significantly more enriched in Th, a trend which extends towards the compositional fields of the sediments and plutons and actually overlaps that of the greywackes. Thus, although the basalts fall within error of the field of normal-type MORB, the andesites fall within the field diagnostic of calcalkaline basalts from convergent margins.

Figure 5-7b builds on the results plotted in Figure 5-7a by incor
Comparison of combined incompatible trace element characteristics of the GRV to possible magmatic sources and to early Tertiary plutons and Cretaceous age flysch sediments of the Kodiak-Sanak shelf (Hill et al., 1981). Symbols as in Figure 5-4. Both diagrams illustrate the correspondence of the GRV basalts to magmas from oceanic spreading centers and of the GRV andesites to calcalkaline volcanic arc magmas. In addition, they illustrate the possible hybrid origin of the andesites by contaminant of MORB with autochthonous materials from within the accretionary prism. a) Ta-Th-Hf (intra-HFSE) tectonic discrimination diagram; fields taken from Wood (1980). Error rhomb shown is for andesites; that for basalts is elongated in Th dimension by approximately factor of two. b) La/Hf versus Th/Hf (REE versus HFSE). Mixing arrays are linear in this diagram. [Data Sources: Batiza and Vanko, 1984; Bougault et al., 1980; Cambon et al., 1980; Cameron et al., 1983; Chen and Frey, 1985; Clague and Frey, 1982; Frey and Clague (1983); Masuda and Aoki, 1979; Nye and Reid, in press; Wood et al., 1979b, 1980.]
porating the behavior of the LREE relative to Th/Hf, the axis of
variation of Figure 5-7a. Compared to magma sources from the north
Pacific, the basalts fall within the fields for data from spreading
ridges and associated small seamounts (East Pacific Rise), back-arc
basins (Philippines and Marianas), and fore-arc lavas (Marianas) (see
Figure 5-7 for sources of data). In contrast, the andesites fall within
the fields of data from the Aleutians and calcalkaline lavas of Japan.
As for the basalts of the GRV, most oceanic sources have La/Th >7 while,
as for the andesites, most arc lavas have La/Th <10 and as low as 2 (see
compilation by Gill (1981), p. 138). Similarly, the andesites are more
depleted in the HFSE relative to the LREE (La/Hf >3) than most oceanic
lavas, a feature typical of, but evidently not restricted to (viz. some
backarc basins and oceanic island basalts), arc magmatism.

Because the denominators along both axes of Figure 5-7b are the
same (Hf), two-component mixing trends will be linear. In addition,
because these elements are largely incompatible, the effect of
fractionation during mixing/ assimilation will not significantly affect
the linearity of the array. It is evident from the trend in the data
that the combined LREE-HFSE characteristics are consistent with
derivation of the andesites by mixing between the basalts and the
plutonic magmas and also possibly with bulk assimilation of argillite-
greywacke mixtures by the basalts. However, bulk assimilation of such
mixtures can be ruled out by comparing the variation in the HREE to the
LREE and Th (Figure 5-8). As for Figure 5-7b, mixing lines in this
figure will be linear because the denominators on both axes are the
same. The Th/Nd ratio of both the greywackes and argillites are too low
Figure 5-8

Comparison of the paired Th/Nd versus Yb/Nd characteristics of the GRV to those of the early Tertiary plutons, Cretaceous age flysch sediments of the Kodiak-Sanak shelf, and possible anatectic melts. Symbols as in Figure 5-4; mixing arrays are linear. Narrowly ruled portion of pluton field indicates range in composition of most of the pluton samples. Also shown are the results of inversion of the combined isotopic and trace element characteristics of the andesites (see text) to yield trace element constraints on two model contaminants having distinct Nd isotopic signatures ($\varepsilon_{\text{Nd}} = -1$ and -2 as shown). Parent magma was permitted to vary in composition from that of S45a by fractional crystallization as illustrated. Crystallizing assemblage taken as 1:1 cpx:plag; D(Nd)=0.196 and D(Yb)=0.344 (compilation of Arth, 1976), D(Th) = 0.01 (compilation of Luhr and Carmichael, 1985). Solutions are for parent magmas containing 5 ppm Nd contaminated by material having 15-45 ppm Nd as shown. A range of parent compositions from 4-10 ppm yields results within 10% of those shown.

Field of possible anatectic melts are shown in upper left hand corner. Garnet, hornblende and biotite were assumed to be completely refractory during melting and abundances are arbitrarily chosen such that La/Yb of the melt equalled that of the solution curves at 40% partial melting. Zircon and apatite saturation constrained by experimental results of Watson and Harrison (1983) and Watson and Capobianco (1981). Zircon saturation was assumed for all melts. 1) Garnet only; 2) Garnet+apatite; 3) Garnet+hornblende+biotite in abundances and proportions similar to sandstone and shale residues of Arth (1976) and Hanson (1980). Melting in the presence of only hornblende produces a melt curve which intersects the melt field at its uppermost right-hand corner. Increasing modal garnet principally decreases Yb/Nd while increasing modal hornblende dramatically increases Th/Nd. REE distribution coefficients from Arth (1976) and Hanson (1980); those for Th assumed to be: garnet: 0; hornblende: 0.1 (Reid, unpub. data); and biotite: 0.16 to preserve Ce/Th partitioning of Mahood and Hildreth (1983); zircon: 91 (Mahood and Hildreth, 1983); apatite: 8 to preserve Ce/Th partitioning of Irving and Frey (1984).
Range of Possible Mixing/Assimilation Endmembers for:

- $\epsilon_{Nd} = -2$ (Solid)
- $\epsilon_{Nd} = 1$ (Dashed)
to fall on an extension of a trend through the basalts and those andesites with high Yb/Nd. The other andesites can easily be related to those with relatively high Yb/Nd by fractional crystallization as illustrated by the trend for fractionation shown in Figure 5-8. However, if partial melting of the sediments produces magmas with higher Th/Nd and with lower La/Hf and/or higher Th/Hf, these melts may also be the source of contamination.

In summary, the isotopic and trace element characteristics vary in generally smooth trends from the basalts through the andesites. These trends are characterized by decreasing $\epsilon_{\text{Nd}}$ (Figures 5-3 and 5-4), increasing abundances in the more incompatible elements, and generally decreasing abundances in the less incompatible elements, particularly Ti and the HREE (Figure 5-6), resulting in relative enrichments between less and more incompatible elements (e.g. higher Th/La, La/Hf, Nd/Yb; Figures 5-7 and 5-8). The nature of isotopic disparity between the basalts and andesites and the inadequacy of likely fractionation trends to produce the magnitude in observed interelement fractionation indicate that these features are not the result of any closed system process nor of alteration. Rather, the andesites may be derived from the basalts by some process of contamination. To a first-order, the isotopic characteristics, relatively low Ti and HREE abundances and more fractionated incompatible element patterns of the sediments and the plutons provide a suitable contaminant. In the following section, some of the key trace element characteristics of the contaminant are constrained and compared to these likely sources of contamination from within the accretionary prism.
Inversion of the trace element data: quantitative evaluation of the plutons and sediments as contaminants

A necessary constraint on the nature of the contaminant is that it simultaneously satisfy the isotopic composition of the andesites at the requisite relative and absolute trace element concentration levels. Thus, the isotopic constraints on the plutons and sediments can be used to evaluate the fit of the intrusive magmas and/or possible anatectic melts to the andesite data. However, because incorporation of material into a magma may be accompanied by fractional crystallization, simple two-component mixing calculations may not be adequate. Moreover, the parent basaltic magma may differ from those analyzed by having experienced a lesser or greater degree of fractionation. In order to pursue a generalized treatment of the data, I have used the equations for combined assimilation-fractional crystallization (AFC; DePaolo (1981)) in conjunction with a range in parent compositions related to those of the GRV basalts by fractional crystallization. Accordingly, the specific case of simple two-component mixing is addressed when \( r \), the ratio of assimilation to fractional crystallization, approaches infinity. The Nd isotope constraints together with Nd concentrations in the andesites eliminate \( r \) and \( F \) (the fraction of magma remaining after AFC) in the equations when the Nd concentrations in the parent magma and the assimilant are specified. As a result, complementary concentrations of other trace elements in the contaminant end-member can be calculated. Their abundances in the parent magma are permitted to vary.
sympathetically with the chosen concentration of Nd according to the equation for Rayleigh fractionation.

Andesites PP33 and 15-2e were analyzed for Nd isotopes and are considered: these samples generally bracket the range in trace element ratios in the andesites as seen in Figures 5-7 and 5-8. Sample S45a was used a parent magma since this basalt is associated with the andesites. The combined results for Th, Yb, and Nd are shown in Figure 5-8. These elements were chosen because they delimit the range in incompatible behavior during crystallization (cf. Figure 5-6), because they exemplify the compositional trends observed between the basalts, andesites, and possible contaminants, and because their behavior during crystallization and melting of a wide range of compositions could be satisfactorily predicted. The specific parameters applied to the calculations are discussed in Figure 5-8.

The contaminants were permitted to have two distinct Nd isotope signatures. The model "sedimentary" contaminant is assumed to have $\epsilon_{\text{Nd}} = -2.5$, consonant with the results of Hill and others (1981) and Hill and Morris (1982) who invoke a 1:3 greywacke to argillite mixture in the evolution of the early Tertiary plutons. The model "plutonic" contaminant is assumed to have $\epsilon_{\text{Nd}} = 0$, a value intermediate to the range in Nd isotopic signatures reported for the plutons ($\epsilon_{\text{Nd}(65\text{Ma})} = -0.9$ to 2.4 for Sm/Nd=0.22; Hill and Morris (1982)). Since the implied trace element characteristics of the contaminant vary fairly smoothly with $\epsilon_{\text{Nd}}$, the effect of varying $\epsilon_{\text{Nd}}$ can be gauged from the results for the two specified here.

A range in Nd concentrations in the assimilant (15-45 ppm)
produces only a limited range in the paired Th/Nd and Yb/Nd characteristics in the contaminant as shown in Figure 5-8. In this figure, solutions to the inverted equations are shown for a parent magma whose Nd concentration equals 5 ppm. This value is well within but somewhat to the low side of REE contents reported in basalts of the East Pacific Rise (Schilling and Bonatti, 1975; Schilling, 1975; Batiza and Vanko, 1984). However, varying the parent concentration from 4-10 ppm produces ratios within 10% of those illustrated; both Th/Nd and Yb/Nd increase with increasing parent Nd concentration. The solution curves lie along a broad extension to the data array, largely because the elements considered are moderately to strongly incompatible.

For the plutonic contaminant, the implied trace element characteristics intersect the field for those of the plutons for contaminants with greater than about 20 ppm. In particular, in spite of the fairly large range in composition exhibited by the individual plutons, the solutions pass through a restricted compositional field common to all of the plutons analyzed. Thus, simultaneous satisfaction of the paired trace element ratios suggests a composition in which most of the plutonic samples fall. Moreover, in spite of the range in $\epsilon_{\text{Nd}}$ measured for the plutons (Hill and Morris, 1982), a satisfactory fit to the model contaminant exists for only a range in $\epsilon_{\text{Nd}}$ from <1.0 to >-2.0, as can be discerned from Figure 5-8.

For the sedimentary contaminant, the implied Yb/Nd characteristics overlap those of the sediments but the Th/Nd characteristics are approximately a factor of two higher. The effect of assimilating more juvenile material (higher $\epsilon_{\text{Nd}}$) does not significantly alter this
conclusion. Therefore, bulk assimilation of the sediments cannot simultaneously satisfy the paired trace element characteristics as expected from Figure 5-7b and, as previously indicated, only a melt produced by partial anatexis of the sediments might suffice. Such magmas are permissable as contaminants if they fractionate Th from Nd to a similar or greater degree than Nd from Yb. Unfortunately, constraints on the evolving mineralogy of sedimentary compositions during anatexis and therefore, on the evolving compositions of the resultant melts, are poorly known. However, it is possible to consider the influence of residual phases likely to be present during melting on these elements. The principal phases to increase Th with respect to Nd in the melt are garnet, hornblende, and accessory phases such as zircon and apatite. All of these phases are likely to occur at some P and T conditions in metamorphosed greywackes and argillites.

The fields of partial melts in equilibrium with the aforementioned phases and which satisfy the requisite trace element characteristics of the contaminant are shown in Figure 5-8. The specific parameters applied to modelling the effects of these minerals are discussed in the figure caption. The solubilities of zircon and apatite have been determined experimentally (Watson and Harrison, 1983; Watson and Capobiano, 1981) and make it possible to adequately characterize their effects on the trace element characteristics of an evolving melt as a function of the degree of partial melting. Of these two, only apatite appears to have a significant effect on the Th/Nd ratio. Garnet strongly concentrates Yb relative to Nd. Thus, the amount of garnet in the residue is severely restricted to less than 3% at 60% partial
melting by the limited fractionation of Yb/Nd in the model contaminants relative to the sediments. Consequently, the fractionation of Th/Nd illustrated by the curve for melting in the presence of garnet is principally controlled by apatite. Hornblende very effectively fractionates Th from Nd and has a much less pronounced effect on Yb/Nd; its melt curve is very steep and defines the upper right hand limit to the melt field. The effect of biotite and other phases common to metamorphosed sedimentary rocks are not so much to fractionate Th/Nd or Yb/Nd as to control the absolute trace element concentrations of the melt. A model partial melting curve is illustrated in Figure 5-8 which, while nonunique, intersects the solution curves at reasonable degrees (35-50%) of partial melting. Thus, some combination of these phases will adequately satisfy the requisite trace element characteristics of the contaminant.

DISCUSSION

The chemistry of basalts from both volcanic belts of the Ghost Rocks Formation is consistent with an origin at or near an oceanic spreading center. In fact, the $\epsilon_{Nd}$ of sample C6b is the highest reported from the Pacific Basin. Aside from this singularly definitive characteristic, many of the geochemical features are also similar to those of some basalts of back-arc basins. However, the compressional nature of synchronous deformation is difficult to reconcile with such an origin.

In view of the intimate spatial and temporal association of the
basalts and andesites and the smooth compositional variations observed between them. I have considered a hybrid origin of the andesite by contamination of the basalt. Both contamination by magmas like those represented by early Tertiary plutons in the adjacent Kodiak Formation and/or possibly by assimilation of anatectic melts of the sediments can simultaneously satisfy the trace element and isotopic characteristics of the andesites. Invoking the plutons as the sources of contamination begs the question of origin of silicic plutonism in a near-trench environment and may seem purely academic since intrusion of the plutons post-dates eruption of the GRV. All workers agree that the isotopic and trace element compositions of the plutons are dominated by those of assimilated sediments (Hill et al., 1981; Hudson et al., 1979). Thus, the plutons probably provide a better average of the geochemical characteristics of sediment anatexis in the accretionary wedge and likely assimilants than can be estimated from considerations based on the limited data for the sediments. Therefore, although I have treated crustal anatexis and assimilation separately from contamination by the plutons, it is likely that they are aspects of a continuum process which produced the andesites and ultimately the more voluminous granodioritic magmas.

Magmatism in an anomalous forearc setting is known from several localities which temporally span the Cenozoic (Chile: Forsythe et al., 1986; Marianas: Bloomer, 1983; Solomon Islands: Perfit and Langmuir, 1984; California: Johnson and O'Neil, 1984 and Echeverria, 1980; Japan: Miyake, 1985; Alaska: Tysdal et al., 1977). A feature common to many of these localities is the presence of high MgO, high Cr lavas, often
andesites. The GRV andesites have Cr contents higher than most arc basalts (Figure 5-9); typical arc andesites have Cr contents less than 40 ppm. Thus, in this particular respect, the GRV differ from those typical of volcanic arc settings. One possible contaminant of the basalts which could satisfy the paired Ti-Cr characteristics of the andesites and which is also known from near-trench settings (Bloomer, 1983; Hickey and Frey, 1982; Cameron et al., 1983) is represented by high MgO, low TiO₂ boninite lavas. However, as constrained by existing data, boninites are too low in SiO₂ and too Th-poor (Figure 5-7b) to satisfy the data. On the other hand, mixing with the plutons will suffice as would mixing with a partial melt of the sediments if the distribution coefficient for Cr during melting is less than that for Ti (Figure 5-9).

An origin for near-trench magmatism by early dehydration of the subducting slab and consequent melting of the trenchward portion of an arc mantle wedge has been proposed (Delong et al., 1979; Jakes and Miyake, 1984). In the case of the Ghost Rocks Formation, the nature of deformation and the likelihood that it was underplated make it difficult to invoke the presence of such a mantle below and in this respect, may make the GRV unique amongst occurrences of near-trench magmatism. Nevertheless, it seems likely that higher than normal heat flow must obtain in the subducting slab (e.g. as in young oceanic lithosphere) in order to drive early slab dehydration. Moreover, several of the documented occurrences of near-trench magmatism can be reasonably well related both temporally and spatially to subduction of an active spreading ridge. In particular, the Pliocene age magmatism of the
Figure 5-9

Cr (in ppm) versus TiO$_2$ (in %). Symbols as in Figure 5-4. Illustrates high Cr contents of andesites relative to those typical of arc basalts; arc andesites generally have less than 40 ppm Cr. Also shown are mixing curves between the basalts and plutonic magmas; the field of the latter extends to lower TiO$_2$ and Cr than shown in figure. Also shown are possible fractionation trends for basalts from same localities (dashed lines). Bulk distribution coefficients (D) calculated from slope of trend; fractionation trends for andesites probably steeper (Gill, 1981). Discrimination line between MORB and arc basalts modified from Garcia (1978) and Pearce (1975). Fields and data points as in Figures 5 and 7 with addition of boninite data (Hickey and Frey, 1982; Cameron et al., 1983) and for near-trench magmatism of Japan, Chile, and So. Alaska (Tysdal et al., 1977; Forsythe et al., 1986; Miyake, 1985).
Taitao Peninsula off southern Chile can be well-correlated to subduction of the Chile Rise (Forsythe and Nelson, 1985). There, magmatism includes mafic and silicic volcanism, ophiolites, and granodioritic intrusions (Forsythe et al., 1986). Thus, by analogy to occurrences such as these, a model for origin of the early Tertiary magmatism of the Ghost Rocks Formation by ridge-trench encounter is preferred.

**Thermal and volumetric considerations**

The viability of a subduction of a spreading center as the ultimate source of magmatism, particularly of the more voluminous plutons, may be assessed in terms of thermal and volumetric constraints. In contrast to other environments, the thermal effects of ridge subduction may prime the sediments of the accretionary wedge for melting, independent of the effects of magma intrusion into the axis of the ridge or into the accretionary wedge. For heat transfer by conduction alone, the 350°C isotherm may penetrate to a depth of less than 5 km within 10 km of the trench when the ridge is subducted parallel to the trench (Delong et al., 1979). At depths of 20 km, temperatures may reach almost 600°C. Extending on the results of Hsui (1981), subduction of a ridge perpendicular to the trench may produce temperatures somewhat less than half of this. These estimates do not consider the important effect of hydrothermal circulation which are a significant source of heat transport out of young oceanic lithosphere. Temperatures of fluids vented along spreading ridges may exceed 350°C. Unfortunately, quantitative modelling of the effect of hydrothermal
circulation on the geothermal gradient in accretionary prisms would require an estimation of its scale, particularly as regards whether exchange occurs with the ocean above, and is beyond the scope of this paper.

Subduction of young oceanic lithosphere ± a spreading ridge may have thermally affected the trench sediments of the Upper Cretaceous Valdez Group of southern Alaska where temperatures of 400-450°C were attained at depths of 7 km in the accretionary complex (Sisson et al., 1986). From this starting point, raising the temperature of the sediments from 450°C to that at which hydrous partial melting can occur (ca. 660°C, Huang and Wyllie, 1981) requires approximately 2/3 km³ of basalt crystallization for each cubic kilometer of sediment melted. To a first approximation, the latent heat of melting of the sediments can be considered equal to that of the latent heat of crystallization of the basalts. Therefore, 1:1 ratios of sediment:basalt are required for actual melting or a ratio of 1:5/3 overall. These estimates are lower but generally consistent with a ratio of assimilation to fractional crystallization of 1:1 estimated by Hill et al. (1981) and Hill and Morris (1982) on the basis of geochemical considerations of the plutons at their current level of exposure.

A minimum volume of basalt required to produce the plutons can be estimated as follows: The areal exposure of the plutons is approximately 6.2 km²/km parallel to the strike of the Kodiak Formation. From the evidence for a subequal ratio of assimilation to fractionation and subequal amounts of basalt and assimilant (Hill and Morris, 1982), it is possible to estimate that about 2/3 of the mass of the pluton must have
been ultimately derived from MORB, or 4.2 km$^2$/km. Engebretson et al. (1984) predict a half-spreading rate of 34 km/Ma for 60 m.y. ago on the Kula-Farallon ridge. For a spreading rate of 11 km/Ma on a portion of the Mid-Atlantic Ridge, Moore et al. (1974) determined a volcanic production rate of 8.6 km$^3$/kmMa (equivalent to the production rate of oceanic layer 2A). Thus, for a reasonable aspect ratio of 1 in the plutons (z=ca. 6 km.), approximately 3 million years of ridge activity are required, well within the time scale dated for the plutons (58 - 62 Ma; Davies and Moore, 1984). Significantly less time is required if the extrusion rates summarized by Crisp (1984) are applied. On the other hand, proportionately more time would be required if the spreading ridge were at a high angle to the trench but quantifying this requires constraints on the amount of subsequent internal reorganization within the formation and on the actual volumes of the plutons. While these calculations are qualitative at best, they do illustrate the volume of near-trench magmatism in the Kodiak Formation and the feasibility of ridge subduction as its ultimate source. For comparison, eruption rates along the axis proper of volcanic arcs are similar (ca. 1-10 km$^3$/kmMa) as are those of oceanic islands (2.5 km$^3$/kmMa; Reymer and Schubert, 1985; Crisp, 1984) although locally eruption volumes of the latter may be as much as 300 km$^3$/kmMa.
Implications for paleotectonic reconstructions

Accumulated paleomagnetic, paleontologic, and geologic studies have established the role of amalgamation of far-travelled terranes in the evolution of southern Alaska (Jones et al., 1981; Coney et al., 1980; Coe et al., 1985). Paleomagnetic studies of the Ghost Rocks volcanic rocks (Plumley et al., 1983) have shown that they erupted in a more southerly latitude than their present location. A fixed hot spot reconstruction of the position of the Kula-Pacific-Farallon spreading center allows extension of the Kula-Farallon spreading ridge into proximity with the Kodiak Island accretionary complex as illustrated in Figure 5-1. Taken together with the geochemical evidence for ridge-trench interaction presented in this paper, the location of the Kodiak Islands accretionary complex during the Late Cretaceous and early Tertiary can be constrained as discussed by Moore et al., 1983. In arriving at a late Cretaceous-Paleocene paleolatitude for the GRV, Plumley et al. (1983) combined paleomagnetic data for andesites from Kiliuda and Alitak Bays (Aliulik Peninsula), in spite of some discrepancies in their NRM which they attributed to tectonic rotation about a vertical axis within the Ghost Rocks Formation. The chemical affinities between andesites from two localities, while nonunique, support such an interpretation.

The time spanned by volcanic and plutonic activity in the Kodiak accretionary complex appears to require an extended period of interaction with a ridge in order to produce both the volcanic and plutonic rocks (>3 Ma). This could be accounted for if some portion of
this activity reflected off-ridge volcanism, if different portions of
the ridge separated by transform faults were subducted, or if the ridge
stalled beneath the complex. Off-ridge volcanism occurs normally, like
that of Cenozoic small seamounts, although depleted MORB-like
compositions are generally restricted to young \( \leq 3 \) Ma old, oceanic crust
(Batiza, 1981); it also might occur anomalously during extension by
bending of young oceanic lithosphere as it enters the trench.
Subduction of the different segments of a ridge may explain the age
range depending on the applicable ridge-trench geometry, as might
coupling of the Kodiak accretionary complex with the ridge for a few
million years.

Delong and others (1979) list various thermal effects which have
been predicted as consequences of ridge subduction; these include
decreased arc magmatism, higher heat flow in the accretionary wedge, and
anomalous near-trench magmatism. The Ghost Rocks volcanics and the
Sanak-Baranof plutonic belt exemplify the last of these. Recent work by
Sisson and others (1986) and by P. Vrolijk (pers. comm. 1986) may
document the effect of ridge subduction on metamorphic gradients within
the accretionary wedge. Finally, although a hiatus in magmatic activity
on the Alaskan Peninsula is temporally well-correlated with the proposed
timing of ridge subduction as shown by Moore and others (1983), recent
paleomagnetic results for the Peninsular terrane have failed to confirm
a spatial link between this terrane and the Ghost Rocks Formation during
the early Tertiary (Thrupp and Coe, 1986).
SUMMARY

Magmatism in the Ghost Rocks and Kodiak Formations probably resulted from the interaction of the Kula-Farallon ridge with the Kodiak Island accretionary complex during the early Tertiary. This interaction resulted in the emplacement of tholeiitic basalts (MORB) and calcalkaline andesites as pillow lavas and of granodioritic magmas as intrusives in flysch sediments. The andesites and granodiorites are interpreted to be the product of sediment assimilation into MORB magma. If other granitoids of the Sanak-Baranof plutonic belt formed by similar means, an extensive early Tertiary ridge-trench encounter is represented. However, the precise geometry of this interaction requires further constraints on the extent of subsequent internal translation. While the andesites have many of the characteristics of arc rocks, this probably reflects the redundant effect of crustal assimilation of material which was dominantly arc-derived. However, this chemical similarity demonstrates the extent to which MORB characteristics may be masked by the effects of sediment assimilation.
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Chapter 6

RAPID AND DIACHRONOUS EFFECTS OF CRUSTAL ASSIMILATION:

ISOTOPIC AND TRACE ELEMENT EVIDENCE
INTRODUCTION

Fluid dynamical considerations have recently been incorporated into the modelling of magmatic evolution. This has galvanized efforts to address more dynamically reasonable models of magmatic behavior with the attendant effect of greatly increasing the range of complexity considered permissible. In spite of this, little is known about the actual kinematics of magmatic evolution. Temporal constraints on magmatic processes should be useful in assessing the appropriateness of the various fluid dynamical models as well as in addressing more fundamental questions pertaining to the scale at which equilibrium obtains. With this in mind, U-series nuclide analyses together with trace element and Sr, Nd, and Pb isotopic analyses of the lavas of Paricutin volcano were undertaken. The range of geologically short half-lives of the U-series nuclides provide realistic time-scales on which to evaluate the role of magma chamber processes.

Retrieval of temporal information from the U-series nuclides depends on disruption of secular disequilibrium by separation of parent from daughter nuclides. Because the U-series nuclides are concentrated in most magmas, they are difficult to fractionate from each other during magmatic evolution which is governed by crystallization. However, in highly siliceous magmas, the effective partition coefficients for these elements increase both absolutely and differentially. Thus, the U-series nuclides are more likely to be fractionated and therefore more interesting where a siliceous magma is involved, as for example, may obtain during crustal assimilation. In view of the importance currently attached to assimilation of sialic crust acting in concert with
fractional crystallization in magmatic evolution, the express purpose of this study was to evaluate the extent to which assimilation fractionated the U-series nuclides and whether they would constrain the timescale over which crustal assimilation occurred. In addition, to the extent that crust-forming processes fractionate U from Th, Th isotopes will become isotopically distinct from mantle signatures faster than Sr, Nd, and Pb isotopes; therefore, they are potentially useful for elucidating the source of crustal contamination.

Rather than study a suite of lavas flows from a single volcano which may have no common magma chamber, the single extended eruption of Paricutin volcano was chosen. The Paricutin lavas are andesite in composition, evidence that they have been modified since extraction from the mantle; the eruption occurred continuously for 9 years, evidence that the lavas are the products of a continuum process and arguably the products of emptying of a single magma chamber. As used in the paper, "magma chamber" refers to any aspect in a magma's evolution which follows initial segregation and coalescence of the magma but which occurs prior to eruption.

In his classic study of the Paricutin lavas, Wilcox (1954) shows that the increasingly evolved character of the lavas with time may be explained as a result of combined assimilation of rhyolitic crust and fractional crystallization. This point has been further corroborated, albeit on similar geochemical grounds, by Bryan (1969) and Miesch (1979). The importance of crustal assimilation in the evolution of the Paricutin lavas is also borne out by oxygen isotope analyses of the lavas (McBirney, pers. comm. 1984). As the results of my study show,
the trends of the data are not the smooth trends typically envisioned for combined assimilation-fractional crystallization. Nevertheless, the magmatic processes at work are quite simple and probably reflect the diachronous effects of thermal equilibration between magma and crust.

RESULTS

Paricutin is an andesite cinder cone and associated lava flows in the Michoacan-Guanajuato Volcanic Field of the western Trans Mexican Volcanic Belt. Paricutin attained notoriety as the volcano "that erupted in the farmer's cornfield" in 1943 and emitted lava until 1952. Samples were collected in early 1982 using a base map which I compiled from maps published periodically during the eruption which indicated its progress. The resulting map (Appendix 6-A) proved satisfactory for identifying key lava flows in the volcanic field and sample localities are indicated on the map. Unfortunately the youngest lava flow which is exposed erupted in 1945 thereby precluding study of the eruptive products from the first two years. One check on the precision of the sampling can be gauged from the agreement in K contents measured in these samples to those measured by Wilcox (1954) on temporally equivalent samples: the correlation coefficient \( r^2 \) is 0.993 (N=8).

Potential ambiguity due to the lack of significant K variation between the earliest lavas is obviated by their distinctive locations in the field.

Sr, Nd and Pb isotopic and U-series analyses as well as trace element analyses of selected Paricutin lavas are presented in Table 6-1. Additional analyses are presented in Appendix 6-A and shown in the
Table 6-1. Representative isotope, trace element and major element analyses, Paricutin volcano, Mexico

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<th>Month, year of eruption:</th>
<th>PR13</th>
<th>PR5</th>
<th>PR6</th>
<th>PR12</th>
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<tr>
<td>1-8, 1944</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>3-8, 1947</td>
<td>~55.2</td>
<td>~57.3</td>
<td>~59.1</td>
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<tr>
<td>3-6, 1948</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>3-10, 1951</td>
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Isotope data

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<tr>
<td>87Sr/86Sr</td>
<td>0.70388</td>
<td>0.70398</td>
<td>0.70401</td>
<td>0.70406</td>
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<tr>
<td>143Nd/144Nd</td>
<td>0.512799(14)</td>
<td>0.512782(12)</td>
<td>0.512758(14)</td>
<td>0.512724(14)</td>
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<tr>
<td>206Pb/204Pb</td>
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<td>18.676</td>
<td>18.676</td>
<td>18.698</td>
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<tr>
<td>207Pb/204Pb</td>
<td>15.621</td>
<td>15.588</td>
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<td>208Pb/204Pb</td>
<td>38.519</td>
<td>38.489</td>
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U series nuclides (dpm/g)

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<tr>
<td>238U</td>
<td>0.409(0.008)</td>
<td>0.388(0.008)</td>
<td>0.457(0.009)</td>
<td>0.486(0.010)</td>
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<tr>
<td>230Th</td>
<td>0.446(0.042)</td>
<td>0.454(0.032)</td>
<td>0.503(0.028)</td>
<td>0.547(0.040)</td>
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<tr>
<td>226Ra</td>
<td>0.802(0.034)</td>
<td>0.688(0.070)</td>
<td>0.752(0.046)</td>
<td>0.838(0.044)</td>
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<td>210Pb (as of 11/1/85)</td>
<td>0.613(0.024)</td>
<td>0.524(0.036)</td>
<td>0.592(0.024)</td>
<td>0.640(0.024)</td>
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<tr>
<td>230Th/232Th</td>
<td>1.164(0.072)</td>
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<td>(210Pb/226Ra)O</td>
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<td>(210Pb/226Ra)T=1943</td>
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<td>0.04 (0.35)</td>
<td>0.14 (0.31)</td>
<td>0.05 (0.27)</td>
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Trace Elements (ppm)

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Analytical techniques: Isotope data: (summarized by Roden et al., 1984); U-series nuclides: U and Th by isotope dilution (Chapter 1), Ra by Rn emanation at WHOI, ²¹⁰Pb by isotope dilution of ²¹¹Po. ²¹⁰Pb and ²³⁰Th/²³²Th by a spectrometry following chemical separation of the nuclides. ²⁰⁸Po spike from M. Bacon. Trace elements: Cs-Th by isotope dilution (Hart and Brooks, 1977; Chapter 1), La-Sc by instrumental neutron activation (Ila and Frey, 1984). Major elements: taken from Wilcox (1954) for temporally equivalent samples.

a) ⁸⁷Sr/⁸⁷Sr corrected for fractionation to ⁸⁶Sr/⁸⁸Sr = 0.1194 and normalized to ⁸⁶Sr/⁸⁶Sr = 0.70800 for Eimer and Amend SrCO₃. Reproducibility = ±0.00004 (2σ); in-run precision <1σ. ¹⁴³Nd/¹⁴⁴Nd corrected for fractionation to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and normalized to ¹⁴⁴Nd/¹⁴⁴Nd = 0.51264 for BCR-1. Reproducibility reduced from that of single runs (±0.00002; 2σ) by multiple analyses; in-run precision <1σ. Pb isotope analyses normalized to NBS 981. Reproducibility = ±0.05% per AMU; in-run precision <0.015%.

b) Activities and activity ratios. Errors (in parentheses) are those of analytical precision at the 2σ confidence level. Error in accuracy of ²¹⁰Pb is ~4% higher due to errors in spike calibration.
figures where relevant. Trace element and isotopic analyses of the
crustal xenoliths as well as lavas are also forthcoming from McBirney
and others (in press).

Sr, Nd, and Pb isotopes

$^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ vary monotonically with time in the
Paricutin lavas (Table 6-1; Figure 6-1) towards higher and lower values
respectively. This trend is altogether expected of assimilation of
somewhat older crust. These results contrast with the early Sr isotopic
analyses of Tilley and coworkers (1969) which yielded a slightly lower
$^{87}\text{Sr}/^{86}\text{Sr}$ ratio for a later eruption than for an early eruption (0.7040
versus 0.7043), possibly due to the erroneous inclusion of a sample
which may not have been part of the eruption (HAB). As can be seen in
Figure 6-1, the data can be fit to a single mixing line. While
assimilation is not required to produce this mixing trend, at least two
components are.

$^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ (not shown) vary slightly and in
opposite directions; as a result, $^{207}\text{Pb}/^{206}\text{Pb}$ exhibits a variation of
statistical significance like that of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$.
However, as presently constrained by the data, this variation occurs
principally in Stage 1 and may indicate that the two components which
undergo mixing are largely similar in Pb isotope characteristics to the
lavas analyzed.

The paired $^{87}\text{Sr}/^{86}\text{Sr}$- $^{143}\text{Nd}/^{144}\text{Nd}$ signatures of the earlier
Paricutin lavas overlap the low $^{143}\text{Nd}/^{144}\text{Nd}$ end of fields for arc lavas
from Japan and Chile, areas which are underlain by Mesozoic to Paleozoic
Figure 6-1

$^{143}$Nd/$^{144}$Nd versus $^{87}$Sr/$^{86}$Sr and their errors for Paricutin lavas. Circled data points are from Table 6-1; eruptive sequence is from left to right. Inset compares Sr-Nd isotope characteristics of the Paricutin lavas to those of intraoceanic and arcs on Mesozoic-Paleozoic crust (continental), Hawaii, and MORB lavas of the East Pacific Rise (EPR). Data sources: Intraoceanic arcs [Cohen and O'Nions, 1982; DePaolo and Johnson, 1979; McCulloch and Perfit, 1981; Nye and Reid, 1986; von Drach et al., 1986; White and Patchett, 1984]; Continental arcs [Japan (Nohda and Wasserburg, 1981); So. Chile (Hickey et al., 1986); Mt. St. Helens (Halliday et al., 1983)]; Hawaii [Chen and Frey, 1985; Roden et al., 1984; Staudigel et al., 1984; Stille et al., 1983; White and Hofmann, 1982]; EPR [MacDougall and Lugmair, 1986].
continental crust (Figure 6-1). The $^{206}\text{Pb}/^{204}\text{Pb}$ characteristics of the Paricutin lavas fall within the relatively restricted range characteristic of arcs from both oceanic and continental environments. They are higher in $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ than other arc lavas with the same $^{206}\text{Pb}/^{204}\text{Pb}$ ratio (e.g. Aleutians, Marianas, Mt. St. Helens). The Pb isotope characteristics of the Paricutin lavas are similar to those of two other lavas from the Trans Mexican Volcanic Belt analyzed by Sun (1980).

**U-series nuclides**

The activities of three U-series nuclides besides $^{238}\text{U}$ were determined: ($^{230}\text{Th}$), ($^{226}\text{Ra}$), and ($^{210}\text{Pb}$). The use of parentheses denotes activities ($\lambda N$), measured in dpm/gram. With sufficient time in a closed system, $^{238}\text{U}$ and its daughters will attain secular equilibrium which is characterized by activity ratios equal to 1. In order to distinguish geochemical effects from those of decay it is useful to normalize each nuclide to another isotope which is at least relatively stable and therefore acts as a geochemical tracer. In the case of ($^{230}\text{Th}$) and ($^{210}\text{Pb}$), ($^{232}\text{Th}$) and Pb abundances (since there is no appreciable Pb isotopic variation) can be used. However, for Ra there is no stable or longer-lived isotope. Consequently, Ba is often chosen as an analog for Ra. In this section I consider the relative variation of the U-series nuclides between the lavas as well as their fractionation with respect to these isotopes.
Figure 6-2

\((^{230}\text{Th})/(^{232}\text{Th})\) in the Paricutin lavas (circled crosses) versus a) \((^{238}\text{U})/(^{232}\text{Th})\); b) \(^{87}\text{Sr}/^{86}\text{Sr}\); and c) \(^{208}\text{Pb}^*/^{206}\text{Pb}\). Also shown are intraoceanic and continental arc lavas (diamonds except in (a) where continental arc lavas shown separately as field) and fields of oceanic lavas. \(^{208}\text{Pb}^*/^{206}\text{Pb}\) is \((^{208}\text{Pb}/^{204}\text{Pb}_{\text{lava}} - ^{208}\text{Pb}/^{204}\text{Pb}_0)/(^{206}\text{Pb}/^{204}\text{Pb}_{\text{lava}} - ^{206}\text{Pb}/^{204}\text{Pb}_0)\) where \((\text{Pb})_0\) are those ratios in Canyon Diablo meteorite. Data sources are: Allegre and Condomines, 1976; Bennett et al., 1982; Condomines et al., 1981a and 1981b; Krishnaswami et al., 1984; Newman et al., 1983, 1984a, 1984b, 1986.
In contrast to the isotope systematics already discussed, \( \frac{^{230}\text{Th}}{^{232}\text{Th}} \) is statistically the same in the Paricutin lavas (Table 6-1; Figure 6-2). Although \( \frac{^{238}\text{U}}{^{230}\text{Th}} \) is only slightly less than 1 (Table 6-1; Figure 6-2a), when the lavas are considered as a whole, \( ^{230}\text{Th} \) is clearly enriched over its ultimate parent \( ^{238}\text{U} \). In this respect, the Paricutin lavas are similar to those from the Cascades which also occur on a continental margin and are different from many intraoceanic arc lavas which are enriched in \( ^{238}\text{U} \) with respect to \( ^{230}\text{Th} \). The fractionation of \( ^{238}\text{U} \) from \( ^{230}\text{Th} \) must have occurred within the last 500,000 years or so.

The Paricutin lavas are similar to slightly more enriched in \( \frac{^{230}\text{Th}}{^{232}\text{Th}} \) than oceanic lavas with similar \( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \) and \( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \) signatures (Figure 6-2b and c; \( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \) is explained in Figure 6-2 and is a means of approximately quantifying the time-integrated \( \text{Th/Th} \) ratio of the mantle). On the average, arc lavas analyzed to date fall to the high \( \frac{^{230}\text{Th}}{^{232}\text{Th}} \) side of the oceanic field; considered in light of the data presented in 6-2a, this appears to reflect evolution in a time-integrated U-enriched environment prior to depletion in U with respect to Th. Judging from the Paricutin data, the latter effect does not appear to be related to crustal assimilation but may have occurred in the source during melt production.

\( \frac{^{226}\text{Ra}}{^{230}\text{Th}} \) in the Paricutin lavas is significantly greater than 1 (~1.6) (Table 6-1). This is also evident in Figure 6-3a as \( \frac{^{226}\text{Ra}}{\text{Ba}} \) ratios above the equiline. Accordingly, they have been enriched in \( ^{226}\text{Ra} \) with respect to \( ^{230}\text{Th} \) since ~8000 years ago. As shown in Figure 6-3b, \( ^{226}\text{Ra} \) both decreases and increases slightly with
Figure 6-3

$^{226}$Ra-$^{230}$Th characteristics of the Paricutin lavas. a) $^{226}$Ra/Ba versus $^{230}$Th/Ba. Dashed line with arrow illustrates variation observed with decreasing age of eruption and is drawn for constant $^{226}$Ra/$^{230}$Th. For most geologic occurrences, a closed system will lie on the equiline within ~8000 years of $^{226}$Ra-$^{230}$Th fractionation. b) Variation in $^{230}$Th and $^{226}$Ra with Ba. Ba increases monotonically with time.
\( \frac{^{226}\text{Ra}}{\text{Ba}} \) vs. \( \frac{^{230}\text{Th}}{\text{Ba}} \)

- Equiline

\( \% \text{M} \)

\( \text{Ba} \)

\( \text{Ba} \)
increasing Ba with the overall effect of significantly reducing the $^{226}_{222}$Ra/Ba ratio (Figure 6-3b). This effect cannot be the result of decay since the slope of a line through the data is $\geq 1$. Thus, not only have the lavas been enriched in Ra with respect to Th but the enrichment trend has been modified by consequent or subsequent magmatic processes.

$^{210}_{210}$Pb The half-life of $^{210}$Pb is 22 years; since $\geq 34$ years have passed since the eruption of Paricutin, any disequilibrium with respect to its parent, $^{226}$Ra, at the time of eruption has been largely erased. $^{(210)}_{(230)}$Pb/$^{(226)}_{(230)}$Th ratios are $>1$ as expected from the enrichment in $^{226}$Ra with respect to $^{230}$Th. Nevertheless, $^{210}$Pb and $^{226}$Ra are significantly out of equilibrium today ($^{(210)}_{(226)}$Pb/$^{(226)}_{(226)}$Ra) $< 0.8$). Existing data for lavas which are up to 100 years old suggest that $^{(210)}_{(226)}$Pb/$^{(226)}_{(226)}$Ra may not be appreciably modified by short-term surficial weathering although significantly older samples have $-10\%$ depletions in $^{(210)}_{(210)}$Pb (Krishnaswami et al., 1984). Therefore, it is likely that the disequilibria observed indicate dramatic disequilibria at the time of eruption. As summarized in Table 6-1, calculated initial ratios are less than 0.3. Due to the large errors which arise in calculating initial $^{210}$Pb activities, the variation in $^{(210)}_{(210)}$Pb over the course of the eruption cannot be delineated. However, disequilibrium of a similar magnitude has been determined in at least one freshly erupted lava (Krishnaswami et al., 1984) suggesting that it is either an eruption-related phenomenon or is intrinsic to the magma.
Trace Element Data: A Tripartite Geochemical Trend

The spread in the Sr and Nd isotopes clearly require the involvement of at least two endmembers in the evolution of the Paricutin lavas. The changing trend in $^{226}\text{Ra}$ with respect to Ba appear to require a third. Thus it is useful to consider whether a third component is required by any of the other data. In fact, three geochemical trends are evident in the trace element data, at least one of which violates conventional wisdom about the behavior of the so-called incompatible elements with increasing magmatic differentiation.

Amongst the incompatible elements, only those which are most incompatible, Cs, Rb, K, increase simply with Ba (Table 6-1; Figure 6-4; additional data in the appendix). At the other extreme, Yb shows a net decrease overall. Like Ra, the REE and HFSE decrease with increasing Ba during Trend 1 (PR13 to PR5), recover dramatically in Trend 2 (PR5 to PR6), and exhibit trends intermediate to those of Trend 1 and 2 in Trend 3 (PR6 to PR12). The interelement behavior during Trend 1 and overall is summarized in Figure 6-5 which compares incompatible element concentrations at the end of Trend 1 and of the eruption to those of the oldest lava analyzed. The overall effect is to fractionate the more incompatible trace elements from the less incompatible ones with increasing magmatic differentiation while producing little change in the concentrations of the light and middle REE.

In general, the major element chemistry of the Paricutin lavas varies monotonically with time. Indicators of differentiation such as K$_2$O, SiO$_2$, and FeO*/MgO increase with time, consistent with fractional
Figure 6-4

Element-element and ratio-ratio plots for representative incompatible elements in the Paricutin lavas. Elements plotted against Ba by analogy to Figure 6-3; Sm chosen as denominator in ratio-ratio plots because it is most distinct from Ba of those of high precision.
crystallization and/or crustal assimilation. However, previous workers (Wilcox, 1954; Bryan, 1969; Miesch, 1979; Reid, 1984) have also recognized a sinuosity in the geochemical trends which can be approximated by a three-stage evolution. This is most apparent in $\text{Al}_2\text{O}_3$ which decreases in Trend 1 and 3 and overall but increases in Trend 2. Moreover, because considerably more lavas have been analyzed for the major elements, it is evident that the tripartite trend in the trace element data is not an artifact of a limited data base and that the samples chosen as endmembers of the individual trends are probably representative.

**INTERPRETATION**

*Probable Origin Of Tripartite Geochemical Trends*

Geochemical variations both within and between eruptions from a single volcanic centers are often assumed to reflect progressive evolution of the magma over the course of the eruption (e.g. compositionally zoned andesite eruptions) or spatial variations extant in the magma chamber prior to eruption (e.g. compositionally zoned rhyolites). The former interpretation is particularly tempting in the case of Paricutin where most of the major elements vary monotonically towards more evolved compositions with time. However, such an interpretation is nonunique and, in view of the diverging trends amongst the U-series nuclide and incompatible element data, may be unrealistic. If the evolution of the magma is not simply a progressive one which acts on the magma as a whole while it is periodically tapped, this leads to the problem of identifying a parental composition from which the other
lavas can be derived. The problem of a parental composition is exacerbated not only by the possibility that it may not be amongst those analyzed but by the possibility that it may lie outside of the range of composition exhibited by the eruption altogether.

The anomalous trace element variations of the Paricutin lavas are not unique to this eruption. The extended eruption of Jorullo volcano which is ~200 years older than Paricutin and occurs ~75 km southeast of Paricutin also exhibits decreasing HREE with anomalously increasing alkalis and SiO₂ over the course of its eruption (Luhr and Carmichael, 1985). In contrast to Paricutin however, Al₂O₃ and Sr increase overall. The Jorullo eruption is also slightly more mafic than that of Paricutin. Volcan Arenal in Costa Rica has been erupting continuously since 1968 and is chemically similar to Paricutin. It exhibits a trend towards increasing alkalis and LREE but decreasing HREE during the third stage of its evolution (Reagan, submitted 1986). Ultimately, case studies of compositionally zoned eruptions such as these need to be considered together in elucidating the deus ex machina which governs their anomalous chemical variations. Although a quantitative treatment of all of the Paricutin data is beyond the scope of this paper, in light of the parity between the incompatible trace element and U-series data it is useful to consider possible explanation for the trends observed in these data. Specifically, it is important to consider the relationships between the endpoints of the three trends since each trend may simply be the result of mixing if the processes which create these endpoints are catastrophic rather than continuous.

Figure 6-5 shows the relative enrichments or depletions of the
Figure 6-5
Enrichments and depletions in the incompatible elements during Trend 1 (solid) and overall (open). Concentrations late in the eruption plotted over those early in the eruption.
incompatible elements observed in Trend 1 as well as those overall. In spite of the dramatic contrast in behavior between the extremes of the incompatible element pattern, the relative changes which occur during Trend 1 and overall are sympathetic. This suggests that little or no change in interelement fractionation is represented by the different trends. This proposition is corroborated by the ratio-ratio plots shown in Figure 6-4. As for the isotope systematics, the ratio-ratio variations can be approximated by straight lines, indicating that only two components are required to explain their variations. Therefore, a third component is required only by the variations in trace element concentrations and must have interelement characteristics similar to those of one of the components.

The most reasonable candidate for a third component is a crystal phase assemblage which either does not appreciably fractionate the incompatible elements or fractionates them in a fashion similar to the trends in the lavas themselves. Accordingly, the tripartite trends in the data may be the result of disruption of a mixing trend by crystal separation or accumulation. The mixing array could reflect crustal assimilation which accompanied the eruption or could reflect a previously established magma chamber which was compositionally zoned. Some of the possible permutations of mixing plus crystal accumulation or settling are illustrated in Figure 6-6: other possibilities are more extreme variants of these. Bowing to Occam's razor, it is simplest to assume that at least two points in the data array lie on the mixing array and that the others have been affected by crystal gain or loss.

Of the scenarios shown in Figure 6-6, the crystal accumulation
Figure 6-6

Variation in Sm with Ba (a) and schematic models for evolution of the incompatible trace element characteristics of the Paricutin lavas. Models involve accumulation (b) or fractionation of crystal phases (c & d) (solid arrows) and crustal assimilation (dashed trend). For simplicity, two of the nodes in the trace element trends are assumed to lie on the trend of assimilation.
Crystal Fractionation

Crystal Accumulation

Crystal Fractionation #1

Crystal Fractionation #2
model has the desirable effect of correlating with an observed increase in modal olivine. However, the amount required (>10%) far exceeds the amount observed (<4%) and therefore, crystal resorption would be required. Of the crystal fractionation models, Model #1 is superficially more acceptable since the implied effect of assimilation is towards increasing incompatible element concentrations. Moreover, the effect of fractionation on SiO$_2$ would be expected to be less severe at lower SiO$_2$ contents, consistent with the smaller change in SiO$_2$ with Rb and Ba observed in Trend 1 than in Trend 3. Finally, according to this model, the least amount of fractionation is implied for those lavas where the amount of undercooling is expected to be the least, that is, those that bridge the olivine-orthopyroxene reaction divide.

In order to evaluate the effect of fractionation on the ~linear trends of the ratio-ratio plots, the composition of the oldest sample analyzed, PR13, was modelled as the sum of vectors for assimilation and fractionation by back-calculating from the beginning of Trend 2 (fractionation model #1). The chemical variations between the beginning of Trend 2 and the end of Trend 3 were treated as an assimilation vector; surface equilibrium (Rayleigh fractionation) was used for the crystal fractionation vector. A range of olivine: plagioclase proportions from 65:35 to 35:65 was considered and the partition coefficients summarized by Luhr and Carmichael (1986) were used. Numerical experiments were used to find an approximate fit to the composition of PR13 but a best fit was not attempted. This resulted in a model involving ~28% fractionation of a composition on the mixing array with a Rb content of 11.5 ppm. The result is compared to that of
Figure 6-7

Graphical illustration of fit of crystal fractionation model #1 (see Figure 6-6) to incompatible trace element characteristics of sample PR13. Parameters of model calculation discussed in text.
Sample PR13

Predicted/Observed

Cs Rb Ba Th U La Hf Ce Ra Nd Sm Eu Ta Yb Lu Sr
sample PR13 in Figure 6-7 and as shown, a fit to within 5% can be made.

This model for the Paricutin data postulates the diachronous interplay of crystal fractionation and crustal assimilation. An estimate of the effect of assimilation from simply comparing the elemental concentrations of the silicic lavas to the more mafic ones would yield an erroneous impression of the true effect and extent of enrichment produced by assimilation. For example, crystal fractionation model #1 predicts -35% more assimilation than would be concluded by simply comparing the latest to the earliest lava. In addition, the incompatible elements all increase monotonically as a result of assimilation according to this model rather than variably. The exact proportion of fractional crystallization to crustal assimilation depends on the steepness of the vector for assimilation (e.g. how much the source of variation in the data approaches that of fractionation model #2 of Figure 6-6). Not surprisingly, similar calculations for fractionation model #2 yielded results which are equally satisfactory indicative of the latitude in interpretation permitted by this model. However, so long as the assimilant has higher concentrations of the incompatible elements than the lavas, the negative trends exhibited by some elements in the earlier lavas require a greater proportion of fractional crystallization to crustal assimilation. Thus, this scenario contrast somewhat with more traditional view of combined assimilation-fractional crystallization which hold that greater crystallization must occur in the more siliceous and therefore cooler lavas in order to drive crustal assimilation.
Other Possible Interpretations

The crystal assemblage which disrupts the mixing array needn’t be in the magma but rather, may be in the assimilant. In this case, it is more reasonable to attribute it to the effect of partial melting. For example, an assimilant which is partially or selectively melted may have low Th, REE, and HFSE abundances due to their retention in the residue thereby explaining Trend 1. At least two possibilities for this exist: one, residence of Th, REE and HFSE in accessory phases ± garnet insoluble at the conditions of melting or two, preferential decomposition of phases in which the abundance of these elements is low but that of the alkalis and Ba is high (e.g. biotite, hornblende, muscovite). Regarding the first, this requires the assimilant to be lower in Th and REE than PR13; high silica rhyolites or granitoids in equilibrium with phases which concentrate these elements are rarely so bereft. Regarding the second, a notable feature in a published description of crustal xenoliths in the Paricutin lavas is the presence of pseudomorphs after mafic phases (Wilcox, 1954). Thus, the preferential decomposition of mafic phases appears to be kinetically favored. It is unlikely, however, that the selective breakdown of mafic phases alone is sufficient to explain the major element trends (e.g. increasing SiO₂) but variations on this theme remain to be tested. Moreover, both of the foregoing models suffer from the improbability that linear variations in the incompatible element ratios would be produced with changing trace element concentrations in the assimilant.

Other processes ultimately controlled by kinetics are those related to diffusion. If the country rocks are generally more enriched
in the incompatible elements overall, the relative enrichments in the incompatible elements overall can be qualitatively correlated to their charge as well as size consistent with diffusional control of assimilation. The problem arises with Trend 1: it is difficult to decrease the concentrations of many of the elements enough by what must essentially be dilution according to this model. However, two-liquid partition coefficients for the REE and HFSE favor the mafic magma. The trend of stage 1 could reflect a diffusion gradient or mixing across a two-liquid diffusion couple if in fact a means of preserving this phenomenon during eruption can be envisioned.

Finally, an alternative explanation for the tripartite trends involves the injection of a new magma into either a zoned magma chamber or one undergoing crustal assimilation. Reagan and others (in press, 1986) have proposed an analogous explanation for stage 2 of the eruption at Volcan Arenal. According to this model Trend 1 would record mixing with a more REE and HFSE-poor but not alkali and Ba-poor magma while Trends 2 and 3 would have to be the result of fractional crystallization and mixing. The specific trace element concentrations of this new magma are somewhat dependent on the amount of fractional crystallization accompanying Trend 1 but the incompatible ratios and isotopic signatures must lie at the end or on an extension of the data array (e.g. like fractional crystallization model #2). These characteristics are qualitatively those of more alkaline magmas, such as lavas near Jorullo volcano, south of Paricutin (Luhr and Carmichael, 1985). Besides typically having higher incompatible element abundances overall, more alkaline magmas usually also have higher \( {^{226}\text{Ra}}/{^{230}\text{Th}} \) ratios. The
lack of significant change in \((\frac{^{226}\text{Ra}}{^{230}\text{Th}})\) overall would therefore require the "new magma" to be an old one: one which has resided in a magma chamber long enough for Ra to decay to \((\frac{^{226}\text{Ra}}{^{230}\text{Th}})\) values \(\leq 1.6\).

A comprehensive examination of all of the data which attempts to simultaneously satisfy the compatible element and major element characteristics with those of the incompatible element characteristics will be forthcoming. However, as I have shown, the variations in the incompatible element characteristics may be quite simply explained in terms of crustal assimilation and fractional crystallization. Consideration of all of the data in the context of this model may yield constraints on whether the apparent composition of the assimilant is likely to be fractionated with respect to representative crustal compositions. This, in turn, should constrain the relative importance of bulk assimilation, partial melting, or kinetically controlled but steady-state phenomenon in the assimilant.

**U-SERIES CONSTRAINTS ON NATURE AND TIMING OF ASSIMILATION**

Based on Pb isotope evolution histories for granulites and actual lower crustal materials, the lower crust appears to have a time-integrated U/Th ratio which is significantly lower than that of the upper crust (e.g. \((^{238}\text{U})/(^{232}\text{Th}) = 0.36-0.80\): Taylor and McLennan, 1985; Weaver and Tarney, 1984). Therefore, the lower crust should also have a significantly lower \((^{230}\text{Th})/(^{232}\text{Th})\) ratio than its upper crustal counterpart. The lack of significant decrease in \((^{230}\text{Th})/(^{232}\text{Th})\) in the Paricutin lavas with increasing assimilation probably precludes the
involvement of the lower crust in this process. Quantifying this depends on the actual amount of assimilation which occurred. For example, using Wilcox's (1954) estimate of 25% assimilation, the incorporation of crust with \((^{230}\text{Th})/(^{232}\text{Th}) \leq 0.85\) is precluded.

All of the parent-daughter pairs show some disequilibrium; those involving \(^{226}\text{Ra}\) are unequivocally significant. The trend of Ra-enrichment follows the tripartite trends discussed above and Ra is satisfied by the model presented for the trace elements (Figure 6-7). The effect of Ra-decay is to reduce the magnitude of differences observed in these trends but it can neither create or destroy them until secular equilibrium is attained. The fact that these trends correlate with that presumed to be related to crustal assimilation means that the enrichment of Ra with respect to Th apparently preceded or attended crustal assimilation. Therefore, crustal assimilation has occurred on a time-scale less than that required for Ra to return to secular equilibrium or less than about 8000 years. The failure of Ra/Th to increase over the course of the eruption indicates that assimilation itself - at least over the interval studied - was probably not the source of Ra enrichment.

The apparent Ba/U ratio of the assimilant is significantly higher than that of the Paricutin magmas. Although it increases overall, Ra increases less than or comparably to U and therefore, significantly less than Ba. If the higher Ba/U of the assimilant is an intrinsic feature of the country rocks, the contribution of \(^{226}\text{Ra}\) to the Paricutin magmas may be governed largely by the abundance of \(^{238}\text{U}\) in the assimilant. In support of this, Ra/U may decrease somewhat over the course of the
eruption and is permissive of a $^{226}\text{Ra}/^{238}\text{U}$ ratio in the assimilant of 1. Moreover, this illustrates that bulk assimilation cannot be precluded on the basis of these U-series nuclides. However, if the Ba/U of the assimilant is high due to fractionation during partial melting, $^{226}\text{Ra}$ may be following U rather than the more geochemically similar Ba. If true, this suggests that Ra is being removed from U and $^{230}\text{Th}$ sites, where it occurs by the grace of U and Th decay, at a rate similar to that of extraction of its parent. Thus, crustal assimilation may be occurring at a rate faster than that of Ra equilibration with the magma. Although Ra equilibration may be slower than that of other alkaline earths and of the alkalis, it is likely to exceed that of the REE and HFSE, depending on their residence sites. Consequently, the potential failure of Ra to equilibrate according to its likely partitioning behavior suggests that the commonly held presumption of equilibrium partial melting (where partial melting is considered at all) during crustal assimilation may be invalid. In any event, Ba is not an appropriate analog for Ra where crustal assimilation is involved.

The temporal significance of the enrichment of $^{226}\text{Ra}$ over $^{210}\text{Pb}$ is shown by a $^{210}\text{Pb}$ evolution diagram (Figure 6-8). This diagram is analogous to the better-known Nd evolution diagram except that the time axis is given in $e^{\lambda t}$. $e^{\lambda t}$ linearizes the exponential effect of decay which in this case governs the rate of in-growth of $^{210}\text{Pb}$. The $^{210}\text{Pb}$ evolution curves give the activity of $^{210}\text{Pb}$ in
Figure 6-8

(210Pb) evolution diagram for the Paricutin lavas. Time axis is plotted as $e^{\lambda t}$. Inset shows the effect of analytical errors including accuracy of 208Po spike on decay correction of (210Pb) and ultimate limits on the timing of 226Ra enrichment.
\((^{210}\text{Pb})_{\text{final}} = (^{226}\text{Ra})\)

\((^{210}\text{Pb})_{\text{measured}}\)

\[e^{\lambda t} = 1, 2, 3, 4\]

TIME

Years before Onset of Eruption

Time of Eruption

PR12 — Illustrating effect of analytical error

\[^{210}\text{Pb} \]

0.8
0.6
0.4
0.2
0.1
0.0

\[^{210}\text{Pb} \]

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

313
the past using the assumption that the lavas have behaved as a closed system both before and after eruption. Although the precise "timing" of Ra-enrichment depends on \(^{210}\text{Pb})_o\), it is clear that an upper limit to this enrichment \((^{210}\text{Pb})_o=0\) is within 30 years of eruption (allowing for analytical error). For \(^{210}\text{Pb})_o\) like that of the lowest \(^{238}\text{U}\) measured (20.4), Ra enrichment may have occurred just prior to, or in the case of the later erupted samples, following the onset of eruption. Although the means of Ra-enrichment remains unresolved, the coherent behavior of Ra (and Pb) with respect to Th and U as well as the other trace elements (Figure 6-5) suggests that the enrichment of Ra (or depletion of Pb) could not have followed assimilation. Therefore, it is possible that crustal assimilation occurred either within a few years of the birth of Paricutin volcano or occurred progressively over the course of the eruption. The geochemical evolution of Paricutin volcano may ultimately have to be interpreted in terms of a predominance of disequilibrium phenomena operative on such a short timescale.

CONCLUSIONS

The apparent effect of crustal assimilation in the Paricutin lavas is to inhibit enrichments in all but the most incompatible elements while producing more fractionated incompatible element patterns overall. This is largely due to the diachronous effect of fractional crystallization. Fractional crystallization also reduces the apparent spread in major element variation produced by crustal assimilation as well as the temperature differential over the eruptive suite as a whole. The effects of fractional crystallization initially dominate those of
crustal assimilation but by the end of the eruption, the opposite is true. Thus, the ratio of crustal assimilation to crystal fractionation varies widely over the course of the eruption, possibly from \(<1\) to almost infinity. In addition, this ratio may vary somewhat sinusoidally if the model preferred above is representative. Once the effect of fractional crystallization is removed, assimilation may be quite simply understood by two-component mixing. The overall result of the diachronous effect is to lead to an underestimation of the amount of assimilation.

The U-series nuclides in the Paricutin lavas are not appreciably fractionated from one another by crustal assimilation. This, together with the decoupling of Ra from Ba and the imprecision of initial \(^{210}\text{Pb}\) make it impossible to quantitatively extract temporal information about assimilation from these data. However, the sympathetic variation in Ra with respect to the other trace elements indicates that assimilation has occurred since \(^{226}\text{Ra}\) was enriched over its parent \(^{230}\text{Th}\), or probably in much less than the last 8000 years. If the \(^{226}\text{Ra}-^{210}\text{Pb}\) systematics have behaved as a closed system since the lavas crystallized, Ra-enrichment may have occurred within years of the onset of eruption. A plausible scenario which incorporates this result is one in which earlier pulses of the ascending magma lose heat to the colder conduit walls with attendant crystallization and little assimilation; later pulses mix with the hotter, now partially molten country rocks. Preliminary calculations indicate that the amount of fractionation estimated for the earlier, more voluminous lavas provides a more than adequate amount of heat for melting of the assimilant.
Studies of the earliest eruptives as well as the crustal xenoliths included in the magmas (courtesy of R. Wilcox) are currently underway. Together with the results of McBirney and others (in press, 1986), an earlier phase of assimilation and limits on the actual magnitude of incompatible element fractionation between the crust and the assimilant will be documented.
REFERENCES


APPENDIX 6A

Figure 6A-1 shows sample locations at Paricutin volcano. Analyses for additional lavas are given in Table 6A.
Figure 6A-1

Plane view of lava flows at Paricutin volcano showing sample locations. Map constructed from compilations of sketch maps published by USGS from 1945-1952.
### Table 6A-1. Additional isotope and trace element analyses, Paricutin volcano, Mexico

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INAA data

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<sup>a</sup> Analytical techniques as described in Table 6-1.