

PETROLOGY AND GEOCHEMISTRY OF HIGH DEGREE MANTLE MELTS

by

STEPHEN WAYNE PARMAN

B.A. Earth and Planetary Sciences
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Submitted to the Department of
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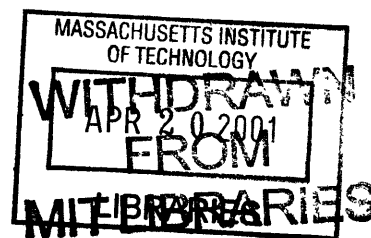
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Signature of Author _____
Department of Earth, Atmospheric, and Planetary Sciences
January 11, 2001

Certified by _____
Timothy L. Grove
Thesis Supervisor

Accepted by _____
Ronald G. Prinn
Department Chairman

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ABSTRACT

Experimental phase equilibria, whole rock major and trace element concentrations, and mineral major and trace element concentrations are used to constrain the petrogenesis of high degree, hydrous melts of the mantle, with particular focus on komatiites from the Barberton Mountainland, South Africa. Chapter 1 presents experiments on a Barberton komatiite composition under anhydrous and H₂O saturated conditions. A comparison of the compositions of augite in the experiments with augite in the samples indicates that at least 4.5 wt.% H₂O was present in the komatiite melts prior to emplacement. The presence of H₂O in the magmas would allow them to be produced at lower temperatures than required by anhydrous models of komatiite genesis, and would obviate the need for extremely high temperatures in the Archean mantle. In Chapter 2, ion probe analyses of augite in Barberton komatiites are used to quantify the effects that metamorphism has had on the bulk rock compositions. The results indicate that high field strength elements and most rare earth elements were not significantly mobilized by metamorphism, while Eu and Sr were mobilized. Some Barberton magmas were enriched in light rare earth elements and Sr, and depleted in high field strength elements, which are the chemical characteristics of modern subduction related magmas. Chapter 3 presents melting experiments that explore the effect of H₂O on melts in equilibrium with olivine and orthopyroxene at 1.2 to 2.4 GPa. The results of the experiments are used to infer the thermodynamic properties of H₂O in silicate melts, and to construct a numerical model that predicts the composition of high degree mantle melts. The model is used to estimate the melting conditions that produced high-MgO andesites, boninites, and komatiites. It is shown that Barberton komatiites can be produced by melting at low pressures (2.4-3.0 GPa) and temperatures (1440-1500°C). Chapter 4 demonstrates that basaltic komatiites overlap the compositions of modern boninites and display nearly identical trace element systematics. Komatiites are also shown to have numerous chemical similarities to boninites as well. It is proposed that komatiites and basaltic komatiites were produced by the same processes that produce modern boninites. The lack of komatiites in modern subduction zones is attributed to ~100°C secular mantle cooling that has occurred since 3.5 Ga.

Thesis Supervisor: Timothy L. Grove
Title: Professor of Geology

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INTRODUCTION

Komatiites are found in greenstone belts that range in age from 2.0 to 3.5 Ga [*de Wit and Ashwal, 1997*]. Their near absence in the post 2.0 Ga rock record is the clearest evidence we have that secular changes in the Earth's mantle have occurred [*Herzberg, 1995*]. This gives komatiites a significance far beyond their physical abundance. Quantifying the secular changes that have occurred requires estimating the melting conditions which produced komatiites. Such estimates are based largely on phase equilibrium experiments [*Green, 1975; Green et al., 1975; Walter, 1998*]. Yet knowing the mantle potential temperatures required to produce komatiites is not enough. The tectonic setting must also be known because potential temperatures are not constant throughout the mantle. For instance, 1500°C is a relatively hot mid-ocean ridge potential temperature, but is low for an ocean island plume. Each of the chapters of this dissertation are aimed at constraining the melt generation conditions of komatiites or their tectonic setting. Chapter 3 is the only one that is not fully given over to komatiites, but instead deals more broadly with the effects of water on mantle melts and the prediction of hydrous melt compositions over a wide range of conditions.

Chapter 1 focuses on the emplacement conditions of Barberton komatiites. A selected composition is crystallized under various conditions, and the composition of augite crystallized from the melt is compared to rare augite in the samples that has escaped the effects of metamorphism. The natural augite compositions are only reproduced when H₂O is present in the melt. This has implications for mantle evolution as the presence of H₂O allows komatiite magmas to be produced at lower temperatures

(80-100°C) lower than under anhydrous conditions, and therefore implies slower cooling of the mantle.

Chapter 2 examines the effect that metamorphism has had on the trace element composition of Barberton komatiites. This is a significant problem because all Barberton komatiites, and all komatiites, have been metamorphosed. Yet trace elements can be useful indicators of tectonic provenance. We calculated the trace element composition of komatiite magmas by analyzing the preserved augite by ion microprobe, and then calculating the trace element concentrations of the melt in equilibrium with the augite using mineral/melt partition coefficients. The results show that the high field strength elements and most rare earth elements are not significantly changed by metamorphism, while Sr and Eu are. Sr contents in the augite imply that the komatiite melts were Sr enriched, and that the Sr depletions seen in many komatiite samples are the result of metamorphism. The pre-metamorphic chemical characteristics of many Barberton komatiites are similar to chemical systematics seen in modern subduction related magmas, including: high field strength element depletions, Sr enrichments, and light rare earth element enrichments [Gill, 1981; Morris and Hart, 1983; Perfit *et al.*, 1980].

Chapter 3 presents experimental data on the effect of H₂O on the composition of melts in equilibrium with olivine and orthopyroxene. The data are used to develop a predictive model for olivine-orthopyroxene-liquid equilibria that is consistent with the hypothesis that H₂O is dissolved primarily as OH. The changes in the mineral/melt partition coefficients can be explained by viewing the melt as having two distinct quasi-lattice sites [Toop and Samis, 1962a; Toop and Samis, 1962b]: one for network formers like SiO₂, and another for network modifiers such as H₂O and MgO. The experimental data are used to construct a numerical model that predicts the compositions of hydrous

and anhydrous melts in equilibrium with olivine and orthopyroxene. The model is used to estimate the melting conditions for high-MgO andesites, boninites, and komatiites. It is shown that Barberton komatiites can be produced by hydrous melting of a depleted source at 2.4-3.0 GPa and 1440-1500°C.

In Chapter 4, the major and trace element chemistry of basaltic komatiites and boninites are shown to largely overlap. The composition of komatiites are also shown to have many similarities to boninites. Taken with the evidence for high concentrations of H₂O in komatiite magmas given in chapters 1 and 3, we propose that komatiites are formed in subduction zones by processes similar to those that produce boninites in modern arcs [Crawford *et al.*, 1989; Stern and Bloomer, 1992]. The melting conditions inferred for komatiites and boninites in chapter 3 are used to show that the spectrum of magma compositions interlayered in komatiite bearing sequences can be explained by melting in a subduction zone that was ~100°C hotter the mantle that produced modern boninites. Phanerozoic sequences that contain basaltic komatiites and boninites, but no komatiites, are argued to represent an intermediate stage of cooling between the komatiite sequences of the Archean and the boninite sequences of the present. Finally, we point out that the mantle residue left by the production of komatiites in subduction zones would have chemical and physical features similar to those of the lithospheric keels beneath cratons which underly most of the greenstone belts in which komatiites are found [Boyd, 1989; Herzberg, 1993; Jordan, 1979].

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Walter, M.J., Melting of garnet peridotite and the origin of komatiite and depleted lithosphere, *J of Petrology*, 39 (1), 29-60, 1998.

CHAPTER 1. EMPLACEMENT CONDITIONS OF KOMATIITE MAGMAS FROM THE 3.49 GA KOMATI FORMATION, BARBERTON GREENSTONE BELT, SOUTH AFRICA

ABSTRACT

This paper provides new constraints on the crystallization conditions of the 3.49 Ga Barberton komatiites. The compositional evidence from igneous pyroxene in the olivine spinifex komatiite units indicates that the magma contained significant quantities of dissolved H₂O. Estimates are made from comparisons of the compositions of pyroxene preserved in Barberton komatiites with pyroxene produced in laboratory experiments at 0.1 MPa (1 bar) under anhydrous conditions and at 100 and 200 MPa (1 and 2 kbar) under H₂O-saturated conditions on an analog Barberton composition. Pyroxene thermobarometry on high-Ca clinopyroxene compositions from ten samples requires a range of minimum magmatic water contents of 6 wt. % or greater at the time of pyroxene crystallization and minimum emplacement pressures of 190 MPa (6 km depth). Since high-Ca pyroxene appears after 30 % crystallization of olivine and spinel, the liquidus H₂O contents could be 4 to 6 wt. % H₂O. The liquidus temperature of the Barberton komatiite composition studied is between 1370 and 1400°C at 200 MPa under H₂O-saturated conditions. When compared to the temperature - depth regime of modern melt generation environments, the komatiite mantle source temperatures are 200°C higher than the hydrous mantle melting temperatures inferred in modern subduction zone environments and 100°C higher than mean mantle melting temperatures estimated at mid-ocean ridges. When compared to previous estimates of komatiite liquidus temperatures, melting under hydrous conditions occurs at temperatures that are ~250 °C lower than

previous estimates for anhydrous komatiite. Mantle melting by near-fractional, adiabatic decompression takes place in a melting column that spans ~38 km depth range under hydrous conditions. This depth interval for melting is only slightly greater than that observed in modern mid-ocean ridge environments. In contrast, anhydrous fractional melting models of komatiite occur over a larger depth range (~130 km) and place the base of the melting column into the transition zone.

INTRODUCTION

Komatiites are high MgO (16-33 wt.%) igneous rocks that are found predominantly in Archean greenstone belts [Arndt and Nisbet, 1982]. They range in age from 3.49 Ga to 0.1 Ga with a peak in preservation in the late Archean (2.0 Ga) [de Wit and Ashwal, 1995; de Wit and Ashwal, 1996]. Because komatiites have high MgO contents, they have high liquidus temperatures. The 0.1 MPa anhydrous liquidus temperature of a 33 wt.% MgO komatiite was estimated to be ~1670°C [Green *et al.*, 1975]. More recent estimates lower the maximum MgO content of the magma to ~29 wt.% and place the liquidus at 1580°C [Nisbet *et al.*, 1993]. To produce the high MgO contents of komatiites by decompression melting of a dry peridotite mantle requires mantle source temperatures that are 200-400°C higher than the modern MORB source [Herzberg, 1992; 1995]. The high inferred mantle melting temperatures of komatiites along with the antiquity of most komatiites (>2.0 Ga) are consistent with a model of progressive cooling of the mantle since the Archean. While heat from meteorite impacts, core formation, and higher concentrations of radioactive nuclides have been used to suggest that the early Earth was hotter than it is today, komatiite liquidus temperatures provide the only quantitative evidence of higher Archean mantle temperatures.

This paper focuses on komatiites from the Barberton Mountain Land, South Africa, because Barberton komatiites have the highest estimated MgO contents of all komatiites and therefore imply the highest Archean mantle temperatures. Furthermore, they are Earth's oldest best-preserved komatiites (3.49 Ga, *Lopez-Martinez et al.*, 1992; *de Ronde and de Wit*, 1994). The correlation between the age of komatiites and their apparent liquidus temperatures has been taken as further evidence of secular cooling of the Earth [*Herzberg*, 1995; *Abbott et al.*, 1994]. The high mantle temperature - oldest age end of this trend is defined by the Barberton komatiites. Therefore, these magmas are the pivotal evidence of extremely high temperatures in the Archean mantle.

The liquidus temperature of a material depends on melt composition, pressure, and volatile content. Quantitative estimates of komatiite liquidus temperatures rely on estimates of their crystallization conditions. Early work concluded that komatiites erupted in a subaqueous environment [*Viljoen and Viljoen*, 1969] dictating a specific set of crystallization conditions, namely near 0.1 MPa, anhydrous conditions. This extrusive hypothesis is based on a number of field observations including: chilled margins, pillows in basaltic rocks interlayered with the komatiites and rare structures resembling pillows in the komatiites. However, none of these features are diagnostic of an extrusive origin. The features previously interpreted as indicative of sub-aqueous extrusion can also be formed in intrusive rocks. For example, a key observation in the extrusive hypothesis is the presence of rare pillow-like chill structures in the komatiites with distinctly lobate and ovoid form. Such pillow structures also form in intrusive settings [*Snyder and Fraser*, 1963; *de Wit and Stern*, 1978]. We have proposed that the pillows in Barberton komatiites are of intrusive origin [*de Wit et al.*, 1987; *Grove et al.*, 1996], and find cross-

cutting spinifex veins and other intrusive structures closely associated with komatiite pillows.

Spinifex textures in komatiites have also been used as evidence for an extrusive emplacement [Green *et al.*, 1975; Viljoen and Viljoen, 1969]. Spinifex describes megacrystic, skeletal and highly elongate olivine or pyroxene crystals. In some Barberton units, individual olivine crystals reach 80 cm in length with a thickness of 1 cm or less. Experiments quenched at 100's of degrees per minute produce dendritic, skeletal olivines that superficially resemble spinifex textures [Green *et al.*, 1975]. Such fast cooling rates appeared to necessitate komatiite emplacement at the surface of the Earth, where air or water could remove heat rapidly by convection. Later work [Donaldson, 1976; 1982] noted that cooling rates fast enough to produce dendritic olivine would only be achieved in the outer 3 cm of komatiite units. Spinifex is found in the center of units that are 7 meters thick [Grove *et al.*, 1996a], where cooling rates were $\ll 0.5^{\circ}\text{C}$ per hour. The discrepancy indicates that spinifex cannot be a 'quench' texture and therefore is not diagnostic of extrusion. Crystallization experiments on a komatiite composition under H_2O -saturated conditions have been successful in reproducing spinifex-like, elongate olivine morphologies at cooling rates relevant to the interior of the units [Grove *et al.*, 1996b]. The influence of dissolved H_2O is to lower nucleation rate and increase growth rate over that found at similar anhydrous cooling rate conditions.

The goal of this paper is to estimate the crystallization conditions by comparing the composition of igneous minerals in Barberton komatiites to the compositions of minerals produced in laboratory experiments. This paper presents analyses of unaltered igneous olivine and clinopyroxene from 10 komatiite samples as well as the experimentally determined phase relations and phase compositions of a Barberton

komatiite composition at 0.1 MPa, anhydrous, and 100 and 200 MPa, H₂O-saturated conditions. This data set provides independent estimates of the emplacement conditions of Barberton komatiites.

ANALYTICAL TECHNIQUES

The minerals in the rock samples and in the experiments have been analyzed with the JEOL 733 Superprobes at MIT. The data were reduced using the corrections of Bence and Albee [1968] modified by Albee and Ray [1970]. A 15 kV accelerating potential was used with a beam current of 10 nA. Anhydrous crystalline phases were analyzed using a spot beam of ~2 microns diameter. Hydrous metamorphic minerals and experimental melts were analyzed with a 10 micron or 20 micron defocused beam to reduce alkali diffusion and devolatilization. H₂O contents were estimated by summation deficit (i.e. 100 - total = H₂O). Sisson and Layne [1993] have shown this method to be accurate to +/- 0.3 wt.% in melts with total H₂O contents around 6 wt. %.

PETROGRAPHY

Sampling

Samples were collected by us from the type area of the Komati Formation east of Spinifex Stream [Viljoen and Viljoen, 1969; Smith *et al.*, 1980]. Our mapping and sampling located outcrops where fresh igneous minerals had escaped metamorphism. Outcrop maps of these komatiites will be presented elsewhere [Dann, in prep.]. Ten samples contain fresh pyroxene, 4 of these also contain fresh olivine. The unaltered olivine and pyroxene are present in their entire spectrum of morphologies from equant to highly elongate laths. Fresh minerals have only been found near the central portions of

cooling units of 1-2 m thickness. A description of the igneous mineral textures in each sample is given in Table 1.

Mineral Compositions

The primary igneous mineralogy of Barberton komatiites consisted of olivine (~55 vol %), clinopyroxene (~25 %), chromite (5 %) set in a glassy groundmass (~15 %). Metamorphism has modified this assemblage and the effects were spatially heterogeneous. On thin section, hand sample, and outcrop scales, completely altered areas are in close association with patches that preserve 80 to 90 % of the igneous mineralogy over areas up to 2 by 2 cm. The glassy groundmass and relict glass inclusions in olivine are always altered to a mixture of serpentine, chlorite, tremolite, and magnetite. Magnetite also occurs as metamorphic overgrowths on chromite. Unaltered mm-sized pyroxene crystals preserve complete core to rim compositional profiles with the outer 25 - 50 microns of the rim usually showing alteration to tremolite. The crystals retain igneous morphologies (Fig. 1) and primary igneous compositions. Fresh pyroxene reacts to tremolite with minor serpentine and chlorite by a reaction front that advances inward from the original outer igneous rim of the pyroxene crystal. Pargasite is also found; presumably as a reaction product of pyroxene and glassy groundmass. Representative compositions of the metamorphic minerals are given in Table 2.

We report on four samples that contain igneous olivine (Table 3). In the freshest minerals an outer 10 to 100 micron border of the original mm- to cm-sized crystal is outlined by metamorphic magnetite. The un-serpentinized olivine remnants inside this outline occur as rounded kernels separated by veins of serpentine, magnetite, and rarely chlorite. The majority of the olivine remnants are zoned from high Mg# ($Mg/(Mg+Fe)$) cores to Fe rich rims. This zoning is associated with the crosscutting veins of serpentine

and represents a metamorphic effect that accompanies serpentinization. Smith et al. [1980] also noted that the compositional zoning does not correspond to the borders of the original crystal. On many fragments, sections of the Fe rich rim are absent. Often in these places, a thin layer or veinlet of magnetite is present. Later serpentine veins, not associated with the zoning, cross cut the zone forming veins.

The percent of the olivine crystal that is serpentinized correlates with the Mg# of the olivine cores. The highest Mg# olivine core (Mg#=94.1) is in the most serpentinized sample. The least serpentinized grains have the lowest Mg# cores (Mg#=92.9). The high Mg# olivine crystals appear to represent metamorphic re-equilibration of olivine with the serpentine and magnetite alteration assemblage. The presence of monticellite lamellae in some olivines indicates low-temperature re-equilibration. Similar Ca endmember olivine exsolution has only been observed in angrite meteorites [Mikouchi *et al.*, 1995], where the FeCa endmember, kirschsteinite is the exsolving phase.

Metamorphism has not affected the composition of the igneous pyroxene. The contacts between pyroxene and associated tremolite and/or serpentine+ chlorite overgrowths are sharp and thin in the fresh minerals (Fig. 1). The metamorphic reaction front does not modify pyroxene compositional zoning. Pyroxene is zoned from high wollastonite (Wo), high Mg# cores to low Wo, low Mg# rims (Fig. 2), though rare reverse zoned crystals are present in melt segregations. In Fig. 2, the composition of the pyroxene cores has been circled for each sample.

METAMORPHISM AND THE BULK COMPOSITION OF BARBERTON KOMATIITES

The effect of metamorphism on the composition of Barberton komatiites must be evaluated prior to choosing an experimental starting composition. A number of studies

have concluded that the chemical variations in the Barberton samples are the result of pre-emplacement olivine fractionation and that the effect of metamorphism has been minimal [Green *et al.*, 1975; Beswick, 1982; Smith and Erlank, 1982]. Other studies have concluded that metamorphism has had significant effects on the chemical compositions [Nisbet *et al.*, 1993; de Wit and Stern, 1978]. For example, de Wit *et al.* [1978] document a correlation between H₂O content (as hosted by metamorphic minerals) and rock composition in Barberton komatiites and also note that the bulk rock compositions are too MgO-rich to be in equilibrium with the fresh olivines found in them. On this basis they suggest an original composition of 23-24 wt. % MgO for Barberton komatiites.

The compositions of Barberton chilled margins suggest that open system metamorphism has had a large effect on bulk sample compositions. In an olivine-clinopyroxene-quartz ternary, the compositions of the chill margins define a tight trend (Fig. 3a). This trend is not collinear with olivine as expected if it were a pre-emplacement olivine fractionation trend. Instead, it is collinear with the metamorphic serpentine and chlorite found in the rocks. This trend is consistent with a metamorphic process that depleted soluble elements (i.e. Na, Ca, K) from the rocks, and left behind an MgO-enriched metamorphic assemblage of serpentine and chlorite. An open system process that involved an H₂O-rich fluid was probably responsible. However, the details of the process are beyond the scope of this paper, and MgO may have also been mobilized in the fluid and added to the rock [de Wit *et al.*, 1987]. The trend towards serpentine + chlorite correlates with H₂O content (Fig. 3b). The H₂O is hosted in metamorphic minerals and so is an indication of the extent of alteration. The correlation between composition and degree of alteration is consistent with the interpretation that the

observed compositional variation is predominantly a result of varying degrees of metasomatism.

An alternative explanation is that the trend in Fig. 3 was originally an olivine fractionation trend, but has been rotated by selective metamorphism [Nisbet *et al.*, 1993]. This process would alter the higher MgO samples (those closer to the Ol corner of Fig. 3a) to a greater extent than the less MgO rich samples because more MgO is available to make serpentine and chlorite. Metamorphism in Barberton is highly variable at all length scales. Rocks with the same initial compositions but with varying degrees of alteration should scatter between the original igneous trend and the observed trend. The lack of scatter contradicts the igneous interpretation of the compositional variations in the Barberton komatiite samples.

The experimental composition used in this study is based on the least altered samples selected on the basis of their low metamorphic H₂O contents. In comparison with the compositions used in previous studies (Table 4), the composition used in this study is notable for its lower MgO and higher CaO contents. All Barberton komatiite rock compositions have been modified by open system metamorphism. The composition used in this study is the best estimate possible at this time. As part of our continuing study, we are searching for fresher bulk rocks and preserved melt inclusions. In future work, petrologic and chemical insights gained from field discoveries and the experimental study will be used to refine estimates of the unaltered composition and potential variability. The issue of bulk composition is re-examined later in this paper when the experimentally determined phase boundaries can be used to illustrate the consequences of choosing various starting compositions.

EXPERIMENTS

Experimental Techniques

A synthetic analog of the starting composition was prepared by mixing high purity oxides [Kinzler and Grove, 1985]. The results of all experiments are reported in Table 5. The compositions of all experimentally produced phases are given in Table 6.

For the 0.1 MPa experiments, 0.6-0.7 mg of the starting material was pressed into pellets along with polyvinyl alcohol (DuPont Elvanol). This pellet was then sintered onto a platinum wire loop (0.008 inch diameter). The loop was pre-annealed with 7-9% Fe to reduce iron loss during the experiment [Grove, 1981]. All 0.1 MPa experiments were performed in a vertical DelTech furnace and drop quenched into water. The fO_2 of all 0.1 MPa experiments was held at the quartz-fayalite-magnetite buffer by mixing CO_2 and H_2 at low flow rates (~ 0.1 ml/s) to avoid Na loss. Experimental fO_2 was measured using a ZrO_2 -CaO electrolyte cell calibrated at the Fe-FeO buffer. All 0.1 MPa isothermal experiments were checked for element loss during the experiment by mass balancing the phases produced with the starting composition.

Cooling rate experiments performed at 0.1 MPa were taken $10^\circ C$ above their liquidus and held there for 1-2 hrs. Then they were cooled at 3 or $10^\circ C$ per hour. Otherwise, the experimental set up was the same as in the 0.1 MPa isothermal experiments.

Hydrous experiments at 100 and 200 MPa were performed in a zirconium - hafnium carbide - molybdenum alloy gas pressure vessel inserted into a vertical DelTech furnace. The fO_2 of the experiment was buffered using powder mixtures of Ni and NiO contained in Pt capsules. The sample was contained in either a Au or $Au_{90}Pd_{10}$ alloy inner capsule. Au was used at temperatures below $1050^\circ C$, $Au_{90}Pd_{10}$ was used at higher

temperatures. The sample capsule and two buffer capsules were enclosed in a $\text{Au}_{80}\text{Pd}_{20}$ outer capsule along with 16-20 microliters of H_2O . H_2O saturation was maintained during the experiment by mixing methane into the argon pressurizing gas. The methane maintains a partial pressure of H_2 on the outside of the capsule, inhibiting H_2O loss through H_2 diffusion. The amount of methane necessary to prevent H_2O loss was determined by trial and error. An experiment was deemed successful if H_2O was present in the capsule at the end of the experiment, both Ni and NiO were still present in the buffer capsules, and mass balance showed little Fe loss.

Attainment of equilibrium

Equilibrium between the sample and the sample container is a requirement for the experimental results to be useful. The primary barrier to this equilibrium is the loss of Fe to the sample containers. In all experiments where good glass analyses were possible, Fe loss was checked by mass balance. The results of the calculations (Table 5) indicate that little Fe was lost to the sample containers.

To assess the degree to which the crystalline phases and the melts approached chemical equilibrium, we performed long duration experiments (240 hrs). These experiments are particularly important in studies of pyroxene fractionation as diffusion is slow in pyroxene [Grove and Bryan, 1983]. Pyroxene compositions are compared from experiments of varying duration but held at the same temperature. The experiments yield similar average Mg#s and Wo contents. The main difference is that the pyroxenes in the long experiments have less variability in both Mg# and Wo content. Such long runs are not feasible for the hydrous experiments as loss of H_2 limits practical run durations to less than 72 hrs. . Fortunately, the presence of H_2O facilitates the approach to equilibrium.

This is indicated by the compositional trends in the 200 MPa pyroxene that are as tight as the 0.1 MPa trends, though run durations were much shorter (6-48 hrs).

All of the pyroxene compositions have been plotted on the pyroxene quadrilateral against the solvus boundaries (Fig. 4) given in Davidson and Lindsley [1989]. The compositions of the high and low-Ca pyroxene indicate they had closely approached equilibrium. We conclude that the pyroxene compositions are close enough to equilibrium to provide useful thermobarometric estimations.

EXPERIMENTAL RESULTS

Effects of H₂O

The conditions and results of the experiments (Table 5) have been used to construct the isothermal phase appearance diagram at 0.1 MPa anhydrous conditions and 100 and 200 MPa H₂O-saturated conditions (Fig. 5). At 0.1 MPa, olivine is the liquidus phase, followed by chromium spinel in minor amounts. Pigeonite is the first pyroxene to crystallize at 1290°C, followed at 1275°C by augite. At 200 MPa H₂O-saturated conditions, olivine is inferred to be the liquidus phase followed by chromium spinel. Compared to the 0.1 MPa experiments, the appearance order of the pyroxene is reversed. Augite is the first pyroxene to crystallize between 1200 and 1257°C. Orthopyroxene is second between 1075 and 1120°C (Table 6).

The presence of H₂O changes the appearance temperature of the silicate phases to varying degrees (Fig. 5). Compared to the 0.1 MPa experiments, the augite appearance temperature in the H₂O-saturated experiments is lowered by 20-70°C while low-Ca pyroxene appearance is lowered by 180-220°C. The thermodynamic explanation of this effect is not fully understood. Because H₂O does not enter the pyroxene structure, the

cause is probably related to a change in melt structure. The most likely effect is that water lowers the activity of SiO_2 in the melt, lowering the nucleation temperature of pigeonite [Kushiro, 1968].

Pyroxene Wo contents in the 200 MPa , H_2O saturated experiments are distinctly higher than the pyroxene Wo contents in the 0.1 MPa experiments (Fig. 6). High Wo contents have been previously recognized as a characteristic of clinopyroxene crystallized from hydrous melts [Sisson and Grove, 1993a; 1993b; Gaetani *et al.*, 1993; Gaetani *et al.*, 1994]. The primary cause of the high Wo contents of augites crystallized from hydrous melts is their lower crystallization temperature. The magnitude of the thermodynamic non-ideality of the high-Ca pyroxene is temperature dependent. At lower temperatures the non-ideal term in the Gibb's free energy of the augite is relatively larger. Therefore, the augite composition closer to the pure Wo endmember composition..

In comparing the pyroxene compositions in the 0.1 MPa anhydrous experiments with the pyroxene compositions in the 200 MPa H_2O -saturated experiments, the effects of pressure and H_2O must be separated. The effect of 200 MPa pressure under anhydrous conditions on the compositions of coexisting low and high-Ca pyroxene is negligible [Davidson and Lindsley, 1989]. The main effect of increased pressure alone is to lower the Wo content of the augites by raising the temperature at which they crystallize.

Effects of crystallization under cooling conditions

In the 0.1 MPa cooling rate experiments olivine is again the liquidus phase followed by chromium spinel. Pyroxene crystals have pigeonite cores and augite rims. This texture indicates that the pigeonite crystallized first. In the 3°C/hr experiment, most of the pyroxene crystals have pigeonite cores. In the 10°C/hr experiment, the pigeonite cores are distinctly smaller and occur only in a few of the pyroxene crystals.

Increased cooling rate lowers the appearance temperature of late forming phases more than early forming phases [Kinzler and Grove, 1985; Walker *et al.*, 1976]. Thus the temperature difference between the first appearance of olivine and the first appearance of pyroxene is larger under cooling conditions than it is under isothermal conditions. This affects the compositions of the pyroxene crystals. Pyroxene in the isothermal experiments has a maximum Mg# of 0.91 (Fig. 6). In the 3°C per hour cooling rate experiments, the maximum pyroxene Mg# is 0.87 and in the 10°C per hour cooling rate experiments the maximum Mg# is 0.86.

The textures of the experimental pyroxene indicate that faster cooling rates suppress pigeonite crystallization more than augite crystallization. The small size of the pigeonite cores in the 10°C/hr experiment implies that at cooling rates faster than 10°C/hr, pigeonite would not crystallize at all. Kinzler and Grove [1985] also studied the effect of varying cooling rates in experiments on komatiitic melts. They also found that increased cooling rate suppresses the nucleation of pigeonite relative to augite. The relative suppression of pigeonite in the cooling rate experiments is a result of crystal/melt disequilibrium. The disequilibrium occurs because increased cooling rate increases crystal growth rates while the lower temperature of crystal growth results in a decrease in melt diffusion rates. The crystals are forced to grow from a melt with higher concentrations of incompatible elements and lower concentrations of compatible elements. Therefore, as cooling rates increase, partition coefficients converge on a value of 1 [Grove and Bence, 1979]. The melt avoids moving elements around by crystallizing a pyroxene with a composition as similar to itself as possible. Augite is closer in composition to the melt than is pigeonite. Therefore the increased disequilibrium at fast cooling rates favors the nucleation of augite over pigeonite.

The pyroxene produced at both 3°C/hr and 10°C/hr cooling rates has a wide range of compositions within a single experiment, in contrast with the results of the isothermal experiments (Table 6 and Fig. 6). The cooling rate experiments produce two types of pyroxene not produced in the 0.1 MPa isothermal experiments: 1) clinopyroxene with intermediate Wo contents at high Mg#'s and 2) clinopyroxene with low Mg#'s (Mg#<75). Both types of pyroxenes are the result of the disequilibrium caused by the cooling conditions.

DISCUSSION

Pyroxene crystallization conditions

The pyroxene compositions produced in the experiments can be used to infer the crystallization conditions of the pyroxene found in Barberton komatiite units as well as the initial emplacement conditions of the units. The experiments indicate that pyroxene appears after crystallization of ~30 % olivine. The interlocking network of elongate olivine blades would have formed at this degree of crystallinity. When pyroxene appeared, it grew within the triangular spaces between elongate, interlocking spinifex olivine. Any post-crystallization movement would have destroyed the delicate spinifex olivine network. The textural constraints indicate that the pyroxene crystallization pressure is the same as the emplacement pressure. Additional evidence that the pyroxenes were not inherited come from the aphyric chilled margins which contain only small (mm-sized, *Grove et al.*, 1996) euhedral olivine phenocrysts.

The compositions of the pyroxene in the samples indicate they crystallized from a hydrous melt at a minimum pressure of 190 MPa. The pyroxene compositional variations (Fig. 6) are produced by crystallization during cooling of the units. The zoning progresses from high Wo, high Mg# cores to low Wo, low Mg# rims. The data are

compilations of 5 to 10 cross sections that define the complete range of compositional variations. Sector zoning and continued nucleation during cooling preclude preservation of the entire zoning trend in a single grain. The highest Mg# cores record the initial pyroxene crystallization conditions, and are circled for each sample in Fig. 2. These core compositions fall within the 200 MPa, H₂O-saturated field, implying that the pyroxene crystallized near these conditions. The width of the augite compositional field creates some uncertainty in the pressure estimate. A linear fit of the experimental augite Wo contents between the 100 MPa values and 200 MPa values yields pressures between 190 and > 400 MPa (Table 3). With experimental constraints at 0.1, 100 and 200 MPa, it is not possible to estimate an upper bound in pressure. The relationship between Wo content and pressure is curved with little increase in Wo expected above 200 MPa. The existing data set does not allow quantitative determination of this curvature. Thus, the estimates in Table 3 should be considered minimum pressures and we can not distinguish the upper limit of $P_{\text{H}_2\text{O}}$. The pressure estimates are best at 200 MPa (Wo₃₉) and the error is expected to grow at higher Wo contents.

The Wo contents of the natural augite cores provide a lower bound on the pressure and water content of the melt during crystallization. The experiments reported here reproduce the natural augite compositions at ~200 MPa under hydrous and isothermal conditions. The Wo contents and Mg#s of the natural augites could also be reproduced at higher pressures under H₂O-saturated conditions if the melt had lower CaO or crystallized at more rapid cooling rates or both. Alternatively, the melt could have crystallized at higher pressures but under H₂O undersaturated conditions. Detailed studies of the compositional effects of cooling during crystallization of a hydrous melt may allow the

various scenarios to be distinguished on the basis of incompatible minor elements such as Al_2O_3 and TiO_2 .

The high Wo contents of the natural augites cannot be produced at 0.1 MPa. Clearly the augites produced in our 0.1 MPa isothermal experiments are not good matches for the natural augites, nor are the augites in the 0.1 MPa cooling rate experiments (Fig. 6). As discussed above, increased cooling rate will produce augites with lower Wo contents than the 0.1 MPa isothermal augites. Therefore, faster cooling rates only increase the compositional discrepancy. In fact, crystallization under anhydrous conditions at any pressure cannot produce the high Wo contents of the augites. Crystallization from a dry melt at pressures >0.1 MPa will raise the melting temperature and thus lower the Wo contents of the augites, relative to the augites in 0.1 MPa experiments [Davidson and Lindsley, 1989].

The compositions of the augites require crystallization from a hydrous melt. We have not explored the influence of cooling rate on Wo content at 200 MPa, H_2O -saturated. Quench overgrowths on some of our 200 MPa isothermal pyroxenes show that the effect of this rapid cooling event is to scatter Wo to lower and higher values and to increase Al_2O_3 to > 4.0 wt. %. The effect of hydrous cooling rate on the emplacement pressure estimates is considered to be small, because the natural pyroxenes were chosen from the slowly cooled interiors of units $> 1\text{m}$ thick and because minor element concentration in the 200 MPa experimental and natural pyroxenes are comparable.

The absence of a low-Ca pyroxene phase in the samples also indicates that Barberton komatiites did not crystallize under anhydrous conditions. At 0.1 MPa, cooling rates greater than 10°C per hour are necessary to suppress pigeonite nucleation completely. Using the equations of conductive heat loss [Jaeger, 1957], this is the

maximum cooling rate that would be achieved 26 cm from the boundary of a komatiite cooling unit. At distances greater than 26 cm from the cooling boundary, cooling rates would be slower. All the described samples cooled at a distance of > 26 cm from a chill margin. If the units crystallized at 0.1 MPa, pigeonite should be present in these samples. The complete absence of pigeonite indicates that the units did not cool at 0.1 MPa. Turner et al. [1986] suggest that komatiite units cooled convectively and so achieved fast ($>200^{\circ}\text{C}$ per hour) cooling rates. Crystallization at these rapid cooling rates would suppress pigeonite, but would also produce a very low Wo content augite quite unlike the natural augite. The combined constraints of the high Wo augite and lack of pigeonite rules out an extrusive emplacement for the spinifex olivine units.

The presence of magmatic water provides an explanation for the absence of low-Ca pyroxene. The experiments show that the presence of H_2O significantly lowers the appearance temperature of low-Ca pyroxene relative to its appearance at 0.1 MPa. Increased cooling rate lowers the appearance temperature of late appearing phases more than early appearing phases. Therefore, the minimum cooling rate necessary to suppress low-Ca pyroxene under H_2O -saturated conditions will be less than the 0.1 MPa value (10°C/hr) and may be low enough to explain the absence of low-Ca pyroxene.

Constraints on the compositions of Barberton komatiites

The experimentally determined phase boundaries show the results of choosing other estimates of Barberton komatiite compositions. The important conclusion is that the results of the pyroxene thermobarometry presented here are not dependent upon choice of starting composition. The other, high-MgO estimates of Barberton komatiite compositions have a greater tendency to crystallize low-Ca pyroxene (Fig. 7). If these high-MgO compositions are appropriate, the lack of pigeonite becomes an even stronger

argument against 0.1 MPa crystallization. The presence of magmatic water may allow the intermediate-MgO estimated liquids to avoid low-Ca pyroxene crystallization, but not the most MgO-rich liquids. The most MgO-rich estimates crystallize orthopyroxene first, even at 1.0 GPa H₂O-saturated conditions [Green *et al.*, 1975].

The preserved olivines provide a further constraint on the melt composition. The composition of the olivines, along with the experimentally determined Fe/Mg partition coefficients, can be used to calculate the Mg# of the melt in equilibrium with them (Table 3). The highest Mg# core should represent the liquidus olivine and provide the Mg# closest to the unfractionated melt. The highest Mg# olivine in the least altered sample yields a melt Mg# of 0.798. This is similar to the Mg# (=0.783) of the least altered chill margins [Smith *et al.*, 1980; Smith and Erlank, 1982] and the starting composition used in this study.

The ultimate goal of any study of the composition of komatiites should be to recognize compositional variations in komatiite parental melts. Such compositional variations in MORB parent melts have been extremely useful in understanding MORB genesis [Klein and Langmuir, 1987]. Recognizing similar compositional complexities in Barberton komatiite melts is a central goal of this research. The present work is a first step towards this goal, but at this time non-metamorphic compositional variations between units have not been identified.

Emplacement conditions of spinifex units

The essential conclusions of this work are that spinifex olivine-bearing komatiite units represent hydrous intrusions and had minimum emplacement pressures of 190 MPa. This corresponds to minimum emplacement depths of 6 km. This should be viewed as a minimum estimate and pressures of 300 to 400 MPa can not be ruled out. The minimum

magmatic H₂O content can be estimated by assuming that the unit was emplaced H₂O-undersaturated and that pyroxene crystallization and H₂O-saturation were simultaneous. Thus, at the liquidus a minimum H₂O content for the liquid accounts for prior interval of olivine + spinel crystallization. This minimum H₂O estimate is 4.2 wt.% at 190 MPa. If the komatiite was H₂O-saturated at its liquidus, the magmatic H₂O content would equal the vapor saturation abundance at the pressure of emplacement. This is inferred to be ~ 6 wt. % H₂O at 190 MPa. Higher pressure estimates require higher H₂O contents.

Anhydrous crystallization of komatiitic melts

Sample B94-4 is a pigeonite-bearing peridotitic komatiite collected from the top of the Komati formation [Viljoen and Viljoen, 1969]. The presence of pigeonite indicates that this komatiite magma contained less H₂O than the melt that produced the spinifex komatiites. The pyroxene compositions resemble pyroxene compositions in the 0.1 MPa cooling rate experiments, exhibiting a continuous variation from pigeonite cores to augite rims (Fig. 6, Table 3). If hydrous komatiite magma was emplaced at shallow levels, the sharp decrease in H₂O solubility with depth would lead to vapor saturation, degassing of H₂O and anhydrous crystallization that produced early pigeonite. Field relations show this unit to be intrusive [J. Dann, unpub.]; presumably at a shallow depth.

Temperature of the Archean Mantle

The liquidus temperature of the komatiite composition at 200 MPa, H₂O-saturated is ~1370-1400°C. This estimate is an extrapolation of the 0.1 MPa komatiite liquidus using the experimentally observed influence of H₂O on basaltic liquids [Sisson and Grove, 1993a; 1993b; Gaetani *et al.*, 1993; 1994]. The H₂O-saturated liquidus of the Barberton komatiite was not determined in this study. The inferred liquidus is 200 to

300°C lower than previous estimates [*Green et al.*, 1975; *Nisbet et al.*, 1993] which assumed 0.1 MPa anhydrous.

The emplacement conditions of Barberton komatiites constrain the potential temperature of their source mantle. Using data from the albite-H₂O system [*Rumble*, 1976] hydrous melts with 4 wt.% H₂O have an adiabatic gradient of 1.4°C/km. Assuming the komatiites were emplaced at 6 km depth, their potential temperatures were between 1362 and 1392 °C. These temperatures are higher than the potential temperatures of modern hydrous andesitic magmas (up to 1270°C, *Baker et al.*, 1994). On the other hand, estimates of the potential temperatures required to produce modern boninites are as high as 1500°C [*Falloon and Danushevsky*, 2000]. Thus Barberton komatiites do not require high mantle temperatures as was previously inferred [*Green et al.*, 1975; *Herzberg*, 1995]. More precise estimates of the melting conditions that produced Barberton komatiites are calculated in Chapter 3, and the genetic relationship between boninites and komatiites is explored in Chapter 4.

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TABLES

Table 1. Mineral Textures in Barberton Komatiites

sample	Olivines	fresh?	Pyroxenes	fresh?	vesicles	% of fresh minerals (visual estimate)
	Textures ^a		Textures			
5-1a	strongly bimodal, spinifex (parallel laths) and clumps of equant crystals	yes	parallel laths and rare elongate to plumose crystals	yes	rare	5% (mostly olivine)
5-10	equant	no	elongate and plumose	yes	abundant (20-30%)	<5%
5-1fd	large skeletal equant and thick elongate	yes	elongate to randomly oriented laths	yes	rare	<5% (mostly pyroxene)
2-15a	spinifex, parallel laths	no	equant with rare laths	yes	rare	<3%
B95-7	chevron/branching laths	no	euhedral elongate to plumose	yes	rare	10%
B95-8	spinifex randomly oriented, not parallel	no	lath to euhedral elongate and plumose	yes	?	5%
B95-9	equant	yes	elongate	yes	no	<5% (only three olivine grains)
B95-10	equant	no	elongate	yes	?	<5%
B95-11	equant	no	equant to elongate	yes	rare	<5%
B95-15	spinifex parallel laths	yes	elongate to lath, texture mostly erased	yes	?	15% (mostly olivine)
B94-4	equant	no	elongate	yes	no	5-10%

^a The term lath refers to crystals with aspect ratios greater than 10. Elongate refers to crystals with aspect ratios between 3 and 10. Equant refers to crystals with aspect ratios less than 3. Plumose refers to a particular crescent-shaped crystal habit of pyroxene which often occurs along with elongate pyroxene.

Table 2. Metamorphic Minerals

	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	Total	H ₂ O ^c
chlorite(7) ^a	34.9(7) ^b	0.049(4)	12.7(8)	-	4.8(3)	0.02(3)	33.3(7)	0.08(6)	-	86.07	13.93
serpentine(49)	44.1(5)	0.046(4)	0.4(3)	-	2.4(5)	0.11(5)	38.6(6)	0.05(6)	-	85.91	14.09
pargasite(26)	48.8(9)	0.6(3)	9.1(6)	0.1(2)	7.0(3)	0.09(4)	18.5(4)	12.1(2)	1.9(2)	98.60	1.40
tremolite(12)	56.6(5)	0.15(6)	1.7(4)	0.2(1)	4.1(7)	0.13(3)	22.4(6)	12.5(5)	0.5(2)	98.40	1.60

FeO* indicates that all Fe is taken as FeO.

^a Value in parentheses indicates number of points averaged. Values of microprobe analyses are reported with 1 sigma standard deviations in parentheses. The entry 35.4(2) should be read 35.4 wt.% $\pm$ 0.2 wt.%. The standard deviation values are based on repeated analyses of the same phase. Therefore they represent a combination of analytical error and real compositional variation. The analytical error has been estimated by repeated analyses of a glass with a known composition. Based on 139 analyses, the percent relative, one standard deviations are SiO₂ = 0.5, TiO₂ = 1.7, Al₂O₃ = 0.9, FeO = 1.3, MnO = 17.6, MgO = 1.1, CaO = 1.0, Na₂O = 1.9, and K₂O = 2.8. Standard deviations larger than this represent real compositional variation in the analyzed phase.

^b Value in parentheses is one sigma deviation. Thus 34.9(7) should be read as 34.9 $\pm$ 0.7.

^c Water contents calculated by summation deficit = 100-Total

Table 3. Electron microprobe analyses of igneous minerals in Barberton komatiites

Sample	Mineral	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO*	MnO	MgO	CaO	NiO	Na ₂ O	Total	Mg#	Wo	Mg _{liq} ^a	Mg _{liq} ^b	P _{calc} ^c
5-1a	ol (core)	41.0	0.0	0.09	0.10	6.30	0.14	51.5	0.19	0.45	-	99.8	0.936	-	0.815	0.810	-
	aug (core)	53.8	0.26	1.81	0.84	6.52	0.16	17.7	20.1	-	0.24	101.3	0.829	0.404	-	-	310
5-10	aug (core)	53.7	0.24	1.24	0.69	4.91	0.14	18.9	20.6	-	0.00	100.4	0.873	0.406	-	-	330
5-1fd	ol (core)	41.2	0.08	0.07	0.14	6.14	0.12	51.4	0.23	0.40	-	99.8	0.937	-	0.818	0.813	-
	aug (core)	54.4	0.15	1.11	0.69	6.11	0.20	18.7	19.9	-	0.07	101.2	0.845	0.393	-	-	200
	aug (rim)	52.6	0.30	2.32	0.11	9.52	0.10	17.0	18.7	-	0.31	100.6	0.760	0.376	-	-	-
2-15a	aug (core)	53.8	0.10	0.85	0.51	4.77	0.17	18.7	20.2	-	0.18	99.3	0.875	0.404	-	-	310
B95-7	aug (core)	53.1	0.22	1.10	0.67	5.17	0.18	17.6	20.6	-	0.17	98.8	0.858	0.419	-	-	460
B95-8s	aug (core)	54.0	0.20	1.53	0.59	5.78	0.13	18.7	19.7	-	0.21	100.9	0.852	0.392	-	-	190
B95-9	ol (core)	41.2	0.0	0.05	0.12	5.76	0.11	51.7	0.22	0.45	-	99.6	0.941	-	0.829	0.824	-
	aug (core)	53.2	0.22	1.19	0.51	5.69	0.15	17.6	20.7	-	0.19	99.4	0.847	0.417	-	-	440
B95-10	aug (core)	53.2	0.17	1.21	0.83	4.95	0.07	17.9	20.4	-	0.18	98.9	0.866	0.415	-	-	420
B95-11	aug (core)	53.2	0.20	1.08	0.55	5.20	0.16	18.9	20.3	-	0.12	99.6	0.867	0.400	-	-	270
	aug (rim)	53.1	0.25	1.10	0.26	7.21	0.23	19.1	18.6	-	0.05	99.8	0.825	0.367	-	-	-
B95-15	ol (core)	41.0	0.0	0.09	0.17	6.96	0.09	51.2	0.21	0.44	-	100.1	0.929	-	0.798	0.793	-
	aug (core)	52.8	0.25	1.42	0.63	5.29	0.13	17.9	20.7	-	0.06	99.2	0.858	0.416	-	-	430
B94-4 ^d	pig (core)	56.8	0.02	0.81	0.58	7.88	0.21	30.8	3.98	-	0.02	101.1	0.875	0.075	-	-	-
	aug (rim)	53.9	0.17	1.31	0.54	5.20	0.14	19.9	18.8	-	0.17	100.1	0.872	0.373	-	-	-

^a Mg#_{liq} is the Mg# of the liquid in equilibrium with the olivine in the rock calculated using the composition of the olivine in the sample and the Fe/Mg K_D for olivine and melt from the anhydrous experiments (=0.302).

^b Mg#_{liq} is the same calculation as in ^a, but using the hydrous K_D (=0.294).

^c P_{calc} was calculated by fitting the Wo contents of the pyroxene in experiments TZM BK19 and TZM BK5. This fit yields the equation P=10,000*Wo-3730. For augites with Wo contents above .393, this fit gives a minimum pressure value.

^d B94-4 is a peridotitic komatiite from the upper Komati formation. See text for further detail.

Table 4. Estimated Barberton Komatiite Compositions

	This Study	Green et al. (1975)	Smith et al. (1980)
SiO ₂	49.1	46.5	47.50
TiO ₂	0.41	0.19	0.36
Al ₂ O ₃	4.65	3.58	3.94
Cr ₂ O ₃	0.37	0.43	0.35
Fe ₂ O ₃	-	-	1.87
FeO	11.4	10.4	9.33
MnO	0.20	0.21	0.19
MgO	23.2	33.0	28.39
CaO	10.2	5.10	7.14
K ₂ O	0.03	0.18	0.03
Na ₂ O	0.28	0.49	0.14
P ₂ O ₅	-	0.01	0.02
NiO	0.16	0.25	0.19
Total	100.0	100.3	100.0

Table 5. Experimental Results

Isothermal Experiments						Sum		
Exp. #	P (MPa)	T (°C)	duration (hours)	phases present	phase proportions	of Residuals Squared	% Fe loss ^a	Fe/Mg K _D
BK4	0.1	1450	2.2	gl	1	-	-	-
BK3	0.1	1435	2.8	gl,ol	94.6(2),5.3(2)	0.04	1	0.306
BK1	0.1	1420	5.3	gl,ol	91.1(2),8.7(2)	0.03	0	0.303
BK5	0.1	1400	12.8	gl,ol	90.2(5),8.3(4)	0.18	3	0.326
BK6	0.1	1300	14.8	gl,ol,chr	75.3(2),23.8(2),tr	0.03	1	0.322
BK12	0.1	1286	29.3	gl,ol,chr,pig	73.3(6),28.5(5),tr,-1.7(9)	0.06	0	0.303
BK10	0.1	1275	41.0	gl,ol,chr,pig,aug	68.1(5),29.4(3),tr,0.0,3.0(6)	0.02	0	0.301
BK15	0.1	1275	240.0	gl,ol,chr,pig,aug	63(2),19.1(9),tr,19(2),0.0	0.25	2	0.296
BK7	0.1	1250	22.0	gl,ol,chr,pig,aug	60.4(7),26.4(5),tr,6(1),7(1)	0.04	1	0.320
BK13	0.1	1250	264.0	gl,ol,chr,pig,aug	53(2),26(2),tr,8(3),12(3)	0.43	4	0.298
BK11	0.1	1237	48.8	gl,ol,chr,pig,aug	46(1),27.2(8),tr,8(2),19(1)	0.10	0	0.303
BK8	0.1	1225	23.0	gl,ol,chr,pig,aug	40.7(5),28.0(4),tr,7.2(8),23.9(7)	0.03	1	0.302

^a Abbreviations: gl(glass), ol(olivine), chr(chromite), pig(pigeonite), aug(augite), opx(orthopyroxene)

^b Phase proportions determined by mass balance.

^c Fe loss is reported as percent relative to starting composition.

^d Glass pockets were too small to analyze accurately.

^e Melt did not quench to a glass.

Table 5 (cont.). Experimental Results

Isothermal Experiments						Sum	% Fe	Fe/Mg	K _D
Exp. #	P (MPa)	T (°C)	duration (hours)	phases present	phase proportions	of Residuals Squared			
TZM BK19	100	1175	6.2	gl,ol,chr,aug ^d		-	-	-	
TZM BK18	100	1150	7.2	gl,ol,chr,aug	50(1),31.8(6),tr,17(2)	0.00	2	0.276	
TZM BK17	100	1125	5,9	gl,ol,chr,aug,pig ^d		-	-	-	
TZM BK11	200	1257	4.7	gl,ol,chr ^e		-	-	-	
TZM BK5	200	1200	6.5	gl,ol,chr,aug	86(3),26.6(6),tr,-8(2)	0.38	4	0.298	
TZM BK4	200	1163	6.3	gl,ol,chr,aug	73(2),33.1(5),tr,0.0	0.22	3	0.292	
TZM BK1	200	1120	6.2	gl,ol,chr,aug	60(1),30.8(4),tr,13(1)	0.19	2	0.291	
TZM BK15	200	1094	35.0	gl,ol,chr,aug,opx	22(1),30(1),tr,37.5(9),11(2)	0.15	0	0.223	
TZM BK10	200	1026	41.1	gl,ol,chr,aug,opx	21.3(9),28.2(9),tr,35.9(7),16(1)	0.10	0	0.235	
Cooling Rate Experiments									
Exp. #	P (MPa)	T (°C) initial	T (°C) final	Rate (°C/hour)	phases present				
BK CR7	0.1	1455	1048	10	gl,ol,chr,pig (cores),aug (rims)				
BK CR9	0.1	1460	1060	3	gl,ol,chr,pig (cores),aug (rims)				

Table 6. Electron microprobe analysis of run products

Exp.	Phase(n)	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO*	MnO	MgO	CaO	NiO	Na ₂ O	Total
BK4	gl(2) ^a	50.1(1) ^b	0.47(2)	4.69(3)	0.44(7)	11.74(4)	0.24(2)	22.68(8)	10.4(1)	0.18(1)	0.27(2)	101.2
BK3	gl(5)	50.3(1)	0.50(5)	4.86(5)	0.44(4)	11.86(6)	0.24(2)	21.8(2)	10.7(1)	0.15(2)	0.22(3)	101.3
	ol(6)	40.9(3)	0.02(3)	0.05(1)	0.16(2)	8.4(1)	0.12(2)	50.5(2)	0.38(3)	0.52(3)	-	101.1
BK1	gl(4)	50.85(9)	0.49(3)	5.05(5)	0.45(4)	11.9(1)	0.21(7)	20.9(1)	11.2(9)	0.16(2)	0.27(8)	101.4
	ol(3)	40.7(3)	0.0	0.061(7)	0.23(3)	8.76(7)	0.14(4)	50.2(1)	0.38(1)	0.54(1)	-	101.0
BK5	gl(5)	50.9(2)	0.47(2)	5.18(5)	0.35(4)	11.5(2)	0.17(3)	21.1(1)	11.24(8)	0.0	0.22(1)	101.1
	ol(4)	40.58(4)	0.0	0.01(1)	0.18(1)	8.8(2)	0.13(4)	49.7(1)	0.35(2)	0.31(2)	-	100.1
BK6	gl(5)	52.6(2)	0.56(5)	6.18(6)	0.27(2)	11.5(2)	0.19(3)	15.62(8)	13.4(2)	0.0	0.29(4)	100.7
	ol(6)	40.0(2)	0.0	0.03(1)	0.19(5)	11.4(1)	0.18(2)	47.9(3)	0.44(3)	0.43(3)	-	100.6
BK12	gl(6)	52.5(2)	0.58(2)	6.3(1)	0.21(3)	11.2(1)	0.19(6)	14.0(3)	13.9(1)	0.0	0.36(5)	99.4
	ol(5)	40.7(2)	0.01(1)	0.07(3)	0.21(3)	11.5(2)	0.13(3)	47.2(4)	0.46(2)	0.41(3)	-	100.7
	pig(5)	57.2(10)	0.05(2)	0.43(8)	0.4(1)	6.9(7)	0.16(1)	31.4(10)	4.2(6)	-	0.0	100.9
BK10	gl(5)	52.7(2)	0.61(3)	6.7(3)	0.20(6)	11.4(2)	0.23(5)	13.2(4)	14.02(9)	0.0	0.41(6)	99.6
	ol(6)	40.7(4)	0.0	0.08(1)	0.22(3)	12.2(2)	0.14(2)	46.8(8)	0.47(2)	0.41(2)	-	100.9
	pig(12)	55.8(6)	0.07(2)	0.5(2)	0.48(6)	7.8(4)	0.18(4)	29.2(8)	5.6(6)	-	0.02(2)	99.71
	aug(11)	54.2(5)	0.10(3)	1.0(2)	0.8(1)	5.3(4)	0.13(2)	20.9(8)	17(1)	-	0.03(3)	99.42
BK15	gl(7)	51.3(1)	0.69(3)	7.7(2)	0.20(3)	11.6(1)	0.23(2)	13.3(3)	13.8(1)	0.03(1)	0.13(3)	99.2
	ol(11)	39.2(3)	0.04(1)	0.08(1)	0.15(3)	12.2(3)	0.20(2)	47.0(5)	0.42(5)	0.34(2)	-	99.6
	pig(4)	55.3(4)	0.06(1)	0.62(9)	0.55(8)	7.7(1)	0.20(3)	29.4(6)	5.6(4)	-	0.0	99.4
	aug(17)	53.8(7)	0.11(4)	0.96(9)	0.84(7)	5.1(2)	0.15(4)	21.3(5)	17.2(6)	-	0.0	99.56

^a Value in parentheses indicates number of points averaged.

^b Value in parentheses is one sigma deviation. The entry 50.1(1) should be read 50.1 wt.% $\pm$ 0.1 wt.%. The standard deviation values are based on repeated analyses of the same phase. Therefore they represent a combination of analytical error and real compositional variation. The analytical error has been estimated by repeated analyses of a glass with a known composition. Based on 139 analyses, the percent relative, one standard deviations are SiO₂ = 0.5, TiO₂ = 1.7, Al₂O₃ = 0.9, FeO = 1.3, MnO = 17.6, MgO = 1.1, CaO = 1.0, Na₂O = 1.9, and K₂O = 2.8. Standard deviations larger than this represent real compositional variation in the analyzed phase.

^c Melt pockets were too small to analyze.

^d Melt did not quench to a glass.

^e Pyroxene core

^f Pyroxene rim

Table 6(cont.). Electron microprobe analysis of run products

Exp.	Phase(n)	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO*	MnO	MgO	CaO	NiO	Na ₂ O	Total
BK7	gl(5)	52.33(9)	0.69(1)	7.7(1)	0.19(2)	11.7(3)	0.21(2)	13.0(1)	14.2(1)	0.0	0.29(2)	100.4
	ol(5)	40.0(7)	0.0	0.05(6)	0.14(3)	13.2(2)	0.23(3)	45.8(6)	0.5(2)	0.45(5)	-	100.5
	pig(18)	55.8(5)	0.09(2)	0.7(2)	0.51(9)	8.2(8)	0.20(2)	29(1)	5.7(7)	-	0.02(2)	99.94
	aug(11)	54.2(7)	0.13(4)	1.3(4)	0.7(2)	6.2(5)	0.15(2)	21(1)	16.7(8)	-	0.02(2)	100.3
BK13	gl(21)	52.0(2)	0.80(3)	9.2(3)	0.22(5)	11.4(1)	0.18(4)	11.7(2)	14.2(1)	0.03(1)	0.16(3)	99.8
	ol(7)	39.9(8)	0.06(1)	0.06(4)	0.21(2)	13.3(4)	0.21(1)	46.0(8)	0.47(3)	0.40(3)	-	100.6
	pig(15)	56.3(3)	0.06(3)	0.61(5)	0.48(4)	8.7(2)	0.15(5)	29.1(5)	5.4(4)	-	0.03(1)	100.8
	aug(11)	54.6(3)	0.08(2)	0.93(5)	0.75(4)	6.0(2)	0.13(3)	21.1(4)	16.9(6)	-	0.07(1)	100.6
BK11	gl(5)	51.8(2)	0.83(2)	9.4(2)	0.14(5)	12.1(1)	0.24(7)	10.85(7)	13.62(5)	0.0	0.40(6)	99.5
	ol(5)	40.3(2)	0.0	0.10(3)	0.18(4)	14.8(2)	0.14(5)	44.1(5)	0.6(4)	0.52(2)	-	100.8
	pig(4)	56.0(3)	0.11(4)	0.6(1)	0.5(1)	8.54(5)	0.14(5)	29.2(7)	5.4(8)	-	0.05(3)	100.6
	aug(3)	54.32(4)	0.16(5)	1.20(7)	0.7(2)	6.1(3)	0.15(1)	21.1(5)	17.4(7)	-	0.03(2)	101.2
BK8	gl(5)	51.9(11)	0.90(2)	10.3(4)	0.10(2)	11.9(2)	0.16(4)	10.1(6)	13.30(9)	0.0	0.44(6)	99.2
	ol(5)	40.0(6)	0.0	0.08(3)	0.21(1)	15.5(2)	0.17(3)	43.5(10)	0.48(7)	0.49(4)	-	100.5
	pig(5)	55.8(6)	0.13(2)	0.9(1)	0.6(1)	9.0(2)	0.21(3)	27.9(6)	6.3(7)	-	0.04(2)	100.9
	aug(4)	54.0(4)	0.15(2)	1.3(1)	0.77(9)	6.4(2)	0.17(2)	21.2(7)	16.7(7)	-	0.04(3)	100.7
TZM-BK19	gl ^c											
	ol(35)	40.0(5)	0.0	0.0	0.10(2)	12.3(1)	0.20(2)	47.3(7)	0.38(7)	0.30(2)	-	100.6
	aug(37)	54.1(5)	0.15(8)	1.2(6)	0.5(1)	5.1(6)	0.14(3)	19.5(8)	19(1)	-	0.02(1)	99.9
TZM-BK18	gl(12)	51.0(2)	0.73(5)	8.2(1)	0.14(3)	11.0(2)	0.18(6)	10.1(3)	12.2(1)	-	0.27(6)	93.9
	ol(16)	40.3(4)	0.09(3)	0.0	0.17(3)	13.7(2)	0.18(3)	45.5(4)	0.41(7)	0.20(5)	-	100.5
	aug(19)	53.7(4)	0.23(6)	1.2(2)	0.56(8)	5.7(5)	0.14(5)	19.5(6)	19.0(9)	-	0.11(6)	100.1
TZM-BK17	gl ^c											
	ol(16)	39.5(6)	0.11(2)	0.0	0.16(2)	15.5(2)	0.18(5)	43.8(7)	0.38(6)	0.40(2)	-	100.0
	aug(40)	53.0(6)	0.33(9)	2.1(7)	0.4(2)	6.3(5)	0.16(4)	17.7(8)	20(1)	-	0.14(6)	99.8
	opx(16)	55.6(7)	0.10(2)	1.1(3)	0.50(5)	10.2(3)	0.22(2)	29(1)	2.7(4)	-	0.0	100.3

Table 6(cont.). Electron microprobe analysis of run products

Exp.	Phase(n)	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO*	MnO	MgO	CaO	NiO	Na ₂ O	Total
TZM-BK11	gl ^d											
	ol(5)	40.3(2)	0.0	0.10(3)	0.18(4)	14.8(2)	0.14(5)	44.1(5)	0.6(4)	0.52(2)	-	100.8
TZM-BK5	gl(6)	49.7(6)	0.59(5)	5.9(1)	0.11(3)	10.0(2)	0.11(5)	13.4(3)	13.3(1)	0.02	0.30(2)	93.4
	ol(5)	40.2(3)	0.02(1)	0.03(2)	0.06(1)	11.0(2)	0.11(5)	49.4(7)	0.39(2)	0.22(3)	-	101.5
TZM-BK4	aug(29)	54.0(4)	0.13(6)	0.7(3)	0.59(7)	4.1(4)	0.12(4)	19.6(6)	20.2(1)	-	0.0	99.4
	gl(5)	49.6(8)	0.64(3)	6.7(2)	0.20(5)	9.8(4)	0.20(4)	10.9(9)	13.9(5)	0.0	0.25(5)	92.2
	ol(5)	40.9(3)	0.0	0.04(2)	0.2(1)	12.1(3)	0.17(3)	46.6(8)	0.35(1)	0.4(1)	-	100.8
TZM-BK1	aug(10)	54.2(8)	0.09(3)	0.52(7)	0.58(5)	4.2(2)	0.11(5)	19.5(4)	20.8(3)	-	0.0	100.1
	gl(6)	49.8(1)	0.72(1)	7.98(5)	0.11(4)	10.64(8)	0.27(3)	10.6(1)	12.44(6)	0.0	0.38(3)	93.1
	ol(5)	39.9(3)	0.03(1)	0.0	0.10(2)	13.6(2)	0.20(2)	46.7(4)	0.32(1)	0.38(7)	-	101.2
TZM-BK15	aug(14)	53.9(7)	0.14(1)	0.73(7)	0.58(5)	4.8(3)	0.12(6)	19.0(4)	20.1(4)	-	0.0	99.5
	gl(14)	52.6(4)	1.11(3)	15.8(2)	0.0	8.9(2)	0.17(4)	4.6(4)	9.2(4)	0.0	0.53(9)	93.0
	ol(22)	39.4(3)	0.0	0.0	0.0	18.2(2)	0.25(2)	42.2(4)	0.4(3)	0.31(4)	-	100.8
TZM-BK10	aug(5)	52.5(4)	0.34(5)	2.5(3)	0.4(1)	6.6(3)	0.18(2)	17.6(2)	20.0(6)	-	0.0	100.0
	opx(4)	54.9(2)	0.16(4)	1.6(4)	0.47(6)	11.9(4)	0.24(5)	29.0(6)	2.5(6)	-	0.0	100.7
	gl(1)	53.065	0.968	15.231	0.084	8.156	0.109	4.309	10.249	0.047	0.358	92.6
BK-CR7	ol(5)	37.8(6)	0.0	0.0	0.08(1)	18.9(3)	0.28(5)	42.3(12)	0.27(4)	0.40(6)	-	100.1
	aug(8)	52.2(7)	0.34(7)	3.1(7)	0.4(2)	6.3(4)	0.15(5)	16(1)	21.1(9)	-	0.07(6)	100.3
	opx(7)	54.1(7)	0.15(5)	2.3(4)	0.52(7)	11.9(3)	0.22(6)	28.3(8)	1.9(1)	-	0.0	99.4
BK-CR9	gl(15)	54.0(2)	1.16(5)	14.5(3)	0.0	15.2(2)	0.23(5)	3.0(1)	11.5(2)	0.0	0.46(4)	100.3
	ol(7)	39.9(6)	0.0	0.027(9)	0.20(5)	10.4(3)	0.11(4)	48.4(9)	0.35(3)	0.0	-	99.6
	cpx(1) ^e	54.7	0.0	0.97	1.00	7.75	0.21	22.9	13.7	-	0.08	101.2
BK-CR7	cpx(1) ^f	50.0	0.61	3.76	0.03	13.6	0.13	12.9	19.8	-	0.13	101.0
	gl(17)	52.8(15)	1.2(1)	15.0(12)	0.0	13.9(13)	0.22(5)	3.7(12)	11.7(2)	0.0	0.0	99.1
	ol(29)	39.8(16)	0.0	0.0	0.22(5)	10.8(40)	0.12(5)	47.6(52)	0.0	0.31(4)	-	99.6
BK-CR9	cpx(1) ^e	56.7	0.0	0.44	0.23	8.7	0.26	30.3	4.74	-	0.0	101.4
	cpx(1) ^f	51.7	0.38	2.8	0.07	12.3	0.23	15.7	17.3	-	0.0	100.5

FIGURE CAPTIONS

Figure 1. Backscattered electron image of fresh augite in sample B95-7. The crystal is zoned from a high-MgO interior to a low-MgO, high-FeO rim. Image is 300 microns wide. Darkest material is a fine-grained mixture of serpentine and chlorite. Dark gray material overgrowing augite is tremolite. Bright material is magnetite. The pattern of compositional zoning preserved augite such as this one indicate that their compositions have not been altered by chemical diffusion during the metamorphism their host rocks.

Figure 2. Compositions of clinopyroxene in olivine spinifex units from Barberton. Different symbols indicate augites from different samples. Average augite compositions are given in Table 3. Mineral textures are given in Table 1. Analyses of augite cores are circled. Arrows extending from the core compositions indicate representative zoning profiles. Shaded fields indicate the compositions of augite experimentally produced under 0.1 MPa anhydrous conditions (lower Wo field) and 200 MPa H₂O saturated conditions (higher Wo field). The compositions augite cores from the Barberton komatiite samples fall within the hydrous experimental field, and do not overlap the anhydrous field, indicating that the komatiite magmas contained at least 6 wt.% H₂O at the time the augite crystallized.

Figure 3. a) Compositions of Barberton komatiite chill margins and aphyric zones (filled circles) projected onto the pseudoternary oliv-cpx-qtz (data from [Smith *et al.*, 1980] and [Smith and Erlank, 1982] reduction method of [Baker *et al.*, 1994]. Also indicated are the compositions of the dominant metamorphic minerals in the rocks,

serpentine and chlorite (filled oval). The thick gray line indicates the data trend expected if the primary compositional control was olivine fractionation with the most olivine normative rocks being the primitive melts. The samples do not fall along the olivine fractionation line, but do trend towards the metamorphic minerals. This suggests that the highest MgO compositions are not igneous, but have been produced by serpentinization. b) The compositions of the chill margins projected onto the ol-cpx join and plotted against their H₂O content (loss on ignition). The H₂O is hosted in the metamorphic mineral assemblage and therefore higher bulk H₂O contents indicate higher extents of alteration. The highest MgO samples (lowest cpx content) are the most highly altered. The good correlation between extent of metamorphism and MgO content corroborates the hypothesis that the high MgO contents are the consequence of metamorphism.

Figure 4. Average experimental pyroxene compositions (Table 6) plotted in the pyroxene quadrilateral. Isotherms from Davidson and Lindsley [1989]. Lines connect coexisting experimental pyroxenes. Filled circles are augites from anhydrous experiments. Filled triangles are augites from H₂O-saturated experiments at 200 MPa. Gray filled triangles are augites from H₂O-saturated experiments at 100 MPa. The data conform well to the predicted isotherms, indicating that equilibrium has been approached.

Figure 5. Phase appearance temperatures at 0.1 MPa (anhydrous) and 100 and 200 MPa (H₂O saturated). Circles are 0.1 MPa experiments. Diamonds are H₂O-saturated experiments. The presence of H₂O depresses the appearance temperature of all phases,

but low-Ca pyroxene is most strongly affected. At 1 atm., low-Ca pyroxene crystallized before high-Ca pyroxene, while at 200 MPa, under H₂O-saturated conditions, low-Ca pyroxene crystallizes ~120°C lower than the first appearance of high-Ca pyroxene.

Figure 6. Wollastonite content versus Mg # ($=\text{MgO}/(\text{MgO}+\text{FeO}^*)$) of pyroxene in Barberton komatiites. Clinopyroxene in olivine spinifex units is shown as open circles. Open squares represent pigeonite and augite in peridotitic komatiite from the upper Komati formation. Shaded regions are pyroxenes produced in isothermal experiments. Inset shows data used to define isothermal fields (shaded regions) and pyroxene compositions produced in 0.1 MPa cooling rate experiments (unshaded region). If the Barberton komatiites were anhydrous, pigeonite is expected to be an early crystallizing phase, yet it is absent in all samples from the lower Komati Fm. . The presence of pigeonite in B94-4, a sample from the upper Komati Fm., may indicate lower H₂O contents in that sample.

Figure 7. Compositions of experimental melts (reduction method of [Baker *et al.*, 1994]) with inferred multiple saturation boundaries at 0.1 MPa (anhydrous, black line) and 200 MPa (H₂O saturated, gray line). The starting compositions used in this study (filled circle) and in Green *et al.* [1975] (filled star) are also indicated. Gray arrow indicates initial liquid line of descent from the starting composition used in this study. Black arrow indicates the initial liquid line of descent using the starting composition from Green *et al.* [1975]. Regardless of the starting composition used, high H₂O contents are required to suppress pigeonite. The high MgO compositions strike the

olivine-pigeonite phase boundary further down than the lower MgO compositions, and therefore require even higher H₂O contents to suppress pigeonite nucleation.

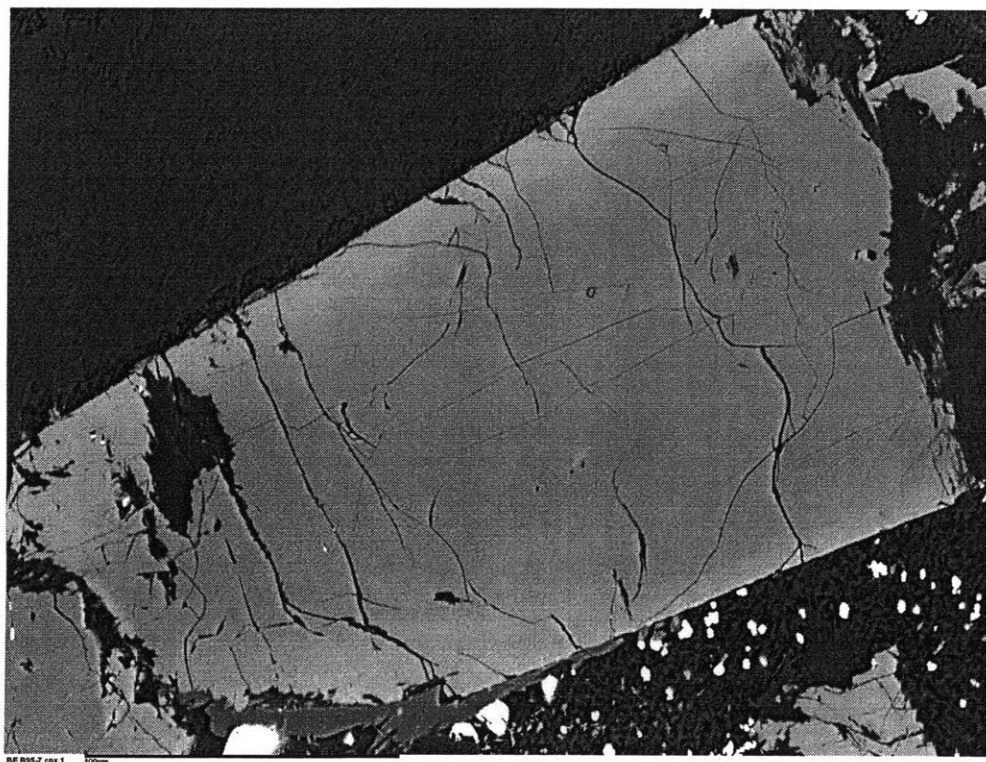
FIGURES**Figure 1**

Figure 2

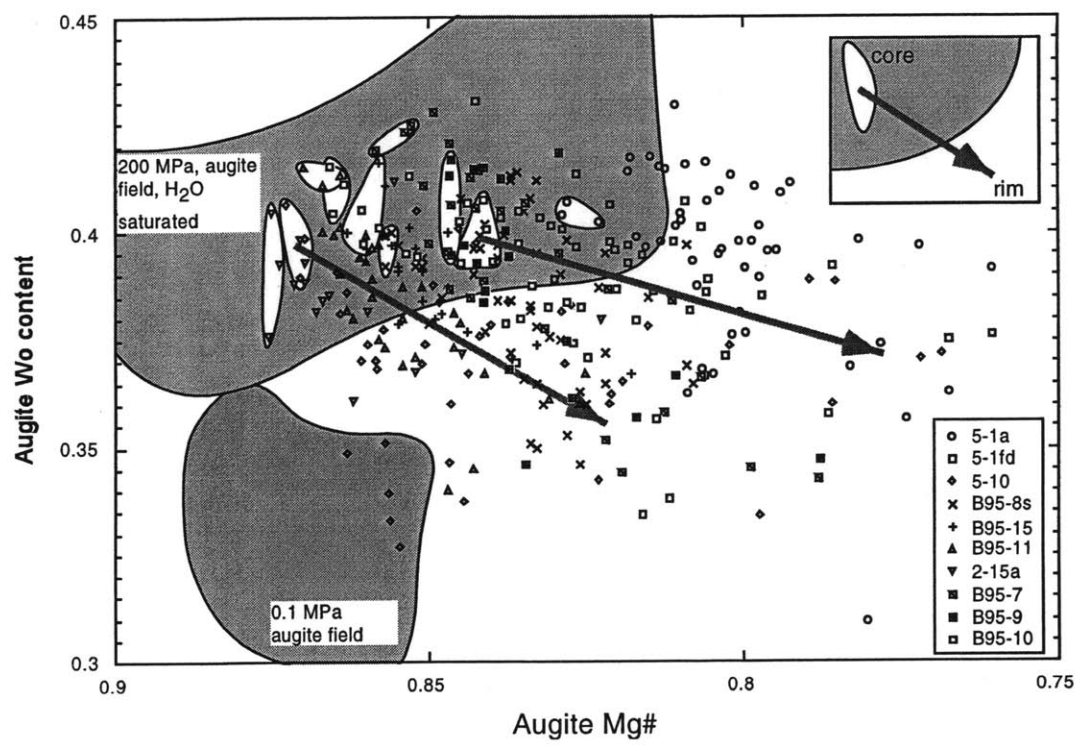


Figure 3

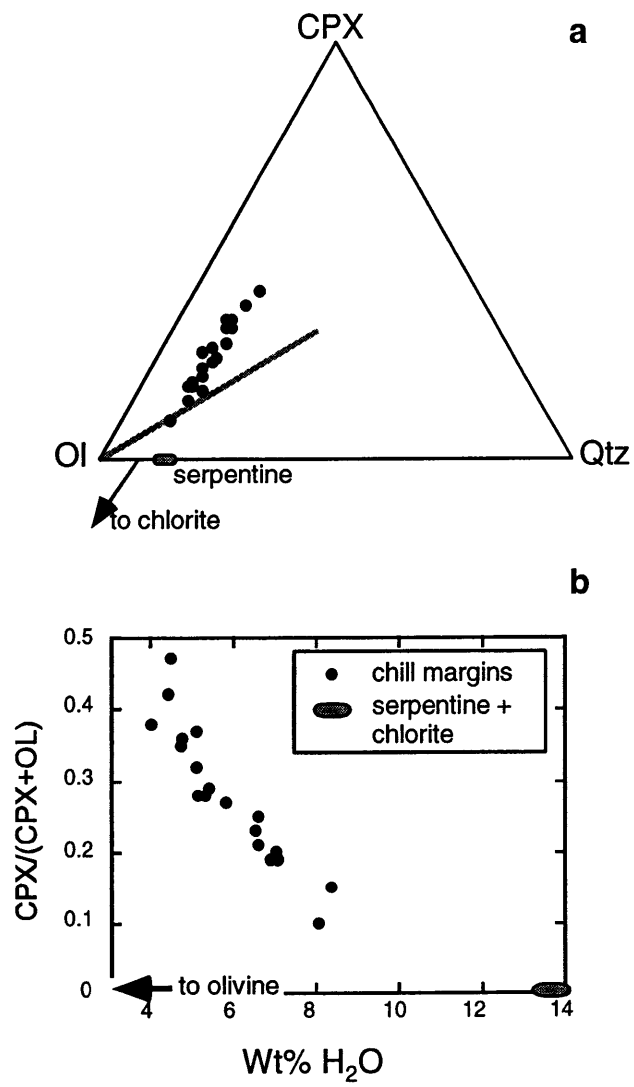


Figure 4

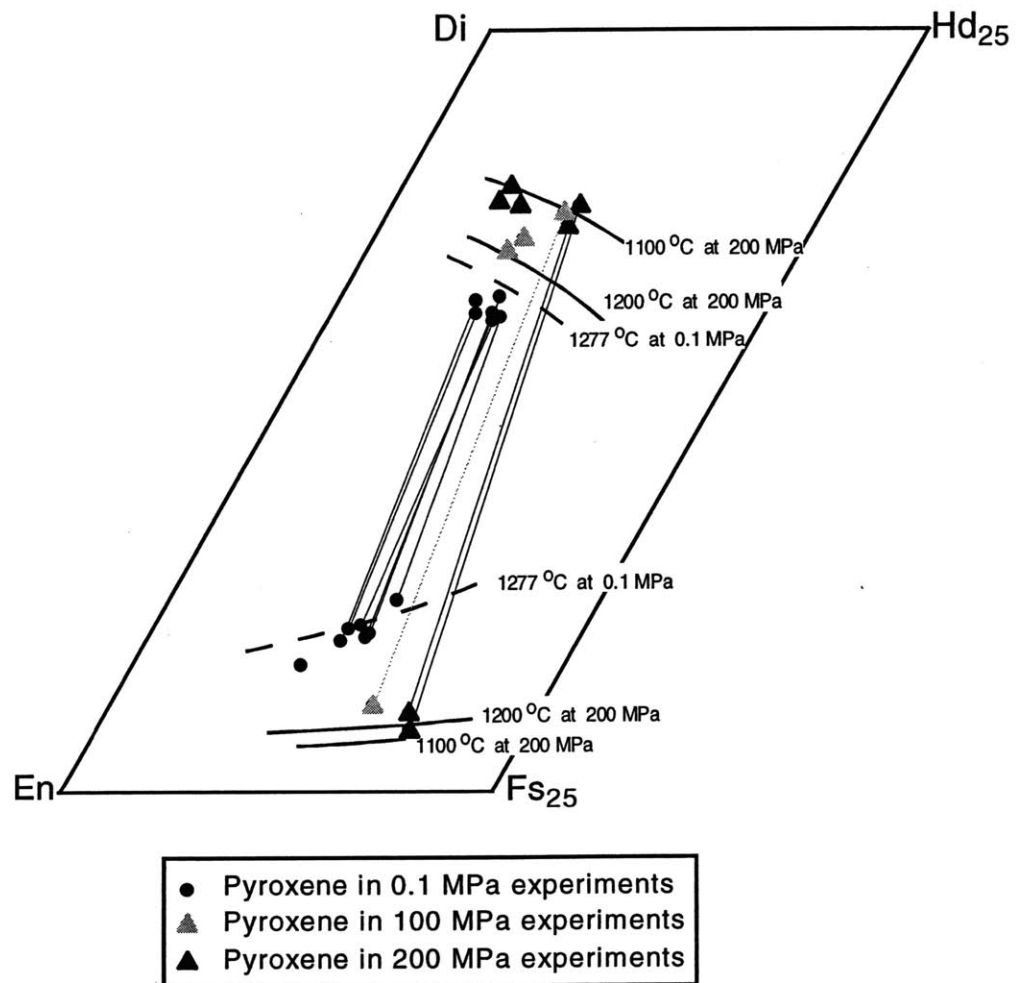


Figure 5

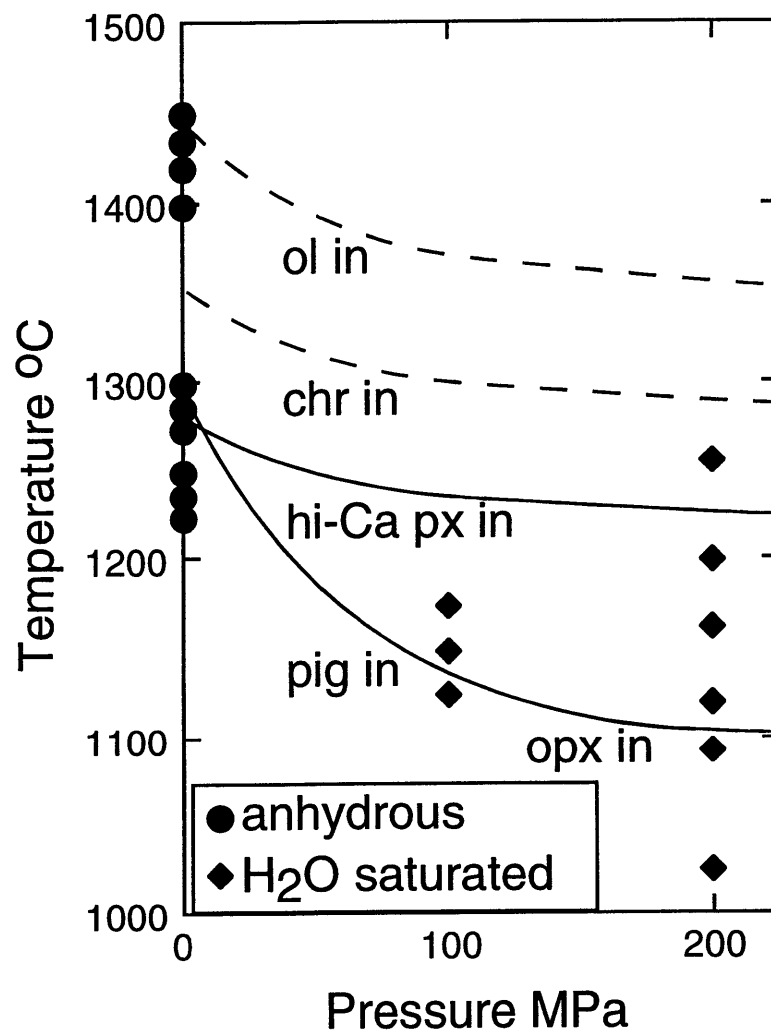


Figure 6

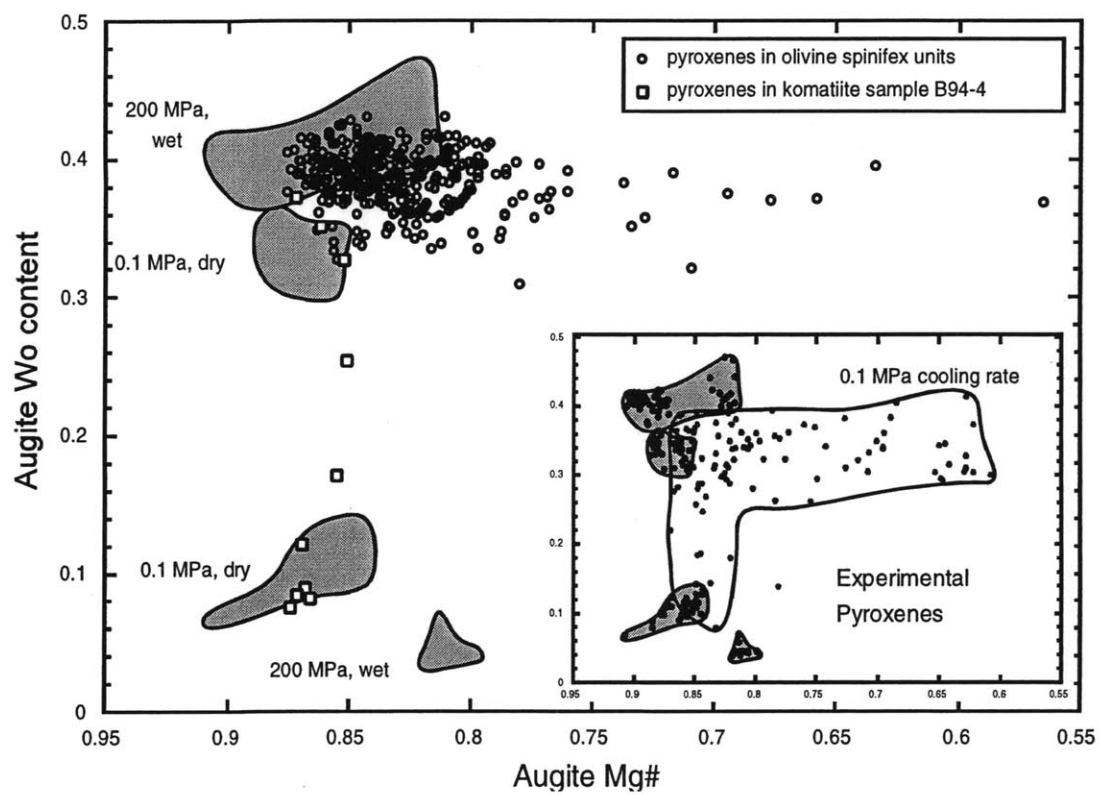
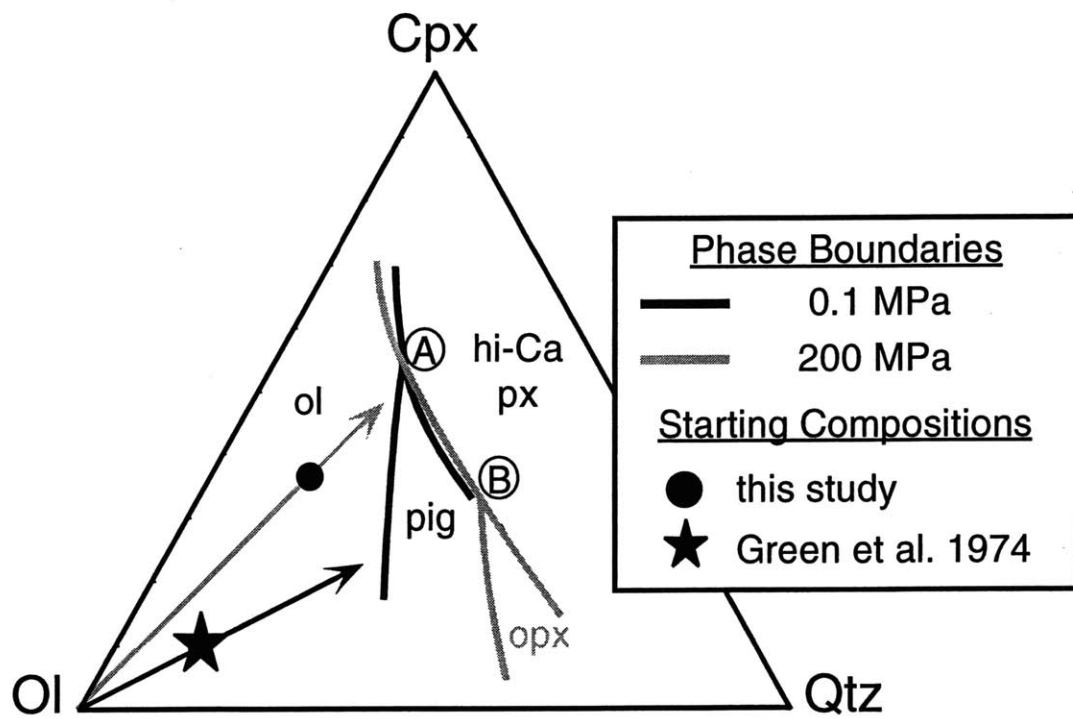


Figure 7



CHAPTER 2. TRACE ELEMENT COMPOSITION OF BARBERTON KOMATIITES

ABSTRACT

The trace element composition of igneous augite preserved in komatiite samples from the lower Komati Fm., Barberton Mountainland, South Africa (3.49 Ga), has been used to estimate the unaltered trace element (TE) composition of the komatiite magmas. The chemical effects of the metamorphism that have affected all Barberton komatiites (BK) are evaluated by comparing the augite analyses with the TE contents of the augite that is calculated to be in equilibrium with the present day composition of the sample. The clinopyroxenes were analyzed by ion microprobe. The augite analyses indicate that the rare earth elements (REE), high field strength elements (HFSE), Y and Ti, were immobile during metamorphism, while Sr and Eu were mobile. Magma compositions reconstructed from the cpx analyses have the same chemical systematics as the bulk sample analyses; namely variable LREE from depleted to enriched, HFSE depletions, and low Ti/Zr. Sr/Nd ratios in the magmas were estimated from the augite Sr/Nd ratios. Three samples were Sr enriched prior to metamorphism (chondrite normalized Sr/Nd = 1.47-1.71), while the remaining two samples had chondritic $(\text{Sr/Nd})_n = 1.1 \pm 0.2$. The compositional features of BK are similar to the TE characteristics of modern subduction zone magmas, and are distinct from the chemical features of mid-ocean ridge basalts and ocean island basalts. Models that produce the HFSE depletions in BK by melting in the majorite garnet stability field in a hot plume are not viable as majorite cannot fractionate Ti from Zr to produce low Ti/Zr. The high Mg# and low Ti/Zr of Barberton komatiites are notably similar to boninites. Boninite-like magmas ($\text{MgO} > 15\text{wt.}\%$, $\text{SiO}_2 > 52\text{wt.}\%$, $\text{TiO}_2 < 0.5\text{wt.}\%$) are found in the Komati and underlying Theespruit Fm., and suggest a close relationship between BK and boninites. In conjunction with the petrologic

estimates of high magmatic H₂O contents and the interlayering of boninitic rocks with komatiites, the TE systematics of BK lead us to conclude that BK were produced in an Archean subduction zone. LREE enriched and HFSE depleted komatiites are present in a number of Proterozoic and Archean greenstone belts, as are boninites, suggesting that the subduction model for BK petrogenesis may be generally applicable.

INTRODUCTION

Komatiites display a wide range of trace element (TE) systematics. The La/Sm ratios vary from >1 to <1, as does Gd/Yb ratios [Arndt and Jenner, 1986; Fan and Kerrich, 1997; Hollings and Kerrich, 1999; Jahn *et al.*, 1982; Jochum *et al.*, 1991; Lahaye *et al.*, 1995; Lecuyer *et al.*, 1994; Sun and Nesbitt, 1978; Xie *et al.*, 1995]. Depletions in high field strength elements (HFSE=Nb, Ta, Zr, Ti), relative to the REE, and large variations in large ion lithophile element (LILE) concentrations are common. The origin of these geochemical variations is not agreed upon. For instance, researchers have proposed that the LREE enrichments are: a) a geochemical feature of the primary komatiite melt [Jochum *et al.*, 1991; Sun and Nesbitt, 1978; Tomlinson *et al.*, 1999], b) a result of chemical changes during metamorphism [Jahn *et al.*, 1982; Lahaye *et al.*, 1995], or c) a result of crustal contamination [Arndt and Jenner, 1986; Cattell, 1987; Hollings and Kerrich, 1999]. Not surprisingly, the TE composition of komatiites have been used to argue that they were produced in nearly all tectonic settings, including plumes [Arndt *et al.*, 1998; Hollings and Kerrich, 1999; Sun and Nesbitt, 1978; Xie *et al.*, 1995], mid-ocean ridges [Gale, 1973; Herrmann *et al.*, 1976], and subduction zones [Wilson and Versfeld, 1994].

A primary barrier to further progress is the pervasive greenschist facies metamorphism that has affected komatiites. All komatiite samples are altered, and only

rarely preserve igneous minerals [Beswick, 1982; Lahaye *et al.*, 1995]. Unaltered glass has not been found. The extent to which the TE have been mobilized by the metamorphism must be evaluated if any confidence is to be placed in the geochemical analyses and interpretations. The most common method used to evaluate the effects of metamorphism is consistency of REE and TE patterns. That is, when element concentrations from a number of samples are plotted together, if they form parallel curves, it is argued that they have not been affected by metamorphism [Lecuyer *et al.*, 1994; Sun and Nesbitt, 1978]. This argument is based on the idea that metamorphism will introduce non-systematic chemical variations. While this may be true in some instances, there are cases where metamorphism has caused parallel shifts in TE patterns [Frey *et al.*, 1974; Hart *et al.*, 1974; Staudigel and Hart, 1983]. More importantly, if metamorphism is the cause of variations of TE concentrations, this method does not distinguish which of the spectrum of TE compositions is closest to the unaltered, igneous composition.

Isotopic ratios have been used to evaluate metamorphism, but are limited to elements with long-lived radioactive isotopes. In some cases, Sm-Nd whole rock isotope data form well constrained pseudo-isochrons that yield consistent ages that agree with independent estimates of the age of komatiites, and suggest little post-emplacement mobilization of Sm or Nd [Jahn *et al.*, 1982]. Other studies have shown variations in initial epsilon Nd, and argue for isotopic exchange between metamorphic fluids and komatiites [Lahaye *et al.*, 1995]. Rb-Sr isotopic data are more scattered than the Sm-Nd data, and rarely form isochrons [Jahn *et al.*, 1982]. The data imply that Sm and Nd, and by inference, all of the middle rare earth elements (MREE), have been less affected than LILE like Rb and Sr, but that neither of the element groups have escaped the effects of

metamorphism completely. Like the consistency arguments, isotopic studies suffer from an inability to quantitatively estimate the pre-metamorphic TE composition of the samples.

This study takes a different approach to identifying metamorphic effects. We have analyzed the trace element composition of the preserved igneous pyroxenes in the rocks. Arguably, these are the only igneous material left in the samples. These crystals have not been affected by metamorphism, and therefore should record the trace element composition of the melt from which they grew. The composition of the melt from which the pyroxene crystallized is calculated using experimentally determined mineral/melt partition coefficients taken from the literature. Any difference between the trace element composition of the magma inferred from the augite and that measured in the whole rock can be attributed to metasomatism. Only an accurate knowledge of crystal/melt TE partition coefficients is needed. This method is attractive because it can be applied to a single sample, and can provide quantitative estimates of the pre-metamorphic igneous TE concentrations.

REGIONAL AND LOCAL GEOLOGY

The mafic to ultramafic Komati Fm. (3.49 Ga) [*Lopez-Martinez et al.*, 1992] forms the lower portion of the Onverwacht group in the Barberton greenstone belt. Olivine spinifex units form five distinct horizons within the lower Komati fm, and are separated by basaltic komatiite and massive komatiite units (Fig. 1). The samples in this study were collected in conjunction with a fine-scale remapping of the area (Dann, in press). In this paper we focus on samples taken from the olivine spinifex units. One sample from the upper Komati Fm. is also included.

PETROGRAPHY

Samples from the interior A (spinifex) and B (cumulate) zones were collected in order to obtain unaltered igneous minerals. Though well-preserved samples usually contain less than 15% relict igneous phases overall, small cm-size areas preserve up to 80% of the original minerals (Fig. 2). In the lower Komati Fm., the igneous phases preserved are olivine and augite. In the upper Komati Fm., pigeonite is found as well. In many cases, nearly complete core to rim profiles are preserved in the clinopyroxene. Olivine is less well preserved, usually occurring only as rounded remnant grains. Chromian spinels are mantled by magnetite overgrowths. The mesostasis surrounding the ol and cpx pseudomorphs consists of a fine-grained mixture of serpentine and chlorite, with variable amounts of tremolite and magnetite. This is interpreted to have been glass prior to metamorphism, though no unaltered glass has been found. In the following discussion, we refer to this as altered glass. Samples with pyroxenes large enough for ion probe study are generally constrained to the lower B section of the komatiite units. Thus most of our mineral TE data comes from cumulate samples B95-11, 5-10, 2-15a, B94-4, that contain equant pyroxene crystals. One spinifex sample, B95-15, contained 2 pyroxene grains large enough to analyze. The pyroxene textures in this sample range from elongate to lathe-like with most being skeletal. B95-7 is from a half-meter wide dike, and has elongated, but not skeletal pyroxenes, with an abundance of curved 'cockscomb' shaped crystals. The positions of samples within the stratigraphy of the Komati Fm. are shown in Fig. 1.

ANALYTICAL METHODS

Ion microprobe

Augite trace element compositions were measured with the Cameca IMS 3f ion microprobe at Woods Hole Oceanographic Institution. Our analyses were focused on obtaining core to rim TE profiles in order to understand the fractionation of TE concentrations during crystallization of the komatiite units. A beam of oxygen ions with an energy of 12.5 kV was used for the analyses. The beam width was 20 μm when analyzing REE (La, Ce, Nd, Sm, Eu, Dy, Er, Yb) and 5 μm when analyzing the other trace elements (Ti, V, Cr, Sr, Y, Zr). Molecular interferences were reduced by offsetting the secondary accelerating voltage by 60V for REE and 90V for the other trace elements. Element abundances were determined by ratioing the ion intensities to Si, then converting this ratio to an abundance using empirical working curves. Shimizu and Hart [1982] provide a more detailed discussion of the ion probe techniques employed.

Analytical precisions are 5-10% for Sc, Ti, Cr, and V, 10-15% for Sr and Zr, 10-12% for light REE, and 10-15% for middle and heavy REE. The accuracy of the ion probe is not as good as its precision, thus the shapes of the REE and TE curves (i.e. the relative abundances) are better constrained than their absolute concentrations. Therefore throughout this paper we will focus on TE ratios such as La/Sm, and Ti/Zr, instead of single element concentrations.

Electron microprobe

Augite major element compositions were measured with a 5-spectrometer JEOL 733 Superprobe at the Massachusetts Institute of Technology (MIT). After ion probe analysis, the gold coating was removed by polishing and the sample was carbon coated for electron probe analysis. 5 to 10 analyses were done around the ion probe pit, which

was readily identifiable in both reflected light and backscattered electron imaging. A 10 nA beam current was used with an accelerating voltage of 15 kV. The beam width was $\sim 1\mu\text{m}$. Data were reduced using the ZAF correction procedure. Maximum counting times were 40 s.

Analytical precision was measured by repeated analysis of a homogenous glass of known composition. Based on 139 analyses, the percent relative, one standard deviations are: $\text{SiO}_2 = 0.5$, $\text{TiO}_2 = 1.7$, $\text{Al}_2\text{O}_3 = 0.9$, $\text{FeO} = 1.3$, $\text{MnO} = 17.6$, $\text{MgO} = 1.1$, $\text{CaO} = 1.0$, $\text{Na}_2\text{O} = 1.9$, and $\text{K}_2\text{O} = 2.8$.

ICP-MS

Trace elements in whole rock samples were determined with the inductively coupled mass spectrometer at MIT. Rock chips were powdered in an Al_2O_3 shatter-box. The powders (100 mg) were dissolved in Teflon Parr bombs in a two step $\text{HF-HNO}_3/\text{HCl}$ process after procedures described in Eggins et al. [Eggins *et al.*, 1997]. When complete digestion was verified, the solutions were diluted to 200 ml. Internal spikes of In, Bi, and Se were used to monitor and correct for drift during analyses. No measurable mass dependent drift was observed. Standard calibrations were done using USGS standards AGV, BCR-1, BHVO, BIR, DTS, and PCC.

Based on repeated analyses of the USGS standards (M Schmitz and K Viskupic, personal comm.), errors for elements with mass >80 amu are 2% (one sigma, relative standard deviation), and for elements with mass <80 amu are 4%. The small magnitude of the errors can also be seen in the repeated analyses of sample BK95-11 (Table 1, Fig. 3). Two separate dissolutions of this sample were made. One solution was analyzed twice. The difference between the three analyses incorporates not only machine error, but

also any powder inhomogeneity and dissolution errors due to the individual user. For all elements, the two analyses agree within 2%.

XRF

Whole rock major elements were measured by x-ray fluorescence (XRF) at the University of Massachusetts at Amherst. A detailed description of the analytical methods can be found in Rhodes [1996]. Sample powders were first ignited at 1000°C to oxidize all FeO to Fe₂O₃. The powders were then fused with La spiked, lithium borate into a glass disc.

Errors on XRF analyses can be estimated from repeated analyses of standard K1919. Based on 13 analyses, the percent relative uncertainties, one standard deviations are: SiO₂=0.26, TiO₂=0.27, Al₂O₃=0.17, Fe₂O₃=0.11, MnO=0.52, MgO=0.44, CaO=0.08, Na₂O=4.58, K₂O=0.35, and P₂O₅=0.62. Previous analyses of ultramafic samples at Amherst have yielded low Na₂O values (M. Rhodes, personal comm.). It is likely that the values reported here are also low and are the cause of the systematically low totals.

RESULTS

The whole rock samples show a range of TE compositions (Fig. 3) typical of published BK analyses [*Jahn et al.*, 1982; *Jochum et al.*, 1991]. The (La/Sm)_n (normalized to CI chondrite of McDonough and Sun [1995]) varies from .78 to 1.17, with (La/Sm)_n ratios <1 being more common. (Gd/Yb)_n ratios for all samples are >1. Ti is depleted relative to the REE in all samples but two (B94-4 and B96-7). The largest Ti depletions are in the samples with the highest TE abundances and highest La/Sm ratios. Nb, Zr, and Hf negative anomalies are seen in all samples except B94-4, which is enriched in Zr and Hf, and has flat Nb and Ti. The U-shaped REE pattern and the Zr and

Hf enrichments in sample B94-4 distinguish it from the other komatiite analyses. TE patterns nearly identical to B94-4 have been reported previously in komatiites and basaltic komatiites from Barberton, as well as in Pilbara, Newton, Alexo, and Wawa komatiites [Jochum *et al.*, 1991], and thus appear to be a common, though volumetrically small, part of komatiite bearing sequences

Ion probe analyses of the BK augite are given in Table 2. Consistent with known partitioning of TE between clinopyroxene and melt, most of the augites are LREE depleted with flat HREE slopes (solid lines, Fig. 4). The majority of the analyses from any one sample define a set of parallel lines in chondrite normalized diagrams (Fig. 4). The concentration of elements increases towards the rims of the crystals, consistent with its production by fractional crystallization. Metamorphic minerals have also been analyzed. The analyses are of the altered glass that surround the augite, which consists of a fine grained intergrowth of serpentine and chlorite. Tremolite is scarce in the studied samples and was not analyzed. The serpentine-chlorite intergrowths have generally flat or slightly concave up REE patterns. In B95-11, the altered glass has an apparent large positive Eu anomaly. The anomaly is an artifact of a peak overlap with Ba, and indicates high Ba concentrations (100s of ppm) in the metamorphosed glass. Smaller apparent Eu anomalies are present in analyses of serpentine-chlorite intergrowths in samples B95-15 and B94-4.

Metamorphic Minerals

The absolute concentrations of REE in the altered glass are variable (Table 2). In B95-11, the altered glass has lower concentrations of MREE and HREE than the augite, and slightly higher LREE concentrations. The altered glass in B95-15 is more variable, and has both higher and lower REE concentrations than the augite. Though, overall, the

concentrations in the metamorphic minerals are comparable to the augite. Compared to B95-11, the altered glass in B95-15 is more enriched in LREE. Fewer analyses of metamorphic minerals were performed on 5-10, B95-7, and B94-4. The analyses are similar to those from B95-11 and B95-15 in having variable REE concentrations that are similar to the concentrations of REE in the augite. The lone exception is an analysis of the altered glass from 5-10. This analysis has REE concentrations between 10 and 30 ppm, much higher than any other analysis of metamorphic minerals or augite. It is possible that this analysis sampled a tremolite grain that was below the surface of the slide, and therefore was not visible in backscattered electron imaging.

Nearly all ion probe pits include some amount of metamorphic veins (Fig. 2). For the majority of analyses, backscattered images of the pits indicate that the amount of contaminating material is <5%, and usually <2%. This amount of contamination will have negligible effects on the augite analyses, as the serpentine-chlorite intergrowths that fill the veins have similar REE concentrations to the augite. A few of the ion probe analyses incorporated larger amounts of metamorphic minerals. These are readily distinguishable as the ion count rate during the analyses fluctuates widely as the beam alternately samples augite and metamorphic minerals. The contamination also shows up in the analyses as higher La/Sm and in B95-11, as pronounced Ba interference peaks at Eu. Eu in uncontaminated analyses does not show anomalies. The following discussion is based upon the uncontaminated analyses (Fig. 4).

Cpx/melt equilibrium calculations

Cpx/melt partition coefficients (D) were used to calculate the TE composition of the augite that first crystallized from the BK magmas, based upon the whole rock compositions. A number of studies report cpx/melt D values. We have chosen those of

Hart and Dunn [1993] because they include all of the elements relevant to the present study and their analyses were obtained using the same machine (Cameca 3f at Woods Hole) and calibration procedures as in this study. The cpx Hart and Dunn studied is higher in Al content than BK pyroxene, which will cause the D values to be high [Gaetani and Grove, 1995], but the relative partitioning of elements is not significantly affected. Therefore we have based our conclusions solely on inter-element ratios. Calculations using the low Al cpx REE D values of McKay et al. [McKay et al., 1986], yield nearly identical results to those using the Hart and Dunn D values, and lead to the same conclusions.

Olivine and trace amounts of spinel are the only phases to crystallize from komatiite magmas prior to the appearance of augite. The amount of olivine that crystallized before pyroxene nucleates is ~30 wt.%, but will vary from sample to sample. All of the samples in this study come from komatiite units which have fractionated into a lower cumulate zone and an upper spinifex zone. The amount of olivine that accumulated into samples from the cumulate layer and fractionated from samples from the spinifex layer is not easily quantified. In addition, the amount of olivine that was carried into a unit after emplacement and the initial amount of olivine carried by the magma as phenocrysts are also unknown. Without an accurate way to estimate the percent of olivine that crystallized, we have chosen not to correct the calculated melt compositions for olivine fractionation. This has a negligible effect on the relative concentrations of elements as olivine and spinel have low crystal/melt partition coefficients, and so does not affect conclusions based upon interelement ratios. On the other hand, the calculated element concentrations for cumulate samples will be high by a

factor of $1/(1-n_{ol})$, where n_{ol} is the percent of olivine. For $n_{ol}=30\%$, this factor is 1.4. For spinifex samples, calculated concentrations will be a factor of $1-n_{ol}$ low, or about 0.7.

Comparison of calculated and measured cpx TE concentrations

The TE patterns of the calculated augites agree well with the analyses of the augite cores (thick solid line, Fig. 4). To a first order, the similarity of the calculated and observed augite suggests that the REE have been immobile in the whole rock samples. Samples B95-11 and B95-15 were sampled within 10 meters of each other and possibly represent the B and A zones of the same komatiite unit, respectively. Their REE patterns are very similar, the only difference is slightly higher La/Sm in B95-15 (Fig. 3). This small difference is recorded in the augite cores. In B95-11, the cores have La/Sm=0.25 while cores in B95-15 have La/Sm=0.35 (Fig. 4), with an error on both values of $\sim 10\%$ relative. Sample 5-10 is significantly more LREE depleted than B95-11 or B95-15, and this is also reflected in its augite cores, which have low La/Sm=0.15. For samples B94-4 and B95-7, there were not a sufficient number of ion probe analyses to allow a meaningful comparison, but are consistent with the results from the other three samples.

In contrast to the relatively straightforward interpretation of the augite core compositions, the core to rim zoning of the REEs in the augites cannot be reproduced using standard crystal/melt partitioning models. In sample B95-11, La/Sm ratios vary from 0.2 to 0.6 and correlate with La concentration which varies from 0.09 to 0.25 ppm (Fig. 5a). Using Rayleigh fractionation and the crystal/melt D values of Hart and Dunn [1993], we have modeled the expected zoning in the augites starting from the core with the lowest TE concentrations. From petrographic data, the maximum amount of crystallization from the time augite appears to the time the rock stops crystallizing is 40-50%. At these amounts of crystallization, the Rayleigh fractionation curves produce

much smaller variations in La concentrations than are observed (Fig. 5a). Over 60% crystallization is required to produce the La enrichments seen in B95-11 augites. More dramatically, the large variation in La/Sm cannot be produced by Rayleigh fractionation by any amount of crystallization. The post-analysis SEM images (Fig. 2) and lack of high Ba concentrations (Fig. 5a) indicate that the analyses have not been contaminated by metamorphic minerals. While the TE zoning in B95-11 is difficult to rationalize with classical partitioning equations, the observed zoning trends point to core compositions that closely match La and La/Sm in the augite calculated to be in equilibrium with the whole rock, indicating that these elements have not been mobilized by the greenschist metamorphism, in the whole rock or in the augite.

Similar La-Sm systematics can be seen in all the samples in which pyroxene has been analyzed (Fig. 5). Augites in sample B95-15 show the strongest fractionation, while the augites in 5-10 fall closest to the Rayleigh fractionation path. B94-4 and B95-7 are intermediate between the two extremes. 5-10 is a cumulate sample which has the largest, most equant augite crystals of all the samples analyzed, while B95-15 is an olivine spinifex sample with highly elongated and skeletal augite. Experimental studies have shown that crystal morphologies are strongly controlled by the rate at which they grew [Lofgren *et al.*, 1979]. The correlation between the texture of the pyroxene and the severity of La-Sm fractionation suggests that kinetics has affected the partitioning of the REEs.

Like B95-11, the augite cores in the other samples correspond to the calculated augite composition. For B95-7 and B94-4, only a limited number of spots were analyzed, so their results are not as clear as the other three samples. An additional complication in B94-4 is that the cores of the crystals are pigeonite, and therefore a different set of D

values must be used to calculate the pigeonite that would be in equilibrium with the whole rock. The pigeonite cores are small and so some amount of augite was also sampled by the ion probe pit, so the core analysis is a mixture of pigeonite and augite, while the rim analyses are entirely augite. We have used the values from McKay et al [1986] to calculate the pigeonite that would be in equilibrium with the bulk analysis and the values of Hart and Dunn [1993] to calculate the equilibrium augite. As expected, the analyzed B94-4 pyroxene core falls between these two points, consistent with it being a mixture of pigeonite and augite (Fig. 5d).

Like La and Sm, the other incompatible elements that were analyzed (Ce, Nd, Dy, Yb, Ti, Sr, Y, and Zr) also display unexpectedly large fractionations (Figs. 6-8). As with the LREE, 5-10 is the closest to the Rayleigh fractionation curve, while the other samples show varying degrees of excess fractionation. For Ti, Y, Zr, and the other REE, the composition of the augite cores agrees with the augite composition calculated to be in equilibrium with the whole rock, implying the REE, HFSE and Y were immobile during metamorphism. This is not true for Sr (Fig. 7). In all cases, the calculated augite has lower Sr/Nd ratios than the analyzed augite. This indicates that Sr has been lost during metamorphism, consistent with the Sr variability in the whole rock analyses and the disturbed Sr isotopic ratios [Jahn *et al.*, 1982]. Like Sr, ratios of Eu to the REE in the calculated augites are lower than in the natural augites, implying that Eu was also lost during metamorphism.

Cr and V are compatible in cpx and show even more unusual zoning than the incompatible elements (Fig. 9). Cr/Ti ratios in augite rims from B95-11 and B95-15 are much higher than expected from the core compositions. In B95-11, the Cr/Ti towards the rim of the crystals not only falls off the calculated Rayleigh fractionation curve, it goes in

the opposite direction. At face value, this implies that Ti was more compatible than Cr. When partitioning is limited by the diffusion of constituent atoms in the melt, rapid crystallization will cause D values to converge to a value of unity as the crystal is forced to incorporate more and more incompatible elements and less compatible elements. Such a process cannot cause an incompatible element to become compatible or vice-versa. Yet this is what the Cr/Ti variations imply has happened. B95-15 augites also don't fit the fractionation curve, though their Cr/Ti ratios at least predict Cr to be more compatible than Ti. Augite in sample 5-10 falls closest to the calculated fractionation curve. Like the incompatible elements, we find that the Cr and V zoning in the more slowly crystallized 5-10 can be fit by equilibrium partitioning, while the zoning in the rapidly crystallized samples cannot.

Control of partitioning by surface attachment processes

This type of complex TE zoning in the BK augites appears to be the rule in augites that crystallized from magmas during, or just prior to, eruption. Shimizu [1981], Shimizu and Le Roex [1986] and Vannucci et al. [1993], have all found TE zoning in pyroxene phenocrysts that cannot be modeled by Rayleigh fractionation, especially in Cr-Ti zoning. To explain the extreme fractionations between TE, these studies concluded that the crystal/melt partition coefficients were affected by disequilibrium. As discussed above, the disequilibrium cannot be controlled by diffusion in the melt as this would cause all partition coefficients to move toward a value of 1. Thus Shimizu [1981] appealed to surface attachment processes to explain the variations. In this model, TE are enriched on the surface of minerals where they attach to lattice protosites [Nakamura, 1973]. These uncompleted lattice sites can more easily accommodate the large TE, and thus the surface concentration of these elements is higher than the equilibrium

concentration in the body of the crystal. When the next layer of crystal is added, the high TE concentrations are buried. Being above the equilibrium concentration, the TE begin to diffuse out of the crystal into the melt. But if the crystal growth rate exceeds the diffusion rate, then the high concentrations will be trapped. Unlike melt diffusion controlled kinetics, surface disequilibrium can cause partition coefficients to switch from incompatible to compatible, and cause partition coefficients of two elements to switch relative compatibilities.

Shimizu [1981] used differences between growth sectors in a natural augite to show that the enrichment of TEs in one sector versus the other is proportional to their ionic potential (charge/radius²). This is in good agreement with theoretical models of surface attachment that indicate high charge elements should preferentially occupy the protosites [Nakamura, 1973]. Thus Ti should be enriched relative to Cr, and the smaller REE should be enriched relative to the larger REE. In the present study, only one sector zoned crystal was found. It is in sample 5-10, and is shown in Fig. 2. In good agreement with Shimizu, one sector (interpreted to be [100]) is systematically enriched in TE (Figs. 5-9). Relative enrichments are Sr<La<Ti<Y<Zr<Cr. Except for Ti, this is the order that is predicted by Shimizu. Why Ti is not more enriched is not understood at this point.

For crystals that are not sector zoned, one can compute the enrichment of an element relative to its concentration in a hypothetical equilibrium crystal. For instance, the higher slope of the observed La/Sm vs La trend in Figure 5 compared to the slope of the curve calculated using the equilibrium D values, implies that the D value for Sm has been raised more than La, and so Sm is enriched less rapidly in the melt, relative to La. Because the surface attachment process affect high ionic potential elements to a greater degree than low ionic potential elements, the hypothetical enrichment factors should correlate with

Z/r^2 . In this case it does, Sm has higher ionic potential than La. The relative enrichments of Yb, Er, Cr, V, and Zr also fit the model, while Sr and Y do not. Sr has a low ionic potential, and yet appears to be enriched relative to Nd. Y has the same size and charge as Er, but is more enriched.

DISCUSSION

The essential conclusion from the above results is that the REE and HFSE concentrations in bulk analyses are representative of the original igneous concentrations, and can be used for petrogenetic interpretations. In contrast, Sr and Eu have been mobile. Their igneous concentrations are only preserved in the cores of augites in the samples. Based upon the augite analyses, BK magmas varied from Sr enriched (chondrite normalized $Sr/Nd = 1.47-1.71$, three samples) to chondritic ($Sr/Nd = 1.1$, 2 samples). Thus enrichments in LILE appear to be a primary igneous chemical feature of BK. The Sr enrichments are consistent with both the arc and plume models of komatiite production. It is tempting to speculate that the high Ba in the altered glass is also an igneous feature. If so, the high Ba would be consistent with an arc origin. Yet, the high concentrations could be the result of metamorphism. Ba in the augite was below detection limits in this study, and so the cause of the high Ba cannot be ascertained.

Tectonic setting inferred from TE systematics

The HFSE depletions seen in BK and related basaltic komatiites are typical of subduction zone magmas, and are often used as a diagnostic tectonic indicator. Xie et al. [Xie and Kerrich, 1994; Xie et al., 1995] have attempted to reconcile the HFSE depletions with the plume model by appealing to majorite. Experimental work shows that this high

pressure (>14 GPa) form of garnet has relatively high D values for the HFSE [Kato *et al.*, 1988a; Kato *et al.*, 1988b; Ohtani *et al.*, 1989; Yurimoto and Ohtani, 1992], relative to the REE, and so could produce negative HFSE anomalies (Fig. 10). One of the characteristics of the HFSE depletion in BK is that Ti is depleted to greater extent than the other HFSE, giving rise to low Ti/Zr ratios. But majorite cannot fractionate Ti from Zr as the majorite/melt D values are nearly equal. Fig. 11 shows that for 20-100% melting using any of the existing partitioning data, majorite cannot explain the HFSE concentrations in Barberton komatiites and basaltic komatiites. Table 3 shows three representative analyses of Barberton komatiites and basaltic komatiites plotted in Fig. 11 (Dann, unpub. data). Moreover, low Ti/Zr is also seen in samples with no HFSE depletions, such as sample B94-4. These sample have low Ti/Zr because they are enriched in Zr and Hf, relative to the REE. Such Zr, Hf enriched samples are seen in komatiites from other greenstone belts as well [Jochum *et al.*, 1991].

The low Ti/Zr of BK is reminiscent of the low Ti/Zr that is a key geochemical feature of boninites [Hickey and Frey, 1982]. Like the Barberton komatiites and basaltic komatiites, most boninites are depleted in both Ti and Zr, but some are notably similar to samples like B94-4 in having enriched Zr [Hickey and Frey, 1982]. These highly magnesian magmas are produced only in subduction zones by hydrous fluxing of a depleted source [Crawford *et al.*, 1989]. The origin of the HFSE anomalies in boninites is a matter of debate. One model is that the depleted source region has low abundances of REE and HFSE. This is enriched by a hydrous slab fluid that is LREE enriched, but has little HFSE as they have low solubility in hydrous fluids [Hickey and Frey, 1982]. The magnitude of the HFSE anomalies in boninites correlates with the La/Sm ratio of the

samples. Remarkably similar trends are seen in Barberton komatiite and basaltic komatiite samples (Fig. 11).

The low Ti/Zr ratios are not the only observation that links Barberton komatiites to boninites. Rocks with very similar compositions to boninites ($\text{SiO}_2 > 52\%$, $\text{MgO} > 12\%$, $\text{TiO}_2 < 0.5\%$) have been found in the Komati Fm. and underlying Theespruit Fm. [Jahn *et al.*, 1982]. Like boninites, komatiites are high in MgO and many have high SiO_2 for their ultramafic compositions. High water contents in Barberton komatiite magmas have been inferred from the major element composition of the igneous augites [Parman *et al.*, 1997], and recent experimental work has shown that magmas with over 20 wt.% MgO can be produced by hydrous melting of depleted mantle at moderate pressures (1.5 - 2.5 GPa) [Falloon and Danyushevsky, 2000; Grove *et al.*, 1999]. Boninites are also interlayered with komatiites in greenstone belts in Central Africa [Poidevin, 1994] and Canada [Kerrick *et al.*, 1998; Fan and Kerrich, 1997], and previous studies have noted the extensive chemical and petrographic similarity between Phanerozoic boninites and Archean basaltic komatiites [Cameron *et al.*, 1979].

Reconciling production of komatiites in plumes with the petrologic, geologic, and geochemical observations is problematic. The difficulty in producing the HFSE systematics has already been discussed. The interlayering of BK with boninite-like magmas, and the repetition of such associations in other greenstone belts is also difficult to explain. Kerrich and co-workers have hypothesized complex interactions between Archean plumes and subduction zones to produce the komatiite-boninite-low Ti tholeiite associations [Fan and Kerrich, 1997; Hollings *et al.*, 1999; Kerrich *et al.*, 1998]. If true, the repetition of these associations implies that some mechanism operated in the Archean that caused subduction zones to be commonly associated with plumes. Finally, the high

H₂O contents inferred from petrologic observations in Barberton and other greenstone belts would imply high H₂O contents in the deep Archean mantle if they were produced by plumes. Producing such high H₂O contents in high degree melts is difficult in a plume because all of the H₂O will be carried away by the first few percents of melt. In the arc model, H₂O is continually supplied by the slab and maintains high H₂O contents.

Despite the above arguments, there is little doubt that a plume based model could be constructed that fits the observations. Such a model would necessarily include a number of secondary processes (crustal contamination, garnet fractionation, variable source composition) and heretofore unobserved processes (high H₂O in plumes, plume/arc attraction) to work. Given this, we find the arc model more appealing because it explains the full range of observations with a single process (hydrous melting) that has produced similar magmas in more recent times (boninites). In this light, komatiites are seen as an extension of modern mantle melting mechanisms observed in arcs, and the interlayering of komatiites and boninites is an unavoidable outcome of these two magmas being produced by the same melting process. In the plume model, komatiites are emphasized to be unusual with little or no connection to modern magmas as they have little chemical similarity to plume related magmas (tholeiites, alkaline basalts, picrites) and are not observed to be interlayered with such rocks.

CONCLUSIONS

- 1) REE, HFSE, Y, Cr, V, and Ti were immobile during the metamorphism of komatiites. Therefore the variations in LREE, from depleted to enriched, are igneous, as are the HFSE depletions.
- 2) Sr and Eu were mobile. Igneous Sr/Nd varied from chondritic to enriched.

3) The TE systematics, combined with petrologic and geologic observations, suggest that BK were produced in an Archean subduction zone by the same, or very similar, melting processes that produces boninites.

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TABLES

Table 1. Whole rock compositions of Barberton komatiites containing unaltered augite

	Sample #									
	B95-11	B95-11A	B95-11B	B95-15	5-10	B95-7	B94-4	B95-13a	B95-18	B96-7
SiO ₂ (wt.%)	47.27	-	-	47.64	47.52	46.22	46.10	50.37	46.76	45.81
TiO ₂	0.29	-	-	0.27	0.23	0.25	0.25	0.41	0.26	0.22
Al ₂ O ₃	3.19	-	-	3.13	2.50	2.68	3.73	3.38	4.46	3.95
FeO*	13.14	-	-	9.79	9.89	9.44	9.93	11.27	11.02	11.60
MnO	0.21	-	-	0.20	0.19	0.17	0.17	0.22	0.20	0.24
MgO	30.99	-	-	31.58	35.12	36.33	33.54	24.26	29.62	30.54
CaO	6.06	-	-	6.51	3.37	3.55	3.80	9.51	5.21	6.12
Na ₂ O	0.00	-	-	0.00	0.03	0.00	0.13	0.04	0.28	0.17
K ₂ O	0.03	-	-	0.02	0.02	0.02	0.07	0.02	0.14	0.03
P ₂ O ₅	0.02	-	-	0.02	0.02	0.02	0.03	0.04	0.02	0.02
Sum	101.2	-	-	99.2	98.9	98.7	97.7	99.5	98.0	98.7
LOI	11.0	-	-	5.0	4.9	4.9	6.0	4.9	5.0	5.8
Mg#	0.808	0.808	0.808	0.852	0.864	0.873	0.858	0.793	0.827	0.824
CaO/Al ₂ O ₃	1.9	1.9	1.9	2.1	1.4	1.3	1.0	2.8	1.2	1.5
CaO/TiO ₂	20.6	20.6	20.6	24.4	14.5	14.3	15.4	23.5	20.4	27.3
Al ₂ O ₃ /TiO ₂	10.9	10.9	10.9	11.7	10.8	10.8	15.1	8.3	17.5	17.7
Cu (ppm)	85	82	81	71	46	31	20	106	6	22
Zn	70	71	70	58	60	53	62	48	70	67
Ni	1430	1720	1350	1560	1950	2160	1270	1060	1890	1670
Cr	2160	2530	1990	1740	1640	1740	6720	5440	2490	2710
V	124	333	114	129	95	253	133	145	362	167
Sc	14.4	11.1	11.1	12.8	10.1	6.5	12.3	22.6	9.4	14.4
Zr	22.4	22.2	22.4	19.0	12.9	12.9	16.2	36.6	15.6	10.9
Nb	1.27	1.27	1.28	1.06	0.65	0.64	0.72	2.01	0.96	0.67
Y	7.6	7.6	7.7	6.5	5.1	5.2	6.3	10.6	6.8	5.0
Sr	19.9	20.1	20.0	16.0	12.3	10.6	24.3	56.6	36.4	32.7
Rb	1.3	1.3	1.2	0.9	1.1	1.5	5.6	0.5	5.2	0.7
Cs	0.59	0.60	0.59	0.56	0.63	0.94	1.76	0.12	3.57	0.35
Ba	15.8	15.8	15.7	16.7	6.6	9.9	1.8	93.5	7.5	8.4
Pb	0.52	0.53	0.55	0.41	0.24	0.22	0.36	0.55	0.36	0.17
Th	0.13	0.13	0.13	0.12	0.05	0.06	0.09	0.23	0.08	0.05
U	0.03	0.03	0.03	0.02	0.01	0.01	0.02	0.05	0.02	0.01
Ti	1740	1770	1750	1610	1400	1500	1510	2440	1560	1360
Ta	0.08	0.08	0.08	0.07	0.04	0.04	0.04	0.13	0.06	0.04
Hf	0.57	0.58	0.58	0.49	0.35	0.35	0.43	0.94	0.41	0.30
La	1.42	1.46	1.45	1.49	0.72	0.80	0.87	2.01	1.17	0.73
Ce	3.79	3.89	3.88	3.69	1.96	2.06	2.22	5.80	2.99	1.93
Pr	0.59	0.61	0.61	0.58	0.34	0.33	0.33	0.92	0.43	0.29

Table 1(cont.).

	Sample #									
	B95-11	B95-11A	B95-11B	B95-15	5-10	B95-7	B94-4	B95-13a	B95-18	B96-7
Nd	2.94	3.02	3.01	2.78	1.79	1.76	1.56	4.53	2.06	1.46
Sm	0.89	0.89	0.90	0.80	0.57	0.55	0.50	1.35	0.62	0.46
Eu	0.29	0.29	0.29	0.28	0.21	0.21	0.18	0.56	0.23	0.16
Gd	1.02	1.05	1.04	0.95	0.68	0.68	0.65	1.72	0.77	0.59
Tb	0.19	0.19	0.19	0.16	0.12	0.12	0.14	0.28	0.14	0.11
Dy	1.18	1.20	1.21	1.05	0.81	0.79	0.94	1.75	1.00	0.78
Ho	0.25	0.25	0.26	0.22	0.17	0.17	0.20	0.37	0.22	0.17
Er	0.72	0.73	0.73	0.63	0.48	0.48	0.62	1.04	0.65	0.50
Tm	0.10	0.11	0.11	0.09	0.07	0.07	0.09	0.16	0.10	0.07
Yb	0.64	0.66	0.66	0.58	0.44	0.41	0.56	0.97	0.62	0.47
Lu	0.09	0.10	0.10	0.08	0.06	0.06	0.08	0.14	0.09	0.07
(La/Sm)n	0.98	1.02	1.00	1.15	0.77	0.89	1.08	0.92	1.17	0.97
(Gd/Yb)n	1.27	1.27	1.27	1.32	1.24	1.32	0.93	1.43	1.00	1.01
(La/Yb)n	1.48	1.49	1.48	1.74	1.09	1.30	1.04	1.40	1.28	1.04
(Sm/Yb)n	1.50	1.45	1.47	1.51	1.40	1.44	0.96	1.52	1.09	1.06
Zr/Zr*	0.93	0.92	0.92	0.86	0.86	0.88	1.24	1.00	0.93	0.89
Hf/Hf*	0.89	0.89	0.89	0.83	0.88	0.89	1.23	0.95	0.93	0.91
Ti/Ti*	0.70	0.71	0.70	0.71	0.86	0.94	1.02	0.62	0.87	1.00
Ti/Zr	77.9	79.8	78.5	85.0	109.2	116.8	93.4	66.7	100.0	124.2

B95-11 was run in triplicate. A and B are duplicate analyses of same dissolution. First analysis is a separate dissolution.

FeO* - all Fe calculated as FeO

(La/Sm)n - chondrite normalized ratio (CI composition from McDonough and Sun)

Zr/Zr*, Hf/Hf*, Ti/Ti* - ratio of chondrite normalized Zr, Hf, Ti to the expected value based upon the concentrations of the nearest neighbors in the spidergram. Order of elements from Sun and McDonough.

Table 2. Individual ion probe analyses of igneous augite in Barberton komatiites

Sample	B95-11															
	xal	1	1	1	1	1	2	2	2	2	2	2	3	3	4	met.
location	core	core	rim	rim	base	rim	core	core	base	rim	rim/tip	int.	core	int.	int.	met.
La (ppm)	0.153	0.176	0.200	0.248	0.126	0.446	0.197	0.165	0.099	0.088	0.205	-	0.122	0.238	0.218	0.234
Ce	0.608	0.753	0.777	0.808	0.579	1.189	0.676	0.618	0.452	0.418	0.704	-	0.394	0.954	0.671	0.557
Nd	0.924	0.992	1.033	0.944	0.887	1.216	0.760	0.780	0.625	0.758	0.852	-	0.581	1.298	0.976	0.417
Sm	0.440	0.448	0.476	0.574	0.430	0.499	0.328	0.407	0.338	0.400	0.415	-	0.261	0.774	0.576	0.203
Eu	0.222	0.232	0.248	0.213	0.165	0.275	0.166	0.188	0.149	0.158	0.196	-	0.117	0.265	0.195	0.169
Dy	0.850	0.858	0.752	0.832	0.713	0.661	0.584	0.749	0.417	0.607	0.662	-	0.418	0.915	0.656	0.196
Er	0.507	0.472	0.429	0.476	0.418	0.576	0.347	0.432	0.333	0.357	0.403	-	0.312	0.492	0.471	0.158
Yb	0.450	0.447	0.433	0.477	0.432	0.430	0.342	0.451	0.368	0.444	0.462	-	0.275	0.417	0.624	0.166
Ti	-	1234	-	956	-	-	-	1166	962	-	-	1212	1053	1023	879	-
V	-	194	-	1560	-	-	-	194	144	-	-	197	1652	148	112	-
Cr	-	5493	-	4294	-	-	-	4674	2175	-	-	4918	4970	2986	2374	-
Sr	-	8.8	-	8.6	-	-	-	10.1	9.2	-	-	8.3	10.8	8.0	4.3	-
Y	-	4.5	-	3.8	-	-	-	4.3	4.0	-	-	4.2	3.4	2.9	1.8	-
Zr	-	5.4	-	7.2	-	-	-	4.3	2.3	-	-	3.2	5.4	2.9	4.4	-

Table 2 (cont.).[illegible]

Table 2 (cont.).

Sample	5-10														
xal	1	1	1	2	2	3	3	3	3	3	4	5	5	met.	met.
location	core	core	tip	int.	int.	int.	int.	int.	int.	core	int.	base	tip		
La (ppm)	0.159	0.080	0.068	0.102	0.094	0.094	0.190	0.094	0.070	0.030	0.092	0.041	0.119	6.675	0.793
Ce	0.342	0.256	0.264	0.565	0.385	0.465	0.864	0.490	0.347	0.155	0.452	0.115	0.598	17.7	1.783
Nd	0.342	0.365	0.440	0.999	0.647	0.868	1.418	0.750	0.656	0.359	0.664	0.201	0.945	12.1	1.325
Sm	0.161	0.257	0.248	0.526	0.342	0.447	0.792	0.538	0.383	0.197	0.483	0.145	0.490	4.327	0.682
Eu	0.079	0.074	0.131	0.229	0.182	0.197	0.384	0.217	0.132	0.108	0.162	0.068	0.255	0.964	0.228
Dy	0.245	0.367	0.466	1.077	0.808	0.879	1.426	0.769	0.591	0.455	0.748	0.172	0.997	3.666	0.763
Er	0.173	0.235	0.308	0.569	0.484	0.515	0.891	0.440	0.331	0.335	0.420	0.130	0.776	1.888	0.534
Yb	0.173	0.242	0.349	0.533	0.545	0.543	0.887	0.434	0.365	0.342	0.433	0.132	0.609	2.138	0.581
Ti	-	-	-	-	-	962	1184	931	928	691	-	-	-	-	-
V	-	-	-	-	-	140	169	135	135	86	-	-	-	-	-
Cr	-	-	-	-	-	2613	418	3744	2848	2454	-	-	-	-	-
Sr	-	-	-	-	-	9.2	7.1	12.5	9.5	5.6	-	-	-	-	-
Y	-	-	-	-	-	5.4	6.5	5.2	4.2	6.9	-	-	-	-	-
Zr	-	-	-	-	-	4.6	6.4	4.6	5.3	5.1	-	-	-	-	-

Table 2 (cont.).

Sample	B95-7		B94-4		B94-52			13-3						
xal location	a rim	b core	a core	b int.	c core	a core	b core	c rim	1 core	1 core	2 core	3 rim	3 int.	4 core
La (ppm)	0.317	0.157	0.143	0.248	0.042	0.198	0.132	0.233	0.737	0.309	0.262	0.883	0.800	0.333
Ce	1.046	0.687	0.580	0.733	0.237	0.683	0.538	0.723	1.620	0.882	0.390	1.967	2.043	0.744
Nd	1.035	0.822	0.980	0.820	0.311	1.366	1.006	1.338	0.743	0.277	0.158	1.031	1.011	0.457
Sm	0.541	0.529	0.622	0.443	0.256	0.902	0.901	0.984	0.130	0.095	0.037	0.373	0.416	0.129
Eu	0.208	0.231	0.135	0.111	0.099	0.406	0.259	0.415	0.165	0.050	0.067	0.155	0.165	0.127
Dy	0.698	0.781	1.062	0.824	0.405	1.668	1.310	1.447	0.275	0.213	0.102	0.417	0.296	0.201
Er	0.483	0.404	0.683	0.634	0.324	0.784	0.687	0.754	0.141	0.122	0.052	0.177	0.250	0.077
Yb	0.459	0.486	0.563	0.630	0.380	0.749	0.628	0.763	0.216	0.169	0.058	0.185	0.337	0.098
Ti	1077	1266	1272	983	593	2035	2522	2153	-	-	-	235	-	165
V	172	220	242	191	107	258	330	276	-	-	-	56	-	78
Cr	6298	6756	2367	1648	3397	5258	5520	6584	-	-	-	3220	-	2921
Sr	9.5	9.3	5.2	5.8	2.3	7.4	58.1	7.8	-	-	-	13.0	-	8.8
Y	4.2	4.2	6.3	4.5	2.2	6.7	7.9	7.3	-	-	-	2.3	-	0.7
Zr	4.2	6.6	5.0	3.0	0.8	7.6	9.4	5.4	-	-	-	4.2	-	4.5

Table 2(cont.).

Sample	2-15a							
xal	1	1	1	2	2	2	2	3
location	core	tip	base	tip	base	int.	int.	core
La (ppm)	0.185	0.360	0.410	0.358	0.166	0.308	0.183	0.214
Ce	0.895	1.169	1.106	1.217	0.839	0.847	0.876	0.708
Nd	0.870	0.830	1.088	1.630	0.867	1.478	0.823	1.045
Sm	0.615	0.544	0.479	0.707	0.332	0.636	0.516	0.536
Eu	0.193	0.207	0.266	0.439	0.157	0.322	0.244	0.169
Dy	0.805	0.870	0.756	1.244	0.441	0.992	0.895	0.858
Er	0.627	0.361	0.360	1.115	0.400	0.665	0.456	0.441
Yb	0.521	0.567	0.281	0.450	0.243	0.610	0.459	0.429
Ti	-	-	-	-	-	850	-	932
V	-	-	-	-	-	123	-	136
Cr	-	-	-	-	-	3108	-	3802
Sr	-	-	-	-	-	8.7	-	9.1
Y	-	-	-	-	-	3.5	-	4.1
Zr	-	-	-	-	-	2.5	-	2.6

FIGURE CAPTIONS

Figure 1. Stratigraphic column of the Upper and Lower Komati Fm., Onverwacht Group, Barberton Greenstone belt, South Africa, after Dann (2000). The five olivine spinifex horizons in the Lower Komati are numbered on the left side of the column, along with the stratigraphic thickness in km. Faults running vertically through the section separate areas of the Lower Komati that have different stratigraphies. Sample locations are labeled in bold letters.

Figure 2. a) Secondary electron image (SEI) of augite (Table 2, grain 3) from sample 5-10, showing that analyses contained <5% metamorphic veins. Nearly 100% of this crystal has been preserved. Large pits are REE analyses and small pits are TE analyses (Ti, Zr, V, Cr, Sr, Y). Light material around augite and filling veins is a microcrystalline mixture of chlorite and serpentine. Slightly darker material overgrowing augite is tremolite. Black material is magnetite. Note that black and white in the image have been reversed. Image is ~800 microns across. b) SEI image of augite (table 2, grain 1) in sample B95-11. Much of the rim of this crystal has been altered to serpentine+chlorite+magnetite. Image is 1600 microns across.

Figure 3. TE spidergram of BK whole rock analyses. TE concentrations are normalized to CI chondrite composition of McDonough and Sun [*McDonough and Sun*, 1995], and ordered according to their apparent partitioning in MORB [*Sun and McDonough*, 1989]. Mg# of the samples is given in the last column and correlates well with overall TE

concentrations. All samples except B94-4 are depleted in Ti, Zr, Hf, and Nb. B94-4 belongs to an unusual group of komatiites with slightly U-shaped REE patterns and positive Zr and Hf, that are found in many komatiite sequences (see text). Samples which contain augite that were analyzed by ion probe are shown with solid symbols and thick lines. Analytical errors for TE are 2%, relative, and error bars are shown for sample B95-11. This sample was analyzed in triplicate, and all analyses are within error of each other.

Figure 4. Chondrite normalized REE composition (thin solid lines) of augite in samples a) B95-11, b) B95-15, c) 5-10, and d) B95-7 and B94-4. Bold lines show composition of augite calculated to be in equilibrium with their respective whole rock compositions. The shape of the augite cores' REE patterns are well matched by the calculated augite patterns. Precision of the analyses and calculated augite are shown by 10% error bars.

Figure 5. La/Sm versus La in BK augites. Lines connect analyses from a single crystal and arrows show direction from core to rim. Open circles are metamorphic mineral analyses, and large filled square is the composition of the augite calculated to be in equilibrium with a BK magma represented by the whole rock TE composition. Hatched line shows Rayleigh fractionation path using D values of Hart and Dunn [*Hart and Dunn*, 1993]. Each hatch represents 10% crystallization. For samples B95-11, B95-15, and 5-10, core compositions are comparable to calculated augite composition and imply little mobility during metamorphism. Samples B95-7 and B94-4 have too few analyses to be conclusive about the effects of metamorphism. Zoning in the augites is not matched by Rayleigh fractionation. The extent of fractionation between La and Sm appears to correlate with crystal morphology and implies that kinetics has effected the partition

coefficients of the REE. Similar systematics are seen for all REE. Error bars for all points are smaller than the square symbol.

Figure 6. Ti/Sm versus Sm in BK augites. Symbols are the same as in Figure 5. The augite calculated to be in equilibrium with the whole rock composition and the analyses of the augite cores in the samples are within error of each other, indicating that Ti and Sm have been immobile during metamorphism. Error bars shown on square is representative of all points shown.

Figure 7. Sr/Nd versus Nd in BK augite. Symbols are the same as in Figure 5. Calculated core compositions are all significantly lower than the analyses of the augite cores, and indicates that Sr has been lost from the samples. Error bars shown on square is representative of all points shown.

Figure 8. Y/Er versus Er in BK augite. Symbols are the same as in Figure 5. Y was immobile in samples B95-11 and 5-10. Error bars shown on square is representative of all points shown.

Figure 9. Cr/Ti versus Ti in BK augites. Symbols are the same as in Figure 5. Cr in the calculated augite cannot be calculated as it is sensitive to both pyroxene and spinel crystallization. The Cr-Ti zoning varies widely and cannot be fit by any equilibrium fractionation model. Similar zoning has been observed in previous studies of TE zoning in igneous cpx [Shimizu, 1981; Shimizu and le Roex, 1986; Vannucci *et al.*, 1993]. Errors are 5% relative on Ti and Cr analyses.

Figure 10. Compilation of experimentally determined TE mineral/melt partition coefficients (D) for majorite garnet [*Kato et al.*, 1988a; *Kato et al.*, 1988b; *Ohtani et al.*, 1989; *Yurimoto and Ohtani*, 1992]. For all studies except Kato [*Kato et al.*, 1988a], the D values of Zr, Hf, and Ti are within error of each other.

Figure 11. Ti/Zr versus La/Sm in Barberton komatiite chill margins (filled circles) and basaltic komatiites (open circles, Dann, unpublished data). Filled squares indicate composition of depleted and undepleted mantle [*Hart and Zindler*, 1986; *Kinzler and Grove*, 1992]. Grids indicate compositions of melts produced by 20 to 100% melting using the range of published majorite/melt D values. The range of Ti/Zr fractionation seen in Barberton samples cannot be reproduced by high degree melting in the presence of majorite garnet. Representative boninite compositions are outlined by gray field. Data from Hickey and Frey (1982). The trend seen in the komatiite and boninite series rocks are very similar.

FIGURES

Figure 1

Komati Formation
 thickness: ~ 3-3.5 km
 age: ~3.48 Ga

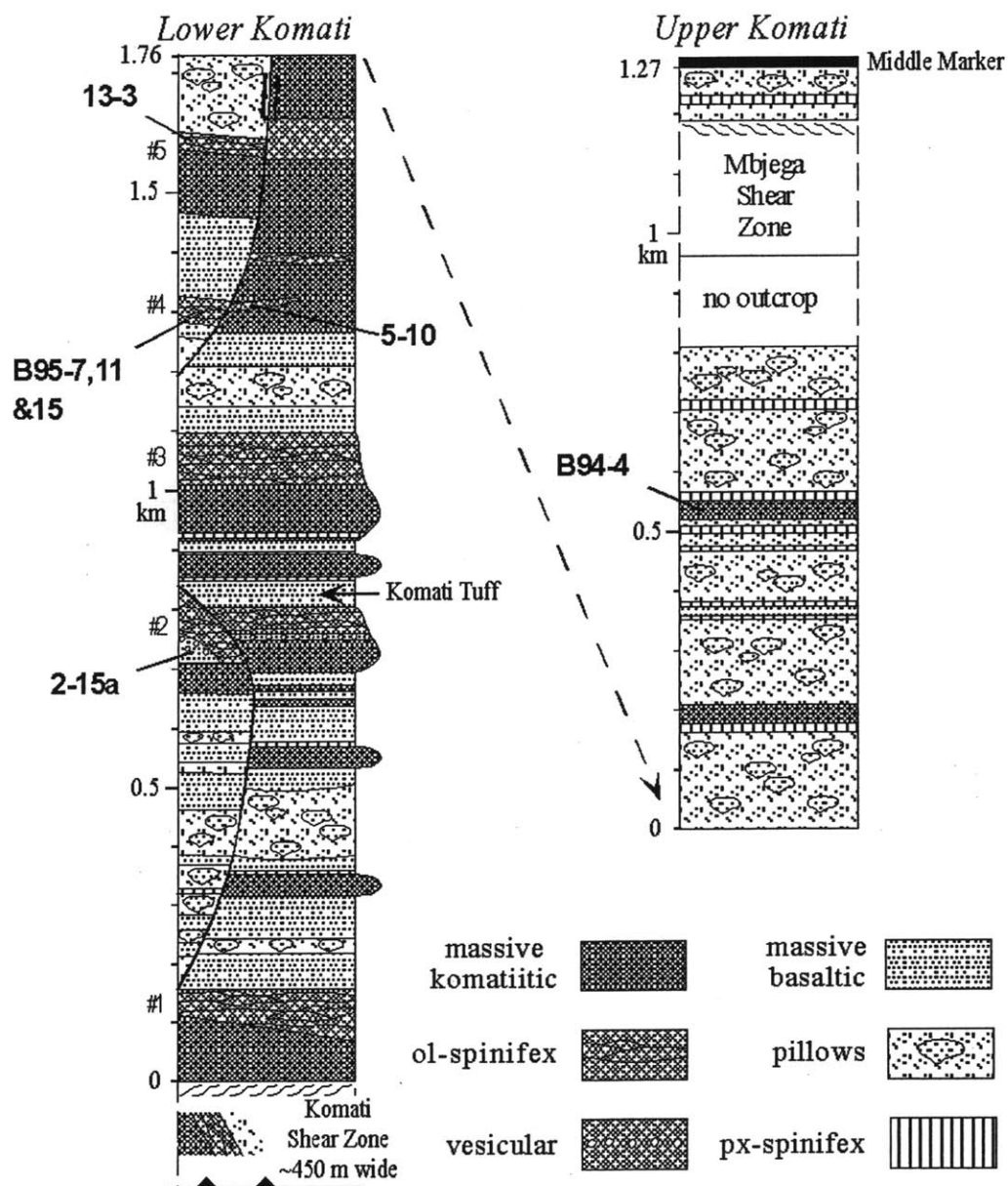


Figure 2a

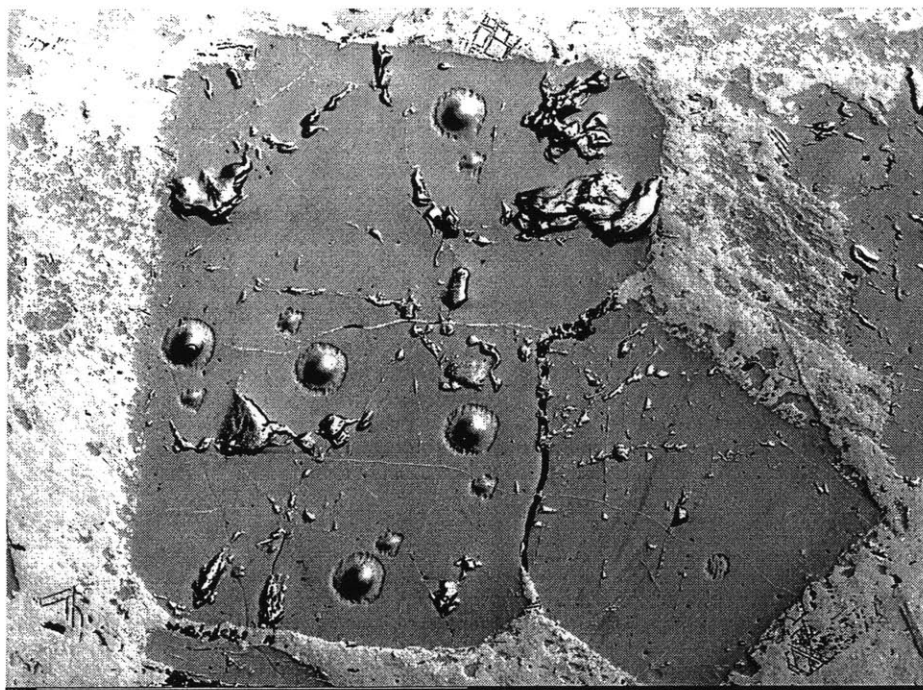


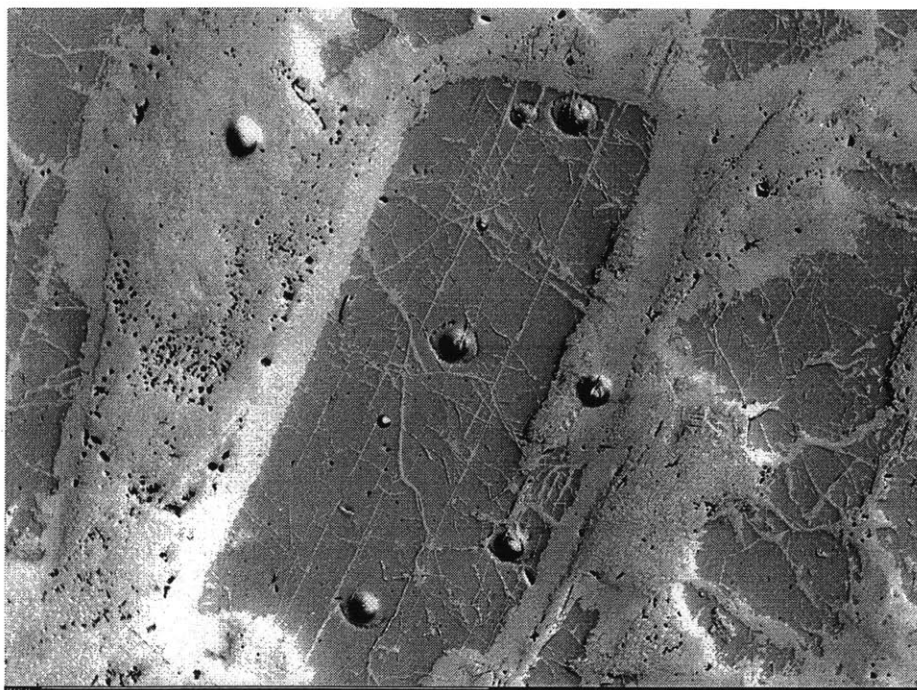
Figure 2b

Figure 3

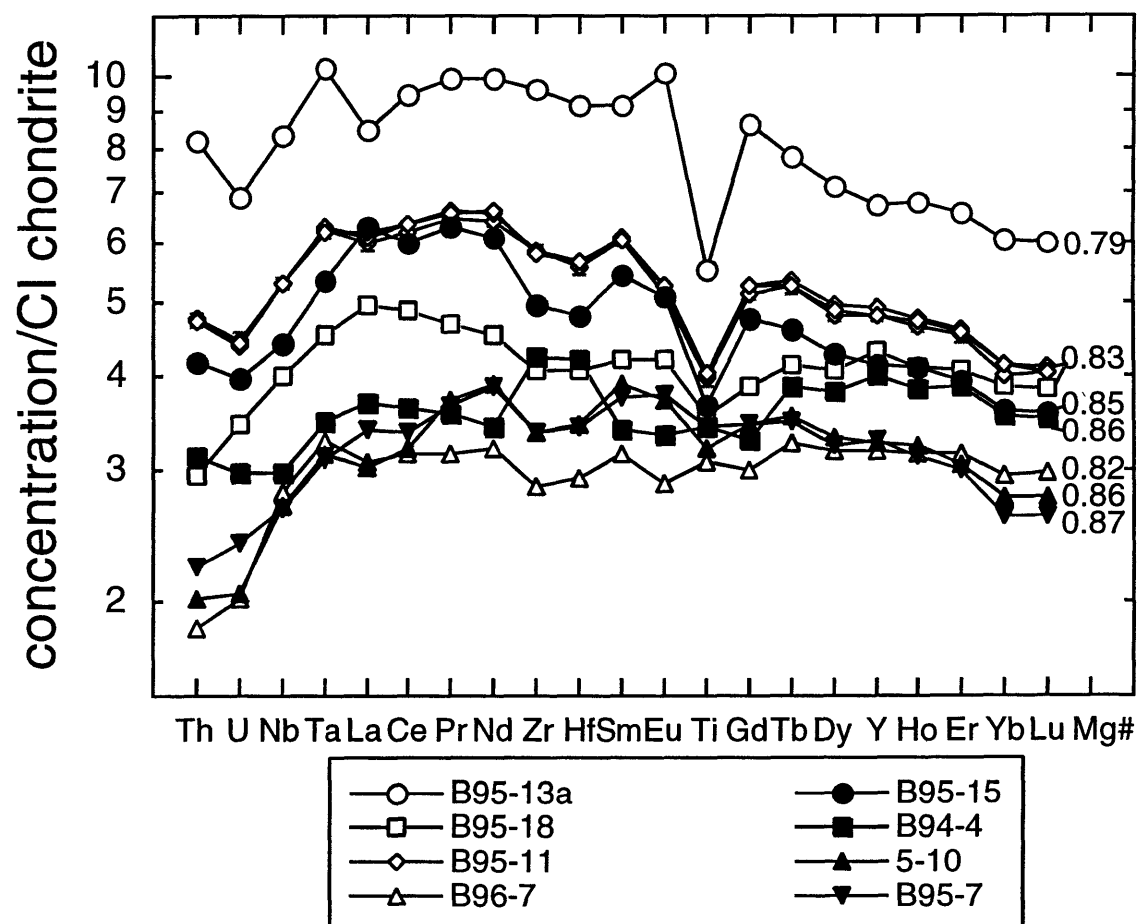


Figure 4

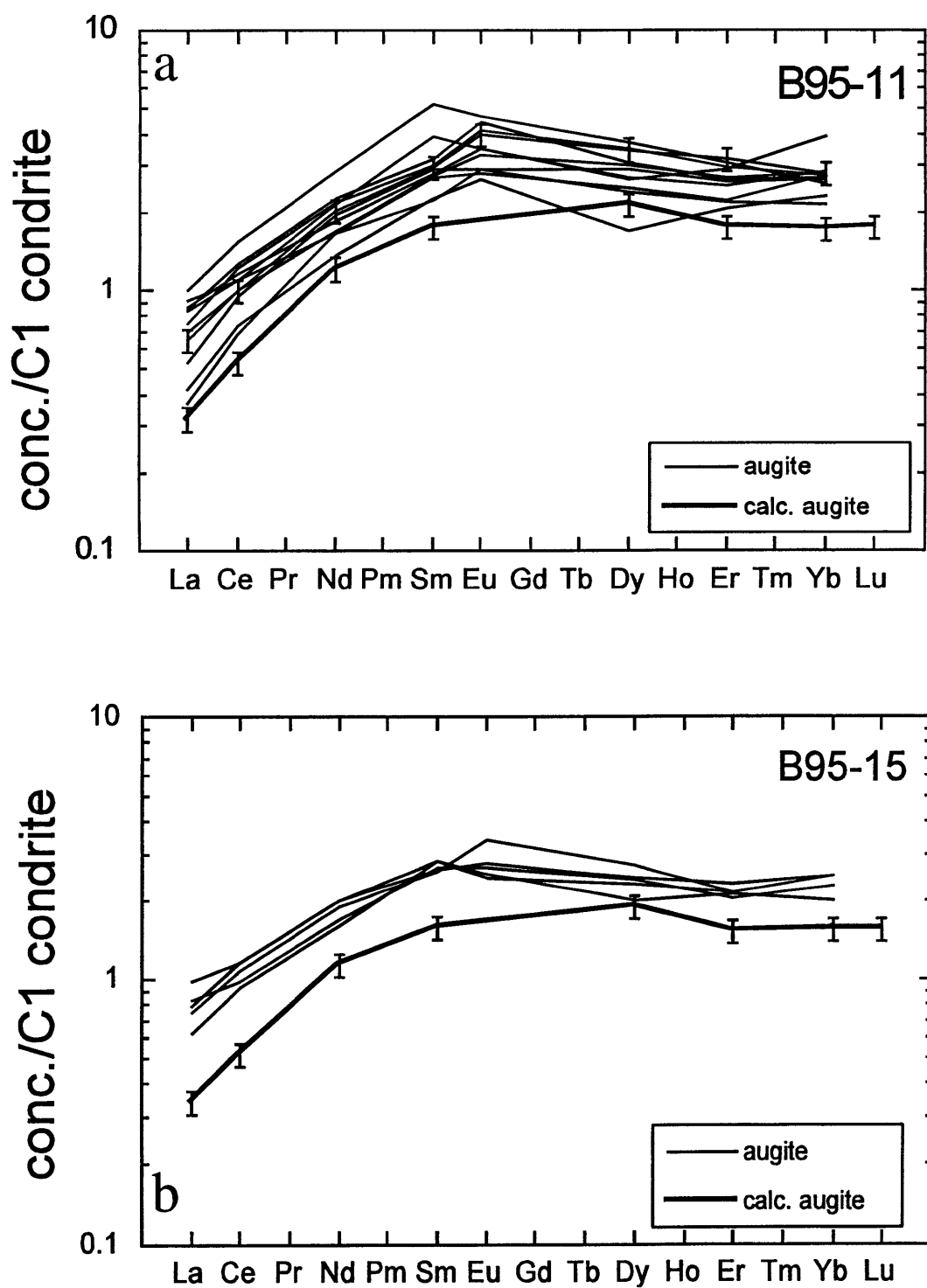


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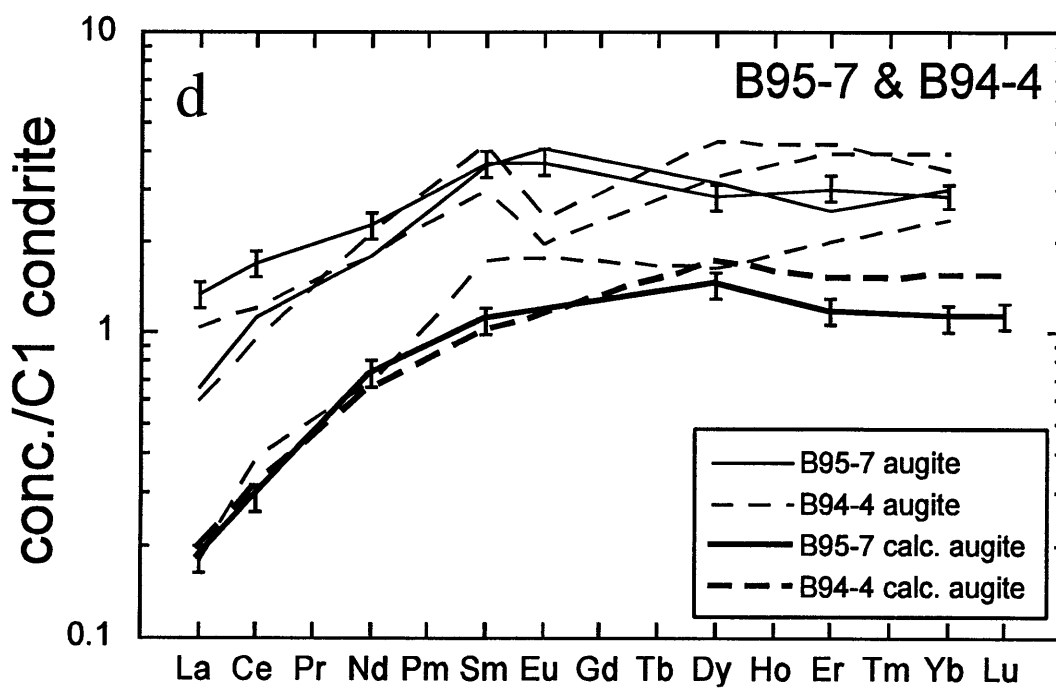
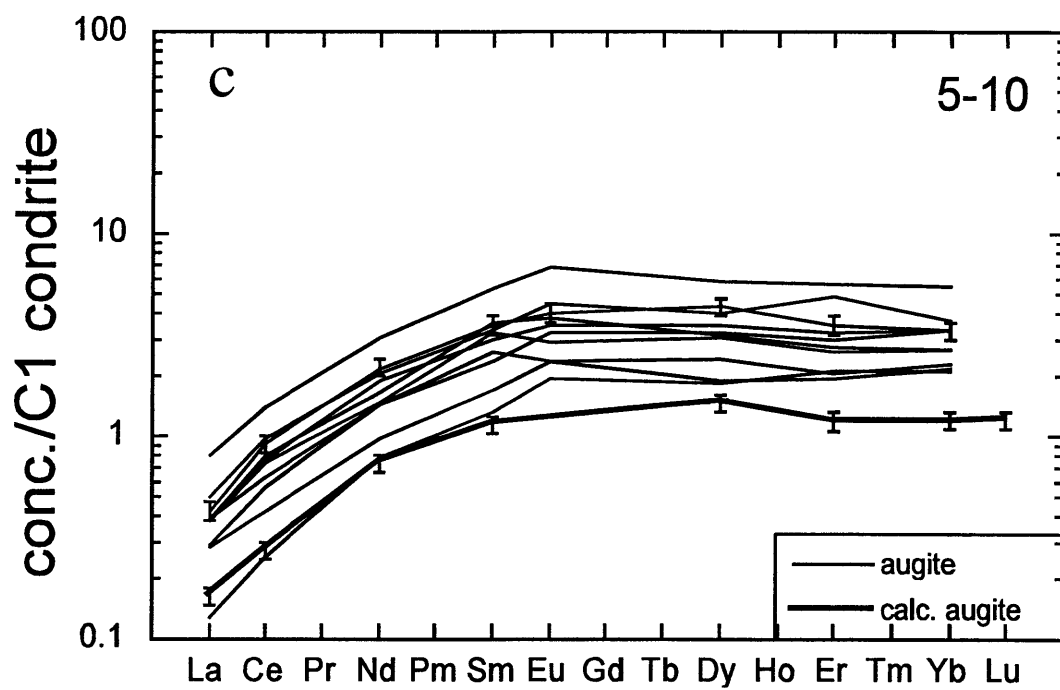


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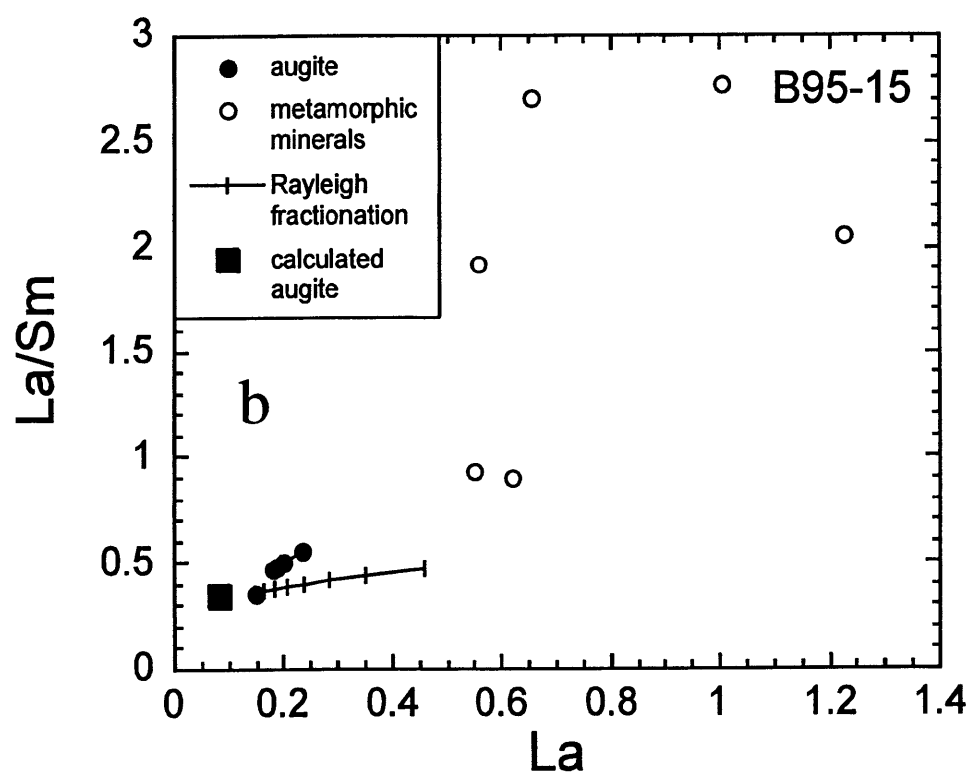
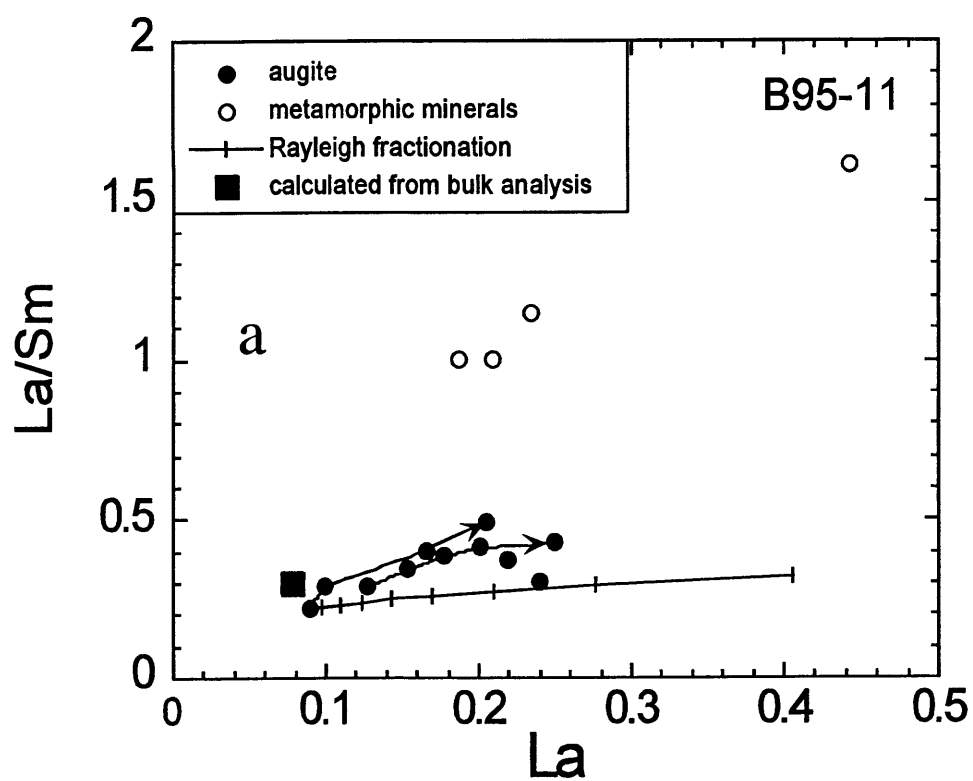


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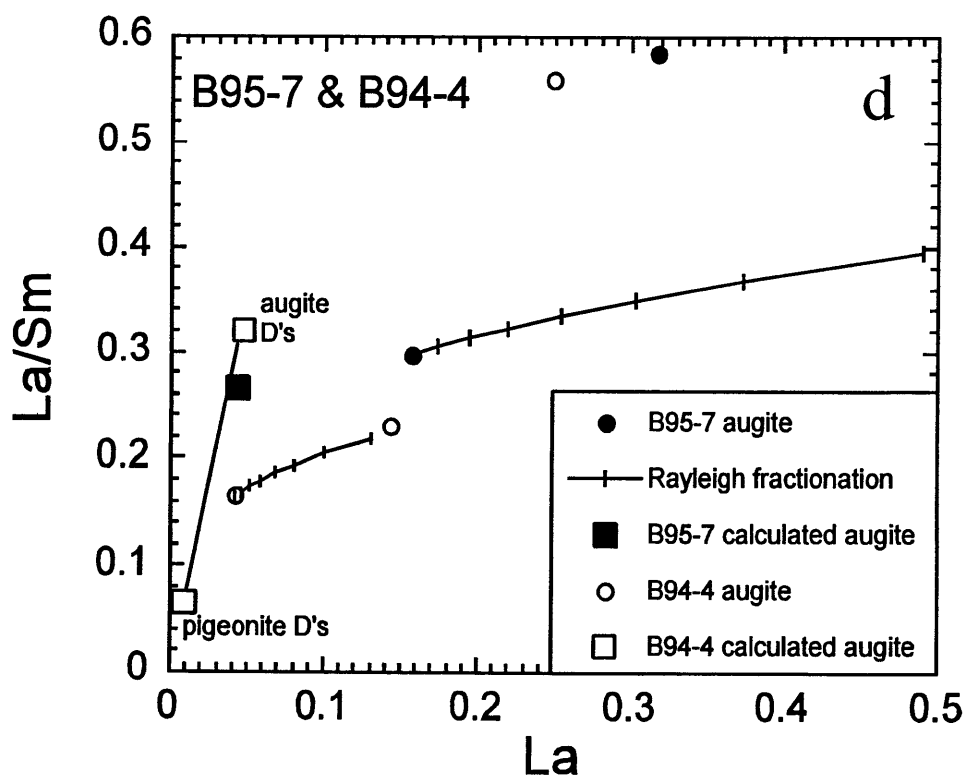
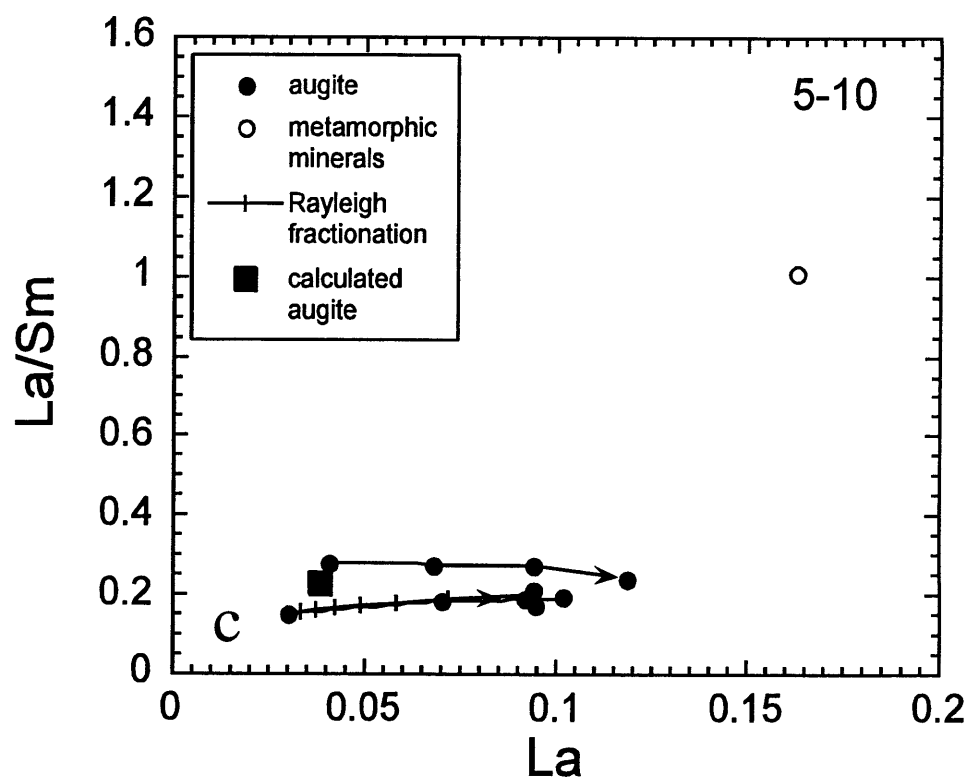


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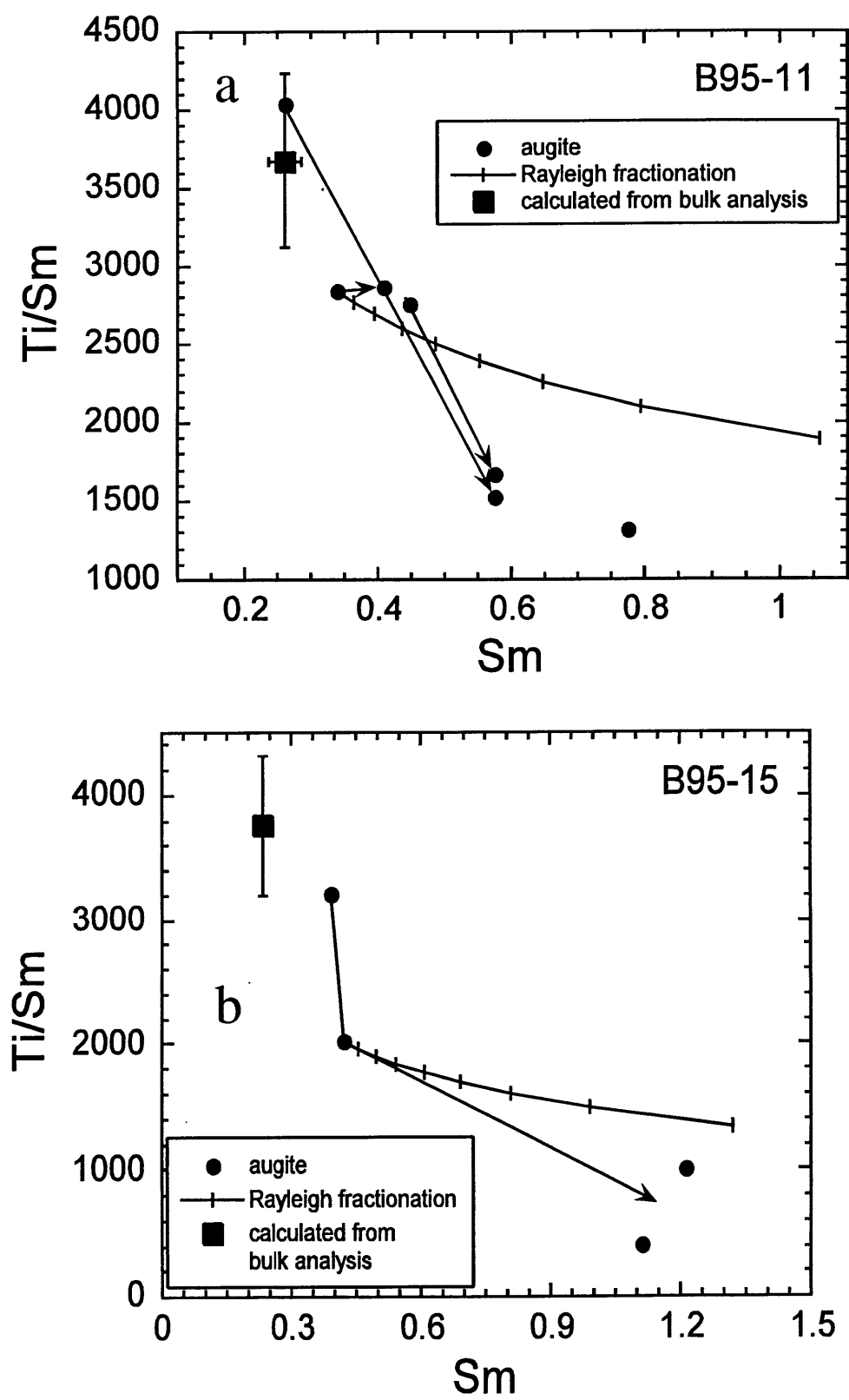


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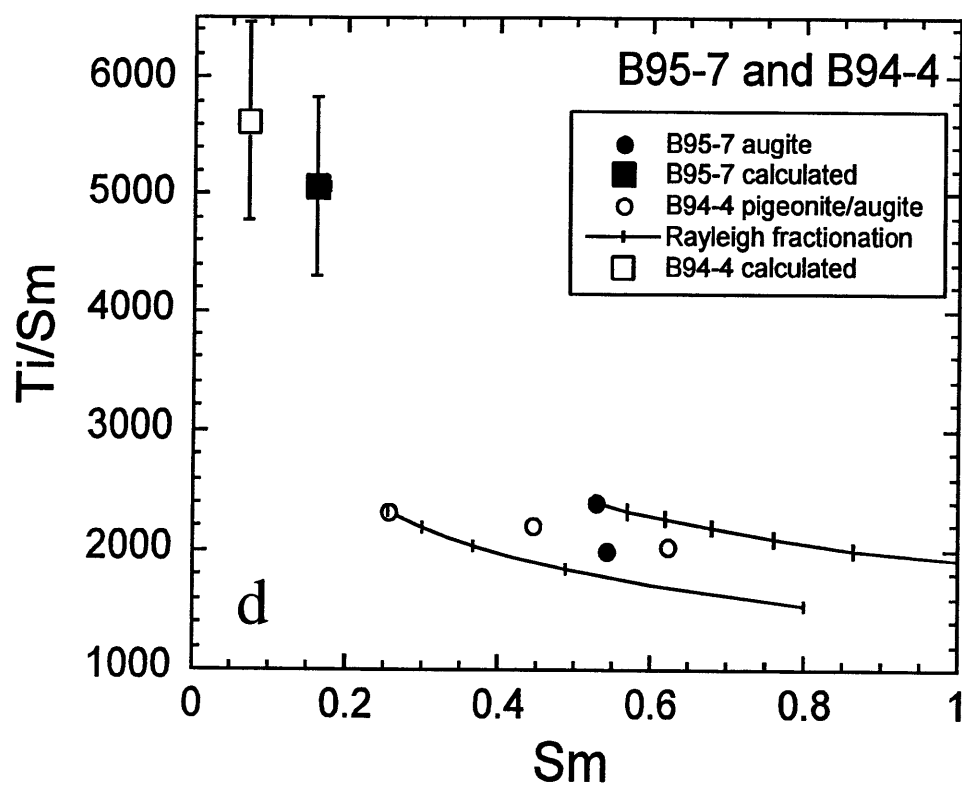
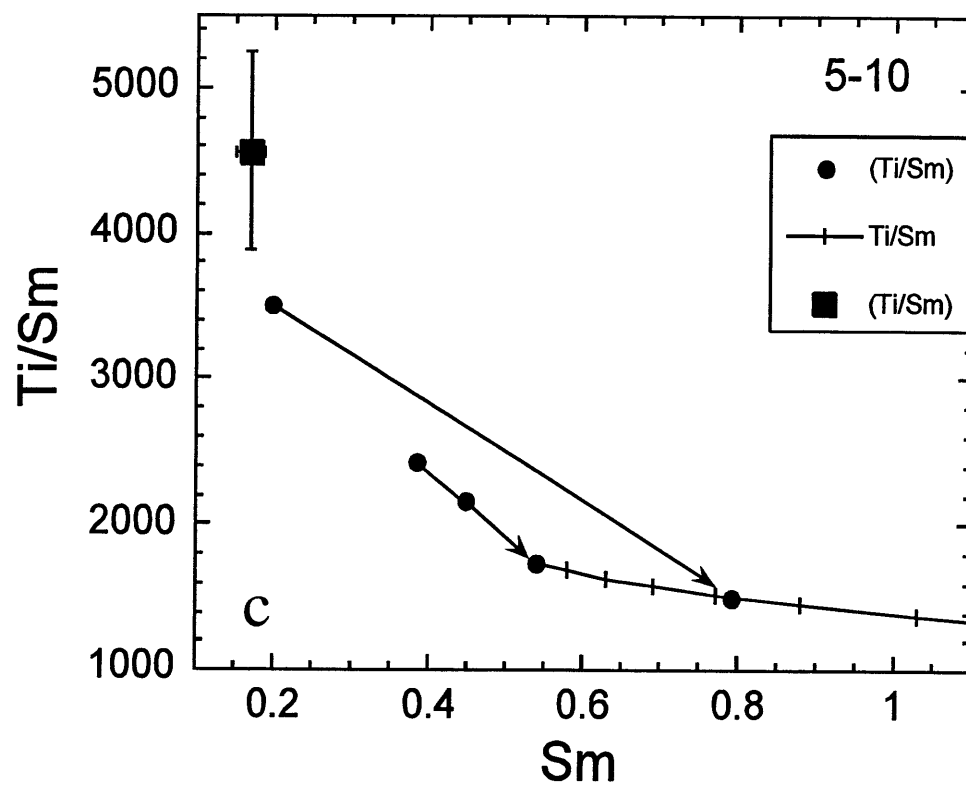


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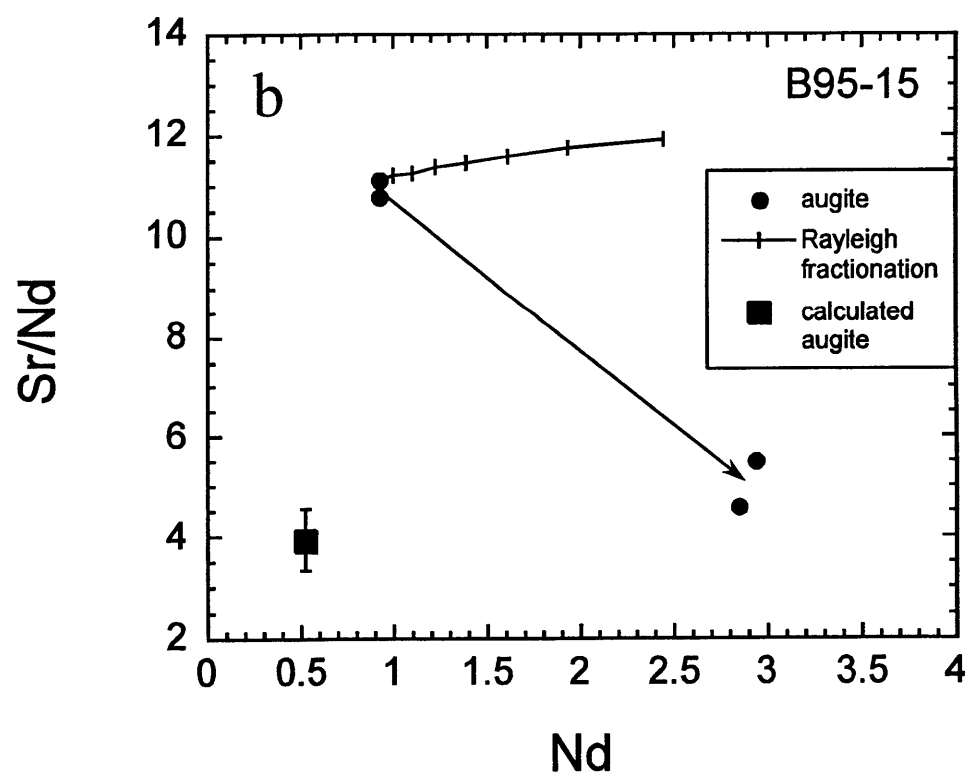
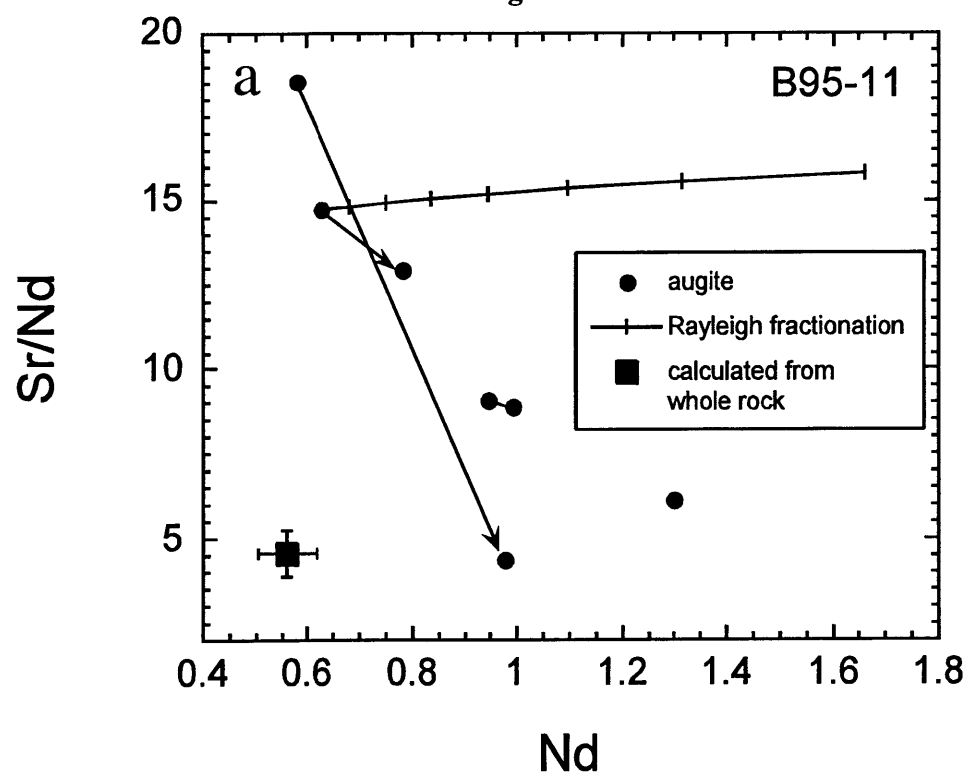


Figure 7(cont.)

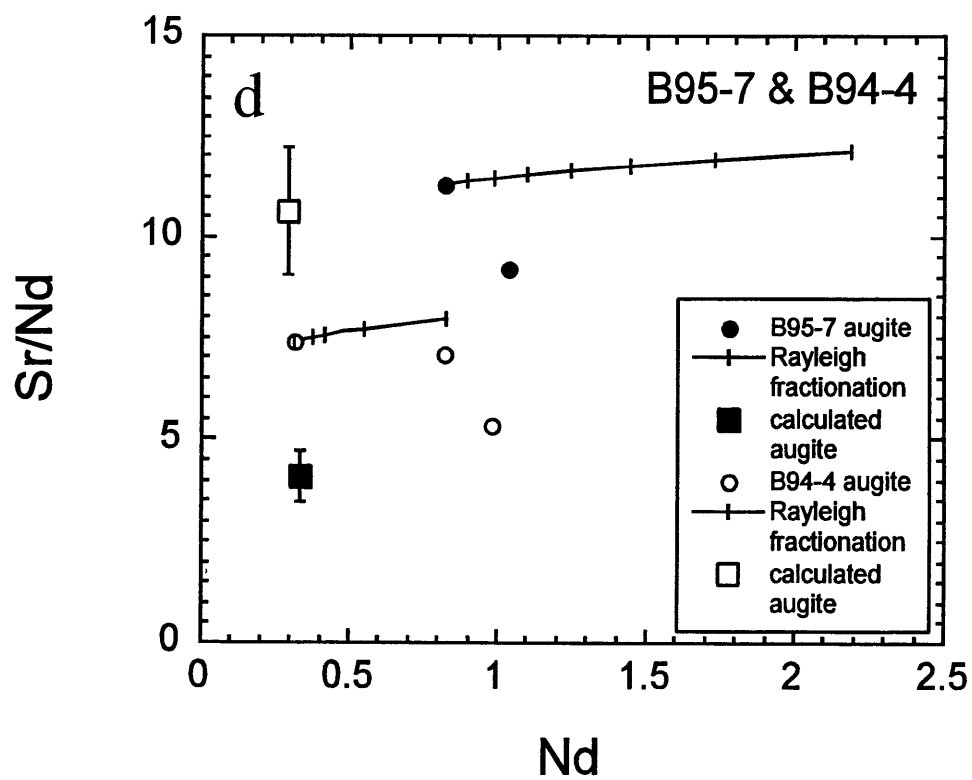
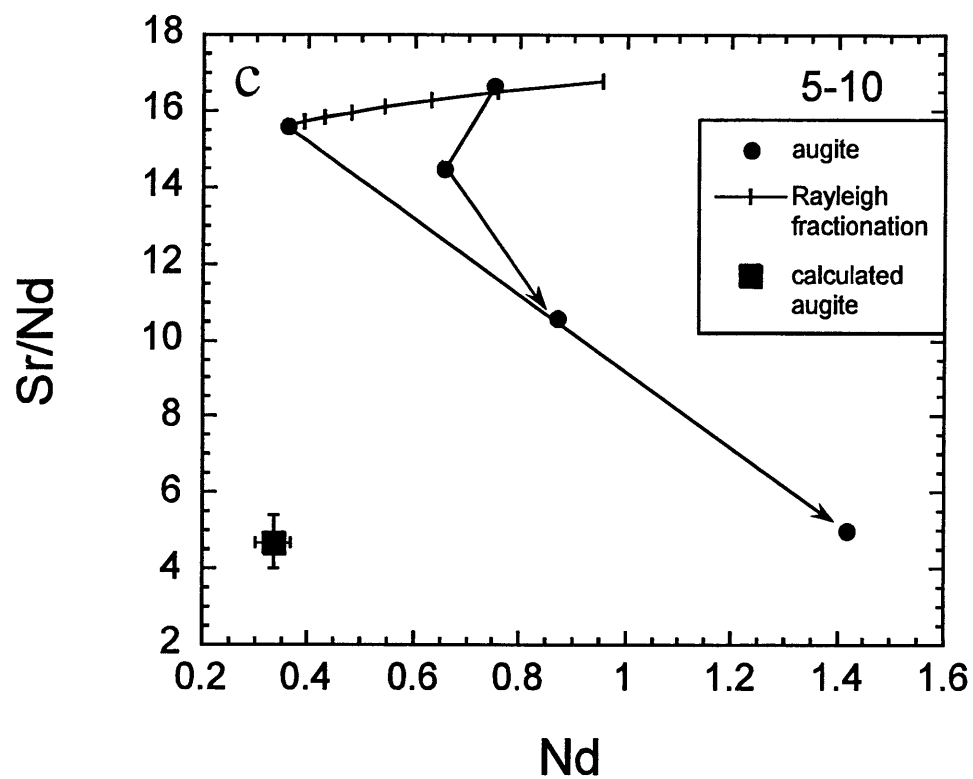


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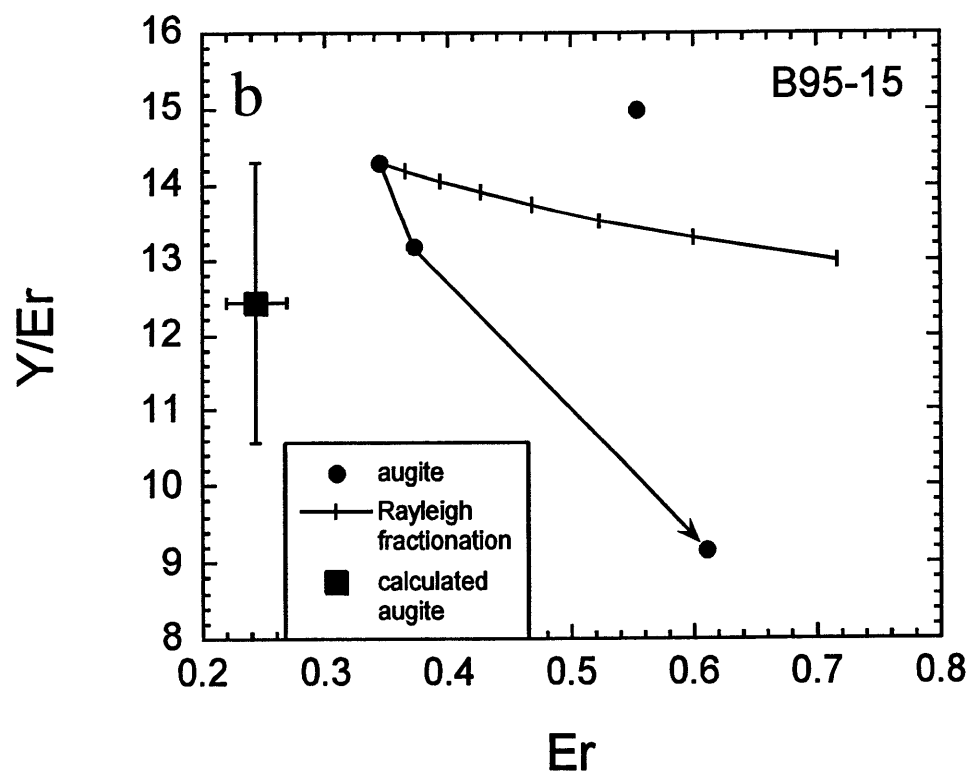
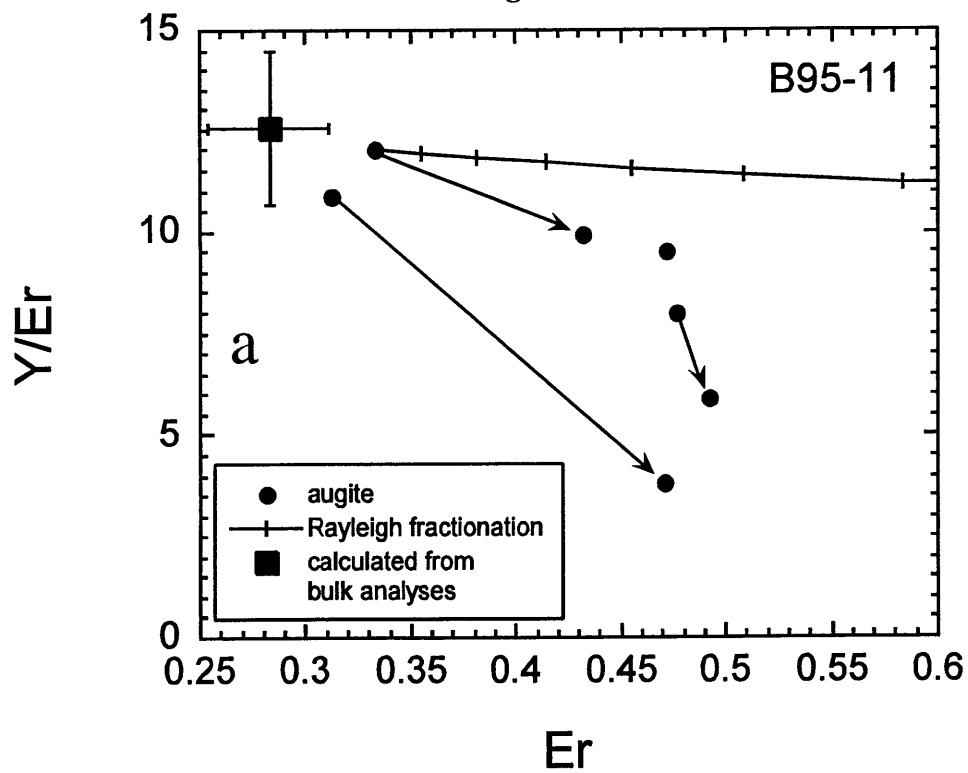


Figure 8(cont.)

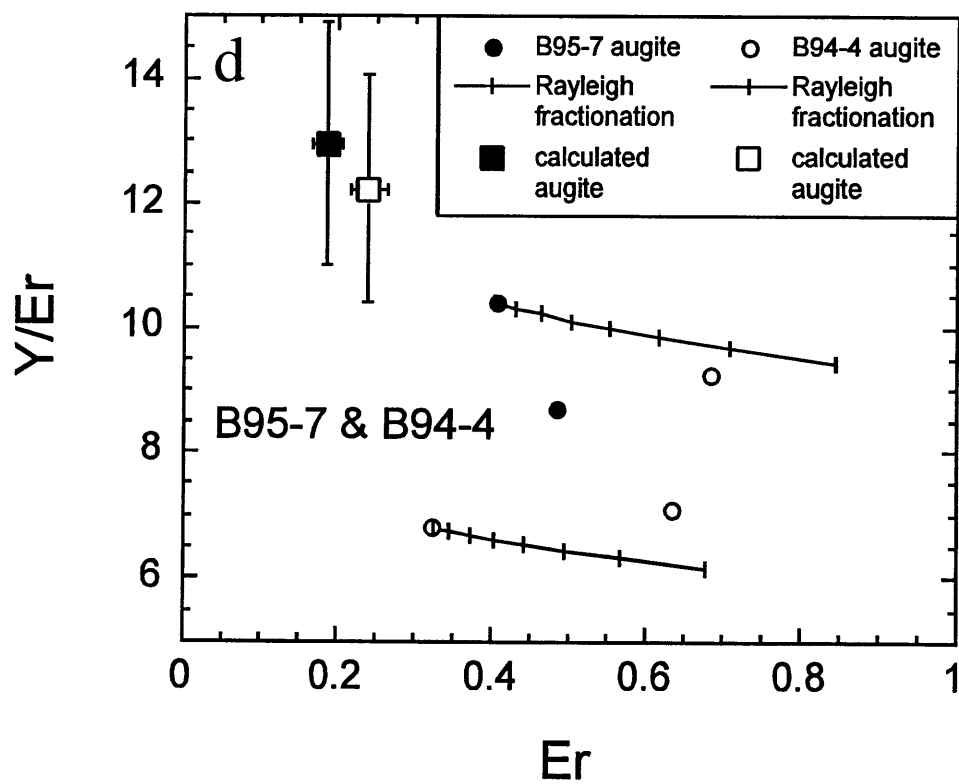
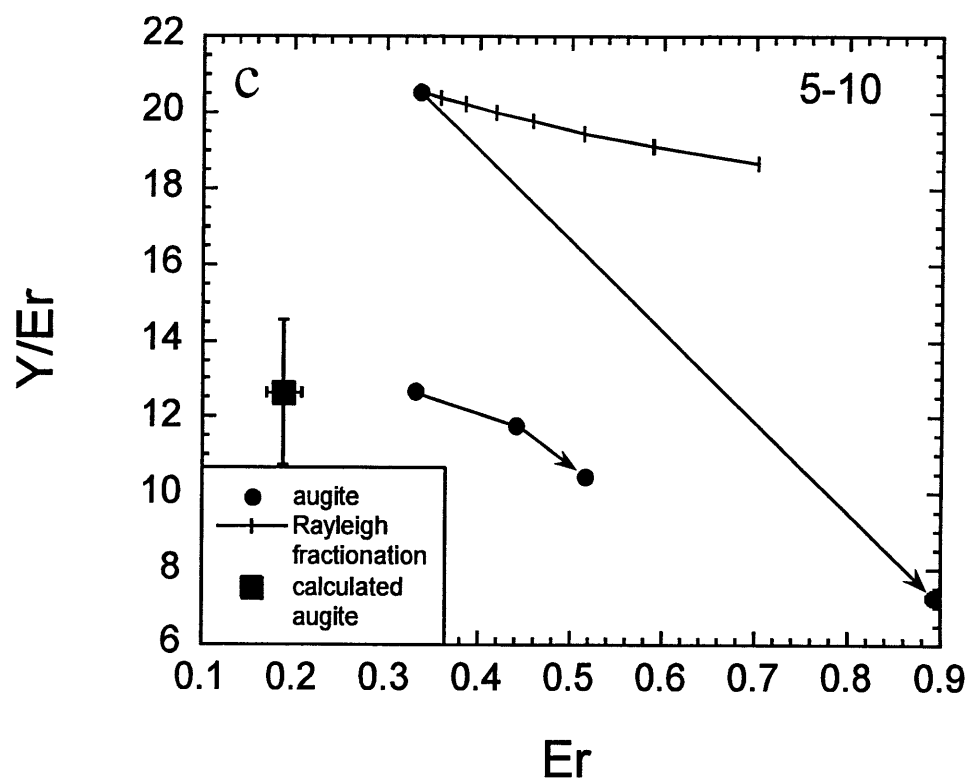


Figure 9

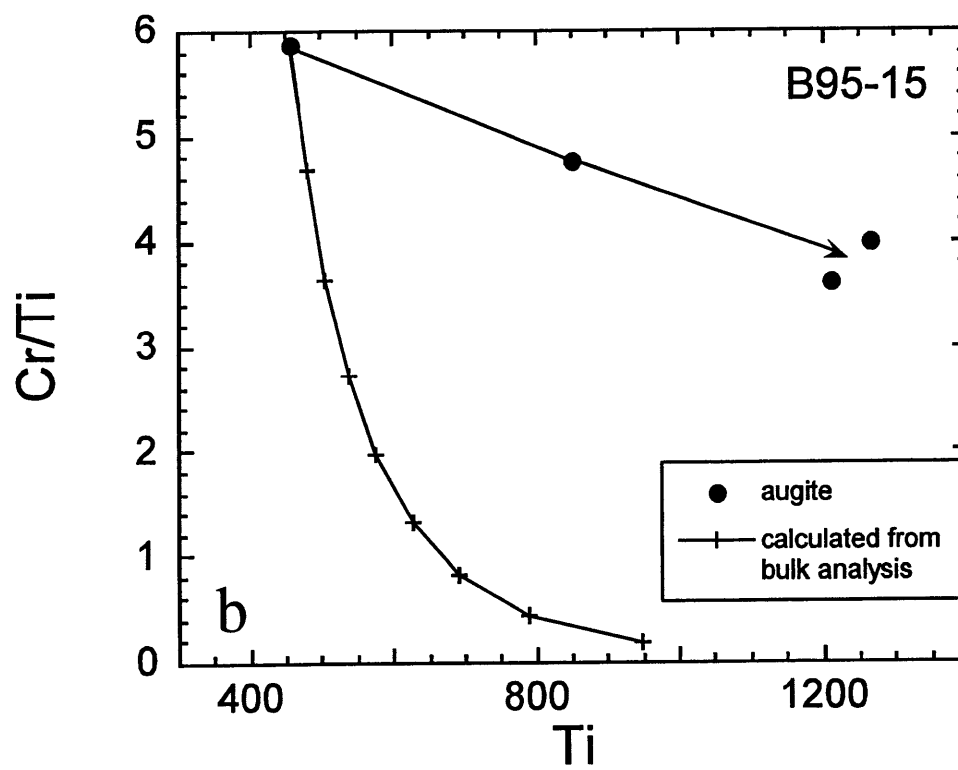
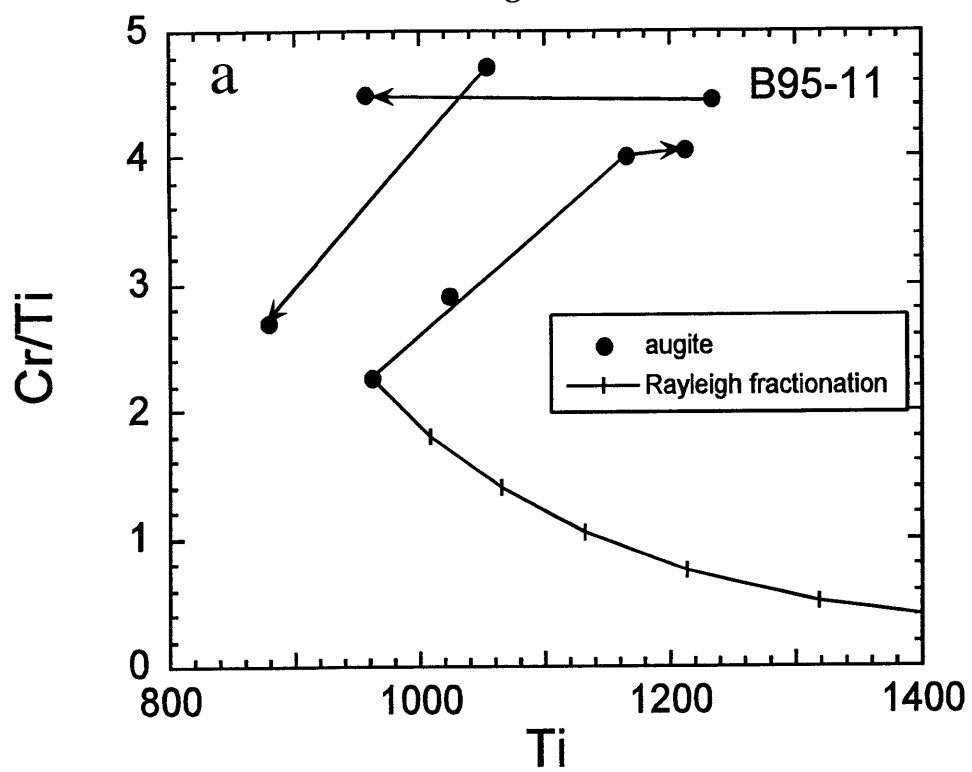


Figure 9(cont.)

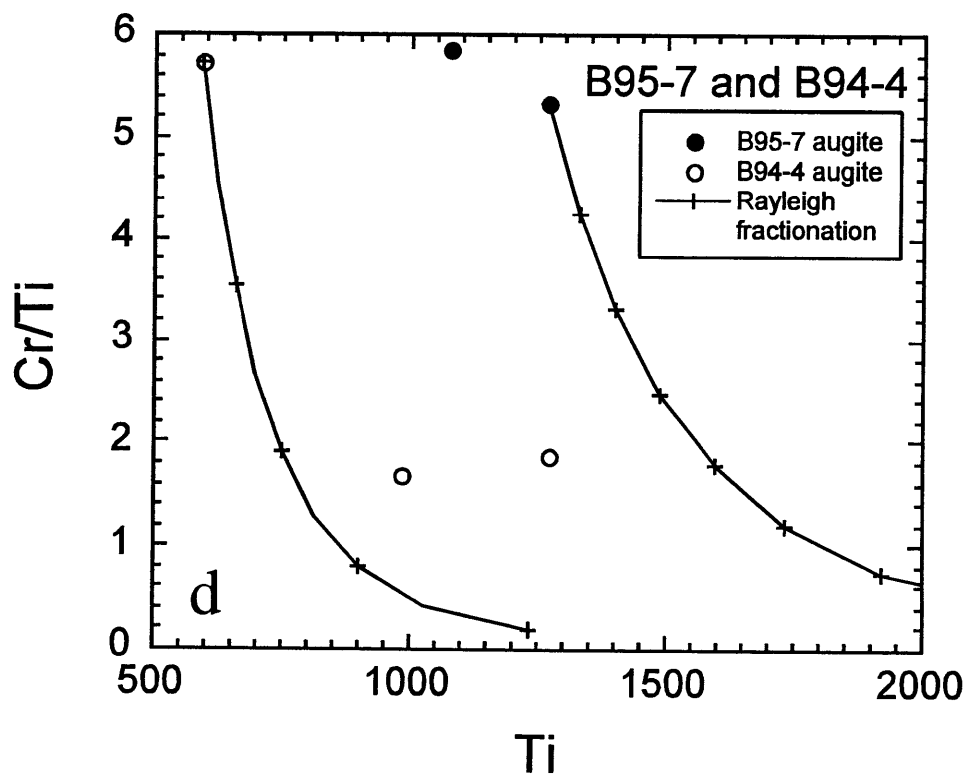
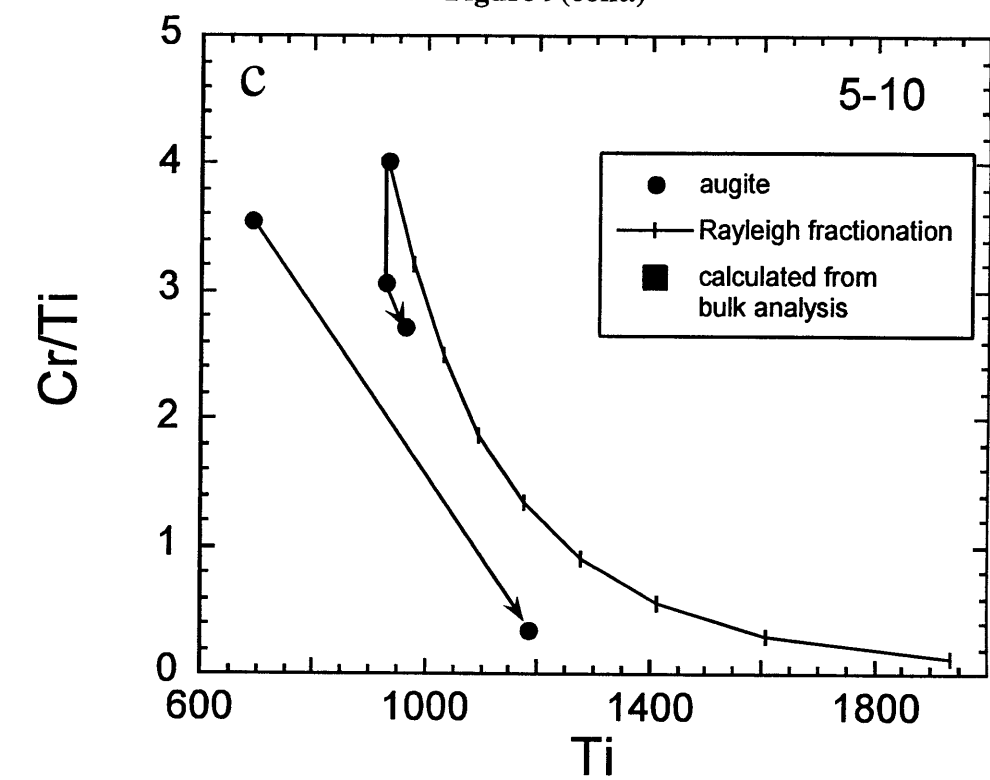


Figure 10

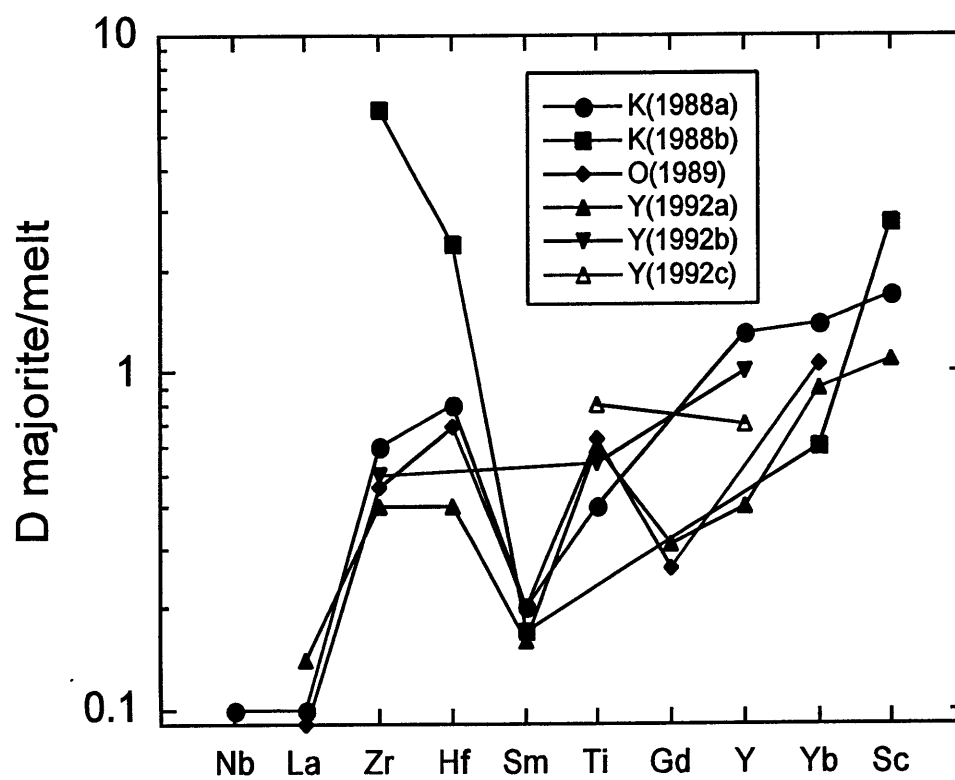
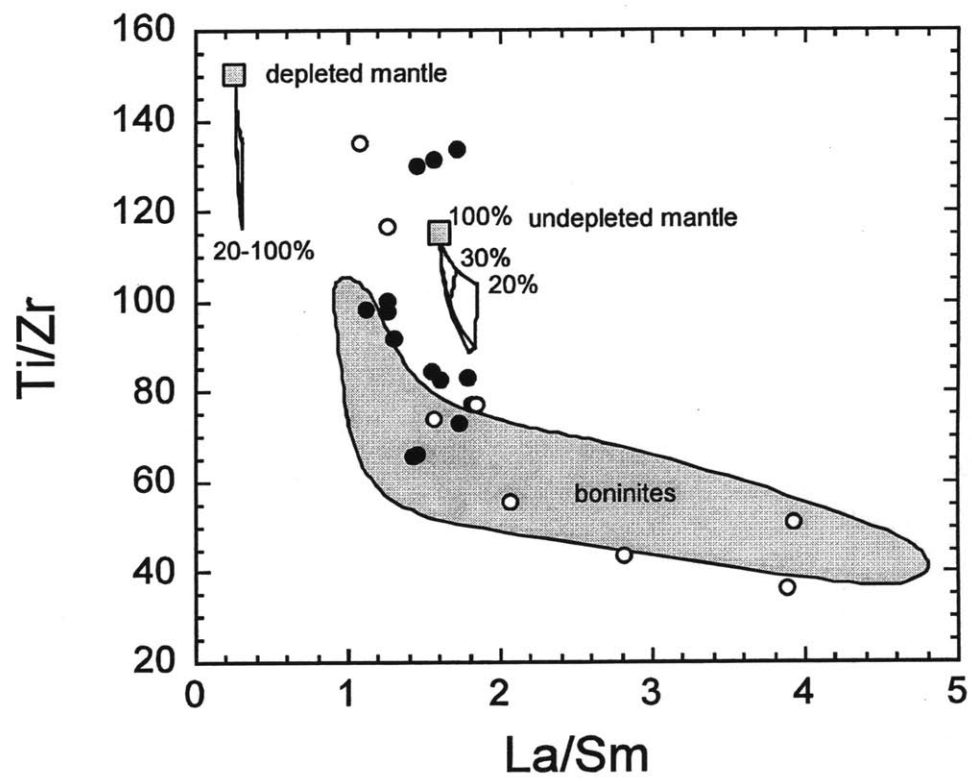


Figure 11



CHAPTER 3. EXPERIMENTALLY DETERMINED COMPOSITIONS OF HYDROUS AND ANHYDROUS MELTS IN EQUILIBRIUM WITH OLIVINE AND ORTHOPYROXENE AND APPLICATIONS TO THE PETROGENESIS OF MAGNESIAN MAGMAS

ABSTRACT

The effect of H₂O on high degree mantle melts has been quantified with a series of hydrous and anhydrous melting experiments. Experimental pressures (P) and temperatures (T) range from 1.2 to 2.2 GPa and 1175 to 1500°C, respectively. Bulk compositions have been chosen to encompass the compositions of high-Mg andesites, boninites, and komatiites. Melt H₂O contents range from 0 to 10 wt.%. The mineral/melt partition coefficients (D) in the experiments can be adequately parameterized in terms of only P, 1/T, and melt H₂O content. The well-behaved systematics of the D values implies that the thermodynamic activity coefficients are relatively constant over the range of conditions explored in this study. The regressions of our D values, supplemented by literature data, have been used as a basis for an iterative numerical model that predicts the compositions of hydrous and anhydrous melts in equilibrium with olivine (ol) and orthopyroxene (opx). The required inputs for the model are P, T, and bulk composition. The predicted melting conditions for near-primary high-magnesium andesites (HMA) from Mount Shasta in the Cascade arc are 1.0 GPa and 1250°C, with 6 to 15 wt.% H₂O. Boninite magmas, such as those in the Mariana fore-arc, require higher temperatures and a more depleted source than HMA. Their estimated melting conditions are 1.0 GPa and 1550°C, with ~2-3 wt.% H₂O. Barberton komatiites (3.5 Ga) were produced by hydrous melting of a depleted source. The estimated melting conditions are 3.0-4.0 GPa and 1440-1500°C if melt H₂O contents were as high as 6 wt.%, and 1560-1600°C if melt H₂O contents were 2-3 wt.%.

INTRODUCTION

The high SiO₂ character of andesites is a fundamental feature of arc volcanism and has been attributed to the effect of H₂O on phase equilibria [Kushiro, 1968; Kushiro, 1972]. By depolymerizing chains of SiO₂ tetrahedra in the melt, H₂O enhances the stability of minerals with similarly depolymerized structures, like olivine. The expansion of the olivine stability field shifts the ol-opx boundary towards more SiO₂ rich compositions [Kushiro, 1975]. This observation was used to hypothesize that hydrous melting of the mantle produces melts with andesitic compositions [Kushiro, 1968; Kushiro, 1972]. While the depolymerizing effects of H₂O are confirmed by studies of melt viscosity [Dingwell, 1987; Shaw, 1963; Stolper, 1982a; Stolper, 1982b], the high SiO₂ contents of hydrous mantle melts has been challenged [Gaetani and Grove, 1998]. The results of H₂O undersaturated (4-6wt.%) lherzolite melting experiments on complex, natural compositions have not produced nearly the increase in melt SiO₂ content as the earlier H₂O saturated melting experiments on simple SiO₂-MgO compositions [Gaetani and Grove, 1998]. This reopens the question, if andesitic melts cannot be produced directly by hydrous mantle melting, then what is the cause of the high SiO₂ character of arc magmas?

An equally important issue is the melt generation conditions that are recorded in the major element compositions of high degree melts such as high-Mg andesites (HMA), boninites, and komatiites. The melting conditions for high degree melts have been estimated using inverse techniques whereby the P and T conditions at which the most primitive sample saturates with olivine (ol) and orthopyroxene (opx) are taken as the melting conditions [Baker *et al.*, 1994; Falloon and Danushevsky, 2000]. The inverse technique has been used with success in the study of low degree melts where the presence

of 5 phases (melt, ol, opx, cpx, spinel) places tight thermodynamic constraints on the melting conditions (*Niu and Batiza, 1991; Kinzler and Grove, 1992a, 1992b*). Once clinopyroxene (cpx) and spinel (sp) have been exhausted from the residue though, the multiple saturation point becomes much less informative. Indeed, nearly all andesitic, boninitic, and komatiitic compositions saturate with ol and opx at some P and T, regardless of whether they have been affected by crystal fractionation, crystal accumulation, or, in some cases, by metasomatism. Thus, it is not clear that the ol-opx saturation point represents the conditions of melt generation. A forward approach is better suited to understanding the melt generation conditions of high degree melts. This involves predicting the compositions of melts that could be produced from estimated mantle compositions, and comparing these melts to naturally occurring magma compositions.

Mantle melt compositions can be estimated by either direct melting experiments on mantle compositions [*Baker and Stolper, 1994; Falloon and Green, 1987; Takahashi, 1986; Walter, 1998*] or by constructing numerical models that predict melt compositions based on a wide range of experimental phase equilibrium data [*Ghiorso, 1994; Ghiorso and Sack, 1995; Kinzler and Grove, 1992a; Kinzler and Grove, 1992b; McKenzie and Bickle, 1988; Niu and Batiza, 1991*]. The first method is most direct, but suffers from a number of difficulties. The primary one is that the percent of melt in the experiments is not large and therefore is difficult to analyze. This problem is greatly compounded by the tendency of hydrous melts to quench not to glass, but a mat of pyroxene, glass, and amphibole. Such 'quench' textures can be analyzed, but only if large areas can be analyzed by defocused electron beams. The direct melting method also suffers because the results can strictly only be applied to the bulk composition studied.

The numerical modeling approach circumvents both these problems. Bulk compositions which produce large amounts of melt can be studied, and once the model is constructed, it can be applied to a wide range of mantle compositions and melting conditions. These gains come at a cost. The need to parameterize a large amount of experimental data and the calculations within the model compound both experimental and analytical errors, with the result that the model results are less accurate. Thus the strengths and weaknesses of such predictive models must be fully understood before applying their results to interpreting magma compositions.

Since much experimental work has been focused on understanding the generation of mid-ocean ridge basalts (MORB), in which melting typically does not progress past cpx-out, little data exists on melts in equilibrium with harzburgite [Falloo and Danyushevsky, 2000]. Thus a primary goal of this study is to increase the data set of high degree, hydrous melt compositions. The second major goal is to construct a model that can predict the compositions of hydrous and anhydrous melts in equilibrium with harzburgite. Existing models are not useable because they are primarily concerned with predicting anhydrous melt compositions, and were made prior to recent advances in techniques for hydrous experiments.

We use our model to estimate the melting conditions that produced modern high degree, hydrous magmas found in subduction zones [Gill, 1981; Crawford, 1989; Baker *et al.*, 1994]. The compositions of many of these magmas, primarily HMA and boninites, show evidence of melting past the clinopyroxene (cpx) out boundary. That is, they left behind a residue consisting only of olivine (ol) and orthopyroxene (opx) [Baker *et al.*, 1994]. In addition to quantifying the melting conditions that produce modern magmas, we will also apply the melting model to komatiites. These are highly magnesian magmas

(up to 29wt.%), and represent the highest degrees of melting observed on Earth [Nisbet *et al.*, 1993]. Their production fell dramatically after the late Proterozoic [de Wit and Ashwal, 1997]. The high MgO contents of komatiites and their restriction to early Earth history are direct evidence of secular cooling of the mantle. The amount of cooling that has taken place since komatiites were produced is a matter of great interest and debate. Estimates vary from 100 to over 500°C [Herzberg, 1992; Parman *et al.*, 1997; Takahashi and Scarfe, 1985; Walter, 1998]. One source of the discrepancies in temperature estimates is the uncertain igneous composition of komatiites, as all have been affected by metamorphism (Parman *et al.*, 1997). Another source of the discrepancies is the assumed tectonic environment that produced komatiites. The most cited model is that they were produced in plumes by anhydrous melting [Arndt *et al.*, 1998; Arndt *et al.*, 1997; Herzberg, 1995; Walter, 1998]. These models estimate that melting started at depths of at least 10 GPa and temperatures of over 1900°C. The alternative hypothesis is that komatiites were produced in subduction zones by hydrous melting in a similar fashion as boninites. This would allow komatiites to be produced at lower temperatures, and decrease the amount of secular cooling required [Allegre, 1982; Brooks and Hart, 1974; Parman *et al.*, 1997]. Yet, to date, no experiment has produced a komatiite melt by hydrous mantle melting. Our model will be used to determine if komatiite magmas could be generated by hydrous melting, and if so, under what pressure and temperature conditions.

EXPERIMENTAL METHODS

Three compositions were chosen as the basis of our study (Table 1). Both anhydrous and hydrous versions of these mixes were prepared. Hydrous mixes contained between 4.5 and 7.7 wt.% H₂O. The first composition is based on a least altered

Barberton komatiite. This is essentially the same composition studied by Parman et al. [Parman et al., 1997]. Using the cpx/melt partitioning data from that study in conjunction with the cpx compositions from the komatiite samples, it was found that the Na₂O content of the estimated komatiite magma was too low to have been the igneous composition, and so it was increased accordingly. This composition will be referred to as BK. The second composition is based upon a hydrous experimental melt in equilibrium with ol and opx reported in Gaetani and Grove [Gaetani and Grove, 1998]. To promote saturation with harzburgite, the melt composition was reconstituted by adding 15% ol and opx. This composition will be referred to as W. The third composition is based upon a high Mg andesite from near Mt. Shasta; sample 85-41 from [Baker et al., 1994]. Its composition has been modified to correct for crystal fractionation and crustal contamination, and is referred to as composition A. BK forms the high MgO, low incompatible element abundance end-member. W is also high MgO, but has higher CaO and Al₂O₃. Composition A has the lowest MgO, and highest SiO₂, and highest amounts of incompatible elements.

Starting Compositions

All of the experimental starting compositions were prepared by mixing high purity oxides. Fe was added as both Fe metal and Fe₂O₃ in the correct stoichiometric proportions to produce FeO. H₂O was added as Mg(OH)₂ (brucite). The brucite was prepared by placing MgO and H₂O in a pressure sealed teflon beaker, which was placed inside an oven at 240°C for 48hrs. Weighing of the powder before and after confirmed that ~96 wt.% of the MgO was converted to Mg(OH)₂. Anhydrous powders were conditioned at log fO₂ = QFM-1 for 24 hrs at 1000°C. Hydrous powders could not be conditioned in this way because the process would dehydrate the powders. Their pre-

experiment fO_2 was set by the oxidation state of Fe in the mix, which was entirely FeO. Composition A was conditioned differently. Because of its low melting temperature, it was possible to melt it completely in a gas pressure vessel at 200 MPa, H_2O saturated conditions. This produced a homogeneous glass with 4.5 wt.% H_2O . This glass was powdered in an agate mortar and used as the starting powder. At pressures above 2.0 GPa, composition W did not saturate with a harzburgite assemblage, so its composition was modified by adding olivine. A Fe_{90} olivine composition was prepared with 6 wt.% H_2O from oxides plus brucite, and added to the W composition.

High pressure procedures

All experiments were performed in piston-cylinder devices at MIT using the hot piston in technique. Pressures for all devices have been calibrated to the Ca-Tschermakite (CATS) breakdown boundary, and pressures are considered accurate to 0.05 GPa. Temperature was measured with a W/Re thermocouple. The temperature gradient across the sample is less than 5 °C. For anhydrous experiments, sample powders were packed into a graphite capsule which was then placed in a Pt capsule and welded shut. Hydrous sample powders were placed in $Au_{80}Pd_{20}$ capsule and welded shut. These capsules were placed inside graphite capsule machined from graphite rod (Fig. 1). The experimental setup is essentially the same as developed by Gaetani and Grove [Gaetani and Grove, 1998]. In some experiments, the graphite outer capsule was replaced with MgO , with the result that ~50 wt.% of the H_2O diffused out of the sample. With the graphite capsules, H_2O loss was 0-10 wt.%, suggesting that it is the graphite that is the most effective barrier to H diffusion. The $Au_{80}Pd_{20}$ capsules were pre-conditioned with Fe before the high pressure experiment. This was done by filling them with an andesite composition and placing them in a 1 ATM furnace at $\log fO_2=QFM-1$ and 1250°C for 72

hrs. The silicate glass was then removed by HF acid. Fluoride residues after HF dissolution were first removed manually with a pick and then by soaking in HCl+nitric acid. The conditions and results of each experiment are given in Table 2.

ANALYTICAL METHODS

Experimental charges were analyzed with the JEOL 733 microprobes at the Massachusetts Inst. of Technology. Data were reduced using a ZAF procedure. The beam current was 10 na with an accelerating voltage of 15 kV for all analyses. A 2 micron beam diameter was used for solid phases, a 20 micron beam for glass, and a 30 micron beam for 'unquenched' melt. The term 'unquenched' refers to melts that do not quench to a glass, but instead form a matrix of lathe shaped pyroxene with interstitial evolved melt (Fig. 2). Due to the high MgO and H₂O contents of the melts studied here, and the high pressure and temperature of the experiments, few of the melts in this study quenched to glass. Unquenched melts are typically analyzed by using a defocused beam or by rastering the beam of the microprobe. We have also followed this method. For each unquenched melt, we perform 30-40 analyses with the defocused beam. In two experiments, half of the melt quenched to glass and the other half did not. Analysis of both sides agree within error for all elements except Al₂O₃, which is slightly overestimated in the unquenched melt. We have also quantified the degree to which the analyses of the unquenched melt represents the true composition of the melt by cutting it out of the experiment and remelting it. This was possible because the small thermal gradient in the experiment causes the melt and crystal to segregate. The cut out unquenched melt was placed in a Pt capsule and melted in a 1 ATM furnace under air at 1300°C for ~20 minutes. The high fO₂ prevents Fe loss to the Pt. These remelts were quenched into water and formed 100% glass. The analyses of the remelted glass also

agrees with the analyses of the unquenched melt to within error, again with the exception of Al_2O_3 . The composition of all experimental products are given in Table 3. H_2O contents of melts that did not quench to glass were calculated using the phase proportion of the melt and the bulk H_2O content of the starting composition.

Attainment of equilibrium

The experiments reported here are all synthesis experiments. No reversals have been performed. While equilibrium has not been proven, it can be assessed by a number of means. The first is mass balance. Loss or gain of mass to the enclosing capsule prohibits equilibrium. All of our experiments have been mass balanced, and only those which have not had significant exchange with their capsules are accepted. Second, the Fe/Mg partitioning between olivine and melt, and between opx and melt are relatively independent of pressure and temperature. So only experiments where the ol-melt $K_D^{\text{Fe-Mg}}$ is 0.31-0.35 have been accepted. Finally, the experimental phases should be unzoned if they are in equilibrium. In reality, some zoning always persists, but only experiments where the zoning is small are accepted. The main elements of concern are FeO and H_2O ; FeO because it is soluble in the AuPd capsules of the hydrous experiments, and H_2O because H atoms can rapidly diffuse through most materials. In practice, it is relatively easy to see when an experiment has failed by one of these mechanisms. FeO loss or gain shows up as strong FeO zoning in both ol and opx. H_2O loss is apparent because of the strong effect it has on melting temperature. Experiments that lose H_2O are much more crystalline than successful hydrous experiments at the same conditions. In fact, if there is H_2O loss, there is typically no melt is present in the experiment. Of the 80 experiments performed, 28 were deemed successful (Table 2). In general, the high temperatures and/or high H_2O contents of the experiments, along with the relatively fast diffusion rates

in ol and opx promote equilibrium. The excellent coherence of the experimental data suggests that equilibrium has been closely approached.

RESULTS

The effect of H₂O on the ol-opx boundary is variable (Fig. 3). For compositions BK, W, and A, H₂O shifts the melts to higher SiO₂ contents. The size of the shift decreases as pressure increases from 1.5 to 2.2 GPa. The amount of the SiO₂ increase agrees with that observed by Gaetani and Grove in hydrous lherzolite melts [Gaetani and Grove, 1998]. Composition W3, the composition with the highest ol component, shows no effect of H₂O on the position of the ol-opx boundary. This is not an artifact of the projection scheme. The anhydrous melt produced in experiment W3.36 is nearly identical composition to the hydrous melt produced in experiment W3.33 (Table 3).

Phase diagrams

The anhydrous and H₂O-undersaturated phase diagrams for BK and W are shown in Figures 4 and 5, respectively. H₂O lowers the appearance temperatures of the crystallizing phases to varying degrees. Opx and cpx phase appearance temperatures are ~200°C lower in the hydrous experiments with 6-10wt.% H₂O in the melt, while ol appears ~100°C lower in the hydrous experiments. The size of the temperature depression is similar for both W and BK compositions. The difference in the effect of H₂O between ol and opx causes the ol-opx liquidus saturation point to move to higher pressures in the hydrous experiments, as would be expected from Fig. 3. The BK composition has ol and opx on the liquidus at 2.3-2.4 GPa and 1425-1450°C with 6wt% H₂O in the melt, and 1.5-1.6 GPa and 1500-1525°C under anhydrous conditions. Composition W has ol and opx on the liquidus at 1.7-1.8 GPa and 1275-1300°C with

6wt% H₂O, and at 1.3-1.4 GPa and 1375-1400°C with no H₂O. Gt appears as a late crystallizing phase in the hydrous W composition at 2.0 GPa (Table 2). This is lower than its stability field in the anhydrous mantle. Gaetani also found gt at low pressure and attributed it to the low temperature of the hydrous experiments and the Clapeyron slope of the sp to gt transition [Gaetani and Grove, 1998].

EFFECT OF H₂O

The experimental results imply that the ol content of the melt has a strong influence on the effect of H₂O on the ol-opx boundary. Thus high SiO₂ compositions such as A and W are more strongly influenced than low SiO₂ compositions such as W3. This is consistent with Kushiro's model that the expansion of the ol stability field is the result of H₂O depolymerizing the melt structure [Kushiro, 1975]. The higher ol melts will be more depolymerized, and should show the least effect of H₂O. Because the ol content of melts increases at higher pressure, the effect of H₂O on melt composition decreases as pressure increases. In this light, the decrease in the effect of H₂O on the ol-opx boundary with increased pressure may primarily be due to the increase of ol content of melts at high pressure.

The Clapeyron slopes of the ol, opx, and cpx phase boundaries are not strongly affected by the addition of H₂O below the saturation point (Figs. 4 and 5). The Clapeyron slope is given by

$$(1) \quad dT/dP = \Delta V / \Delta S$$

where T is temperature, P is pressure, delta V is the volume of fusion, and delta S is the entropy of fusion. The similarity of the Clapeyron slopes between the wet and dry experiments implies that either the changes in delta V and delta S are small, or that the

increases in their values with increasing water content are of similar magnitude and offset each other.

Pairs of experiments have been used to calculate the melting reaction of the solid phases (Table 4). The results show that opx dominates the melt reaction during harzburgite melting in both H₂O undersaturated and anhydrous experiments. At 1.5 GPa, 18% ol is consumed per unit of melt produced. At high pressure, ol and opx are in a reaction relationship and melting of harzburgite produces ol, driving the melts towards higher SiO₂ contents. Melting of lherzolite is dominated by cpx. The results are in good agreement with previous studies of mantle melt reactions [*Baker and Stolper, 1994; Walter, 1998*].

MINERAL/MELT PARTITIONING

The effect of water on phase equilibria can be evaluated by examining the mineral/melt partition coefficients (D). At equilibrium,

$$(2) \quad \mu_a^i = \mu_b^i$$

$$(3) \quad \mu_a^{i,0} + RT \ln a_a^i = \mu_b^{i,0} + RT \ln a_b^i$$

where μ_a^i is the chemical potential of component i in phase a, $\mu_a^{i,0}$ is the standard state chemical potential, R is the gas constant, T is temperature, and a_a^i is the activity of component i in phase a. Activity is related to composition by

$$(4) \quad a_a^i = \gamma_a^i x_a^i$$

where x_a^i is mole fraction and γ_a^i is the activity coefficient of component i in phase a.

Substituting (4) into (3), and solving for the solid melt D value yields

$$(5) \quad \ln D^{\text{solid/melt}} = \Delta\mu_i^{a-b}/RT + \ln (\gamma_i^b/\gamma_i^a)$$

where D is the ratio of the single cation mole percent of an element in the solid to its single cation mole percent in the melt. If mixing of an element in the crystal and melt follows Raoult's law ($\gamma=1$) or Henry's law ($\gamma = \text{constant}$), then plots of $\ln D$ versus $1/T$ should produce straight lines. Conservative single cation oxide components (e.g. MgO, $\text{AlO}_{1.5}$, $\text{HO}_{.5}$) are used in all regressions and in the melting model. Model results are converted to weight percent units when comparing them with natural magma compositions.

For FeO and MgO in both ol and opx, $\ln D$ shows an excellent correlation with $1/T$, suggesting that the activity coefficients for these elements are nearly constant (Figs. 6b and 7b). No difference is seen between the hydrous and anhydrous experiments, implying that H_2O has no effect on the activity coefficients of FeO and MgO in the liquid. Neither is there a difference between experiments with different starting compositions. The tightness of the fits is a good indication that the experiments have closely approached equilibrium, while the parallel slopes of the FeO and MgO lines for both ol and opx indicate that near constant Fe/Mg K_D have been maintained.

Minor element (TiO, $\text{AlO}_{1.5}$, $\text{CrO}_{1.5}$, and CaO) partitioning in ol also forms lines in the Arrhenius plots (Fig. 6). The data scatter more than the FeO and MgO data, due to their lower concentrations. There is a slight offset of the BK experiments from the W experiments. This implies that the D values vary with bulk composition and that the activity coefficients are not constant for these elements, though the change is small. No effect of H_2O is apparent. Though a small H_2O effect could be obscured by the scatter in the data and the lack of T overlap between the hydrous and anhydrous experiments.

Arrhenius correlations are also seen for minor elements (TiO, $\text{AlO}_{1.5}$, $\text{CrO}_{1.5}$, and CaO) in opx (Fig. 7). The correlations are better for $\text{CrO}_{1.5}$ and $\text{NaO}_{.5}$ than for TiO_2 and $\text{AlO}_{1.5}$.

$\text{CrO}_{1.5}$ and $\text{AlO}_{1.5}$ show large variations with bulk composition, implying that their activity coefficients are not constant.

The D values for SiO_2 do not display Arrhenius relationships in either ol or opx (Figs. 6a and 7a). $D \text{ SiO}_2$ for both ol and opx are distinctly higher when H_2O is present, though no difference is apparent between the W and BK experiments (Fig. 8). Because H_2O has a very low solubility in ol and opx, the change in $D \text{ SiO}_2$ must be due to changes in the melt, and implies a rise in the activity coefficient of SiO_2 in the melt.

H₂O dissolution mechanisms

The difference in partitioning behavior of SiO_2 compared to the remaining elements belies their differing roles in the structure of the melt. Si is a network former and is located in tetrahedral units, while the other elements act as network modifiers and are weakly bonded to the network forming polyhedra. The melt model of Toop and Samis proposes that the network formers and network modifiers can be treated as occupying different quasi-lattice sites in the melt [Toop and Samis, 1962a; Toop and Samis, 1962b]. The rather constant activity coefficients of the network modifiers is due to the highly depolymerized structure of high degree melts. There are no SiO_2 polymer chains to be broken. Complications can arise in the tetrahedral site when $\text{AlO}_{1.5}$ is charge balanced by a Na atom and becomes a network former. Both $\text{NaO}_{0.5}$ and $\text{AlO}_{1.5}$ have low concentrations in the melts studied here, and so the proportion of tetrahedral Al to tetrahedral Si is negligible.

H_2O (treated here as $\text{HO}_{0.5}$) is a network modifier. Therefore, when calculating D values for network modifiers (MgO , FeO , CaO) in hydrous melts, it should be included, as its presence dilutes those elements. But when comparing partitioning of SiO_2 in anhydrous and hydrous melts, it should be excluded because H atoms do not partition

onto the tetrahedral site, and therefore do not dilute SiO_2 . The artificial dilution of SiO_2 by H_2O is the cause of the break between the hydrous and anhydrous SiO_2 D values in Figs. 6a and 7a. When the hydrous melts are renormalized on an anhydrous basis, the SiO_2 D values form well-defined linear trends on Arrhenius plots (Fig. 9). Thus the difference in the effect of H_2O on SiO_2 partitioning versus the partitioning of all other elements can be rationalized within the framework of a Toop and Samis type model in which elements partition onto distinct sites within the melt structure.

The speciation of H_2O in the melt can also be addressed with the partitioning data. Burnham argued that the linear relationship between the fugacity of H_2O and the square of the H_2O concentration in experimental melts implies that all H_2O is dissolved as OH in silicate melts [Burnham, 1975]. Stolper demonstrated that silicate glasses contained significant amounts of molecular H_2O [Stolper, 1982a; Stolper, 1982b]. He proposed that the OH/ H_2O ratios in the glasses were indicative of the ratios in the melts from which they were quenched and also that this speciation could also produce the observed relationship between H_2O fugacity and concentration. Subsequent in situ analyses of H_2O speciation in melts have gone far to resolve this issue. They show a steep temperature dependence to the OH/ H_2O ratio [Shen and Keppler, 1995]. Extrapolation of this temperature dependence to the temperature of mantle melting experiments indicates that nearly all H_2O is present as OH. The high molecular H_2O in glasses records the speciation of H_2O of the melt at the glass transition, which occurs at low (600-700°C) temperatures [Dingwell and Webb, 1990]. When D values for the network modifiers are calculated assuming all H_2O as $\text{HO}_{.5}$, linear trends are observed in Figs 6 and 7. But when treated as all molecular H_2O , a distinct break occurs between the hydrous and anhydrous data (see Gaetani and Grove, Fig. 5) [Gaetani and Grove, 1998]. This

corroborates Burnham's model and in situ observations that H₂O predominantly dissolves as the monoxide OH.

MELTING MODEL

Theory

The relatively well behaved element partitioning in high degree melts can be used to advantage in constructing a predictive melting model. The following model is based on that of Langmuir and Hanson and Weaver and Langmuir [*Langmuir and Hanson*, 1981; *Weaver and Langmuir*, 1990]. Three equations constrain the composition and weight proportions of phases in equilibrium with each other. The first is mass balance, which states that the mass of an element in each phase must sum to the mass of that element in the bulk composition:

$$6) \quad \sum_j n_j x_j^i = x_{\text{bulk}}^i$$

where n_j is the weight fraction of phase j , x_j^i is the weight percent of element i in phase j , and x_{bulk}^i is the weight percent of i in the bulk composition. The second constraint is that each phase must be stoichiometric:

$$7) \quad \sum_i x_j^i = 1$$

where the summation is over all elements i in phase j . The third constraint is the equilibrium condition given in equation 2, stating that the partial molar Gibb's free energy of a component in phase j must equal to the partial molar Gibb's free energy of the component in phase k . Equation 5 recasts this constraint in terms of mineral/melt partition coefficients (D). When the bulk composition of the system is prescribed, equations 5-7 leave only two independent variables [*Spear*, 1993]. For modeling purposes, we have chosen these two variables to be pressure and temperature.

Parameterization of partition coefficients

The core of the model is a parameterization of the ol/melt and opx/melt D values. Equations for the mineral/melt partition coefficients have been obtained using a step-wise regression method with P , $1/T$, and melt composition as the independent variables. Using only P , $1/T$, and the H_2O content of the melt, the partition coefficient data is recovered with a high degree of accuracy (Table 5). Four different fits are shown in Table 5. The first includes terms for P , $1/T$, and melt H_2O , the second only $1/T$ and H_2O , the third P and H_2O , and the fourth only $1/T$. The first row of data for each oxide shows the values for the fit parameters, the second shows the relative errors (1 sigma), and the third shows the values for R^2 and the significance value F . The regressions capture the behavior seen in the experimental data. H_2O has a large effect (i.e. large coefficient value and low error) on SiO_2 partitioning, and little effect (i.e. small coefficient values and high errors) on the partitioning of network modifiers in olivine or in orthopyroxene. In the model developed, fits including H_2O are only used for SiO_2 partitioning. A pressure term is only used for partitioning of SiO_2 and Al_2O_3 between melt and opx. All other elements have only the $1/T$ term.

Table 5 shows the results of regressing two different data sets. One includes a large number (226) of experiments from various experimental laboratories. The other data set includes only data from the present study, and the anhydrous melting study of Walter [Walter, 1998]. This second data set encompasses the widest range of P , T , and melt H_2O content, with the fewest experiments. Regressions of both data sets yield similar results. The fit parameters for all major elements, and the majority of minor elements, are within error of one another. This indicates that the values of the parameters are robust, and not artifacts of the data set chosen. For our model, we have used the

regression from the larger data set, as the errors on the fit parameters are smaller, and the significance values (F) are slightly higher. The fits to Cr_2O_3 and MnO partitioning are significantly worse than for the other elements, so they have not been included in the model.

MODEL RESULTS

The Newton-Raphson method is used to solve the system of equations 5-7. The P, T, and bulk composition of the system is set, as is an initial guess at the melt composition. The P, T, and melt H_2O are used to calculate a set of ol/melt and opx/melt D values. The system of equations is iteratively solved until a minimum level of convergence is reached for all values (0.01% relative). A new set of D values is calculated at each step.

The output of the model is in good agreement with the input data. Both the predicted phase percentages and melt compositions match the experimental data (Figs. 10 and 11, Table 6). The best fits are for anhydrous experiments between 1.0 and 3.0 GPa, where data coverage is best. The difference between observed and predicted melt composition are ~10% relative or less. The least accurate predictions are for pressures above 3.0 GPa, and hydrous conditions, where data are sparse. At these pressures, the errors in melt composition are as high as 20% relative.

An important test of the model is to predict the composition of experimental melts not included in the data set used to construct the model. The mantle melting study of Falloon et al. was not included in our data set [Falloon *et al.*, 1999]. The model does an excellent job of reproducing their melt compositions (Table 6). For SiO_2 , FeO , and MgO , the relative errors are less than 5%.

The main deficiency of the model is temperature prediction. The model systematically overestimates temperatures by 20-100°C (Table 6). The error is one of accuracy, instead of precision. For example, the model overestimates the temperatures for the two experiments from Falloon et al. [Falloon et al., 1999] (Table 6) by 100°C. On the other hand, the 40°C temperature difference between the two experiments is precisely matched by the model. Thus the accuracy of the model is ~100°C, while its precision is approximately 10-20°C. In sum, we conclude that the model accurately predicts melt compositions and relative temperatures, but absolute temperature estimates are likely to be high.

Fig. 12 shows the modeled results of melting fertile mantle past the cpx-out boundary at 1.0 GPa with varying bulk H₂O contents. The hydrous melts produced have 0-17 wt.% H₂O, which varies as a function of both bulk H₂O content and melt extent. As expected, the magmatic H₂O lowers equilibration temperatures between minerals and melt. H₂O also increases the SiO₂ content of the melts at a given MgO content, and lowers the concentration of incompatible elements. These differences are largely due to the higher extents of melting at a given MgO content under H₂O-undersaturated conditions, which is in turn due to the lower temperatures at which the hydrous equilibrium occurs.

APPLICATION OF MODEL TO HIGH DEGREE MANTLE MELTS

High-Mg Andesites

The compositions of andesites and high-magnesium andesites (HMA) from the Mt. Shasta area are compared with the predicted compositions of hydrous mantle melts in Fig. 12. Shasta is one of the most intensively studied volcanoes, and an uncommonly

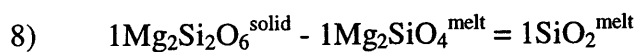
detailed knowledge of the chemical variations are available [*Baker et al.*, 1994]. Most of the andesitic magmas have SiO₂ contents well above the predicted melt compositions (>55 wt.%), and cannot be primary or near-primary mantle melts. They must have evolved high SiO₂ contents by fractionation of olivine and/or orthopyroxene. Previous studies have argued the thermodynamic effects of H₂O on melt composition produced the high SiO₂ contents in these andesitic magmas, and that they could be generated by hydrous melting of peridotite [*Kushiro*, 1968; *Kushiro*, 1972]. In contrast, the results of this and other subsequent experimental studies indicate that the effect of H₂O on melt SiO₂ content is small [*Gaetani and Grove*, 1998].

Primitive Shasta lavas such as sample 85-44 can be produced directly by mantle melting. In plots of MgO versus SiO₂, TiO₂, and Al₂O₃, they fall on or near the predicted compositions of melts produced at 1.0 GPa and temperatures of 1200°C (Fig. 12). The predicted H₂O contents are 15 wt.%. This value is quite high, more than twice that of previous estimates [*Baker et al.*, 1994]. The high water contents could be in error if 85-44 was not a primary melt, but instead derived from a more magnesian, lower H₂O melt by olivine fractionation. The estimated concentration of FeO is lower and of CaO is higher than in 85-44. Both discrepancies suggest that the mantle source of 85-44 was more depleted than the fertile mantle composition used in the modeling. The high Na₂O of both Shasta samples suggests, in contrast, that their sources were not depleted. But it is likely the Na₂O was introduced with the hydrous slab fluid that instigated the melting event.

Rare primitive magma compositions, such as 85-41c, are unusual in having both high SiO₂ and high MgO; 56 and 11 wt.%, respectively [*Baker et al.*, 1994]. These compositions cannot be derived from magmas like 85-44 by fractionation. Instead, their

compositions are consistent with derivation from a parent magma with 15-20% MgO by fractionation of orthopyroxene and olivine (Fig. 12). Indeed, the compositions of HMA are very similar fractionated boninites (Fig. 13). Yet, it is unlikely that these HMA are produced from boninites as no boninite magmas have been found at Mt. Shasta or anywhere else in recent Cascadian volcanism, and their trace element systematics are dissimilar [Anderson, 1974; Gill, 1981; Hickey and Frey, 1982].

Alternatively, melt-wall rock interaction could produce 85-41c from basaltic andesite compositions such as 85-44. Kelemen has argued that melts rising through the mantle will become saturated with ol and undersaturated in opx as the ol-opx boundary shifts with decreasing pressure [Kelemen, 1990; Kelemen *et al.*, 1997]. Qualitatively, the assimilation of opx with precipitation of ol can raise the SiO₂ content of a magma without significantly affecting the other major and minor elements. This can be seen by rearranging the opx formation reaction in the form:



More quantitatively, addition of 50 wt.% opx and subtraction of 31 wt.% olivine from 85-44 produces a melt quite similar to 85-41c in all elements except FeO (Table 7). FeO is significantly lower in 85-41c than the predicted composition. The low FeO could be the result of magnetite fractionation, but this process is unconstrained. Thus the unusual compositions of magmas such as 85-41c are broadly consistent with melt-wallrock interaction.

Boninites

Boninites have high MgO and H₂O contents, and record unusually high degrees of melting during the early stages of subduction [Crawford *et al.*, 1989; Stern and Bloomer, 1992]. The compositions of boninites dredged from the North Tonga Trench are shown

in Fig. 13 [Cameron *et al.*, 1983]. We focus on North Tonga because the boninites there have been extensively studied and have some of the highest MgO contents of any boninites [Cameron *et al.*, 1983; Falloon and Danyushevsky, 2000; Sobolev and Danyushevsky, 1994]. The samples contain up to 30% phenocrysts of ol and pyroxene, so it is possible that their compositions do not represent magma compositions. Primary boninite magma compositions have been estimated from melt inclusion studies [Sobolev and Danyushevsky, 1994]. The calculated primary melt compositions overlap the compositions of the most magnesian whole rock samples, suggesting that the highest MgO samples have not been significantly affected by crystal accumulation or fractionation. The melt inclusion studies imply melt H₂O contents of ~ 3 wt.% [Sobolev and Danyushevsky, 1994].

The composition of the most primitive boninite sample lies on the 1.0 GPa hydrous melting curve for moderately depleted mantle (Fig. 13). The estimated melt temperature is ~1550°C for a melt with 3 wt.% H₂O and a melt extent of 25%. The source composition used in the model is a 50/50 mixture of fertile lherzolite [Walter, 1998] and depleted harzburgite [Falloon and Danyushevsky, 2000], and represents a moderately depleted mantle. Like previous studies, the most striking feature of boninite petrogenesis is the high temperatures required to be present at shallow levels in the sub-arc mantle.

Unlike the HMA, the compositional trends in the North Tonga boninites can be reproduced by ol fractionation from the most primitive sample (Fig. 13). No melt/wallrock interaction is indicated. The difference in chemical systematics between the North Tonga boninites and Shasta HMA may be caused by differences in their tectonic settings. The boninites were erupted through highly extended ocean crust with a

presumably thin lithosphere, while the HMA were erupted through continental crust. Thus the HMA traversed a much thicker thermal boundary layer and had a greater opportunity to cool and interact with their surroundings.

Komatiites

Komatiites have yet higher MgO contents than boninites, implying even higher melting temperatures. Chill margin samples of Barberton komatiites have between 24 and 33 wt.% MgO (Fig. 14). Barberton komatiites, like all komatiites, have been metamorphosed. The concentrations of mobile elements such as Na₂O, K₂O, and CaO, are scattered and generally cannot be explained by igneous processes. Their concentrations were disturbed during metamorphism. MgO concentrations in at least some samples were also affected [*de Wit et al.*, 1987; *Nisbet et al.*, 1993; *Parman et al.*, 1997]. The most magnesian olivines in Barberton samples is Fo₉₄. Assuming 1) an oxygen fugacity was QFM ($\text{Fe}_2\text{O}_3/(\text{FeO}+\text{Fe}_2\text{O}_3)=0.11$) when the melt equilibrated with the olivine, 2) a melt FeO content of 11.5%, and 3) an ol/melt Fe-Mg K_D of 0.32, the melt in equilibrium with Fo₉₄ olivine has 29 wt.% MgO. This is also the maximum MgO content calculated for Barberton komatiites by Nisbet et al. (1993). Therefore the komatiite samples with 30-33 wt.% MgO do not represent magma compositions. The FeO concentrations in Barberton komatiites are a bit scattered (Fig. 14). Some have as low as 10% FeO, which would imply a maximum MgO content of 26 wt.%. Thus we consider the maximum MgO content of Barberton komatiites to be between 26 and 29 wt. %.

The H₂O contents of Barberton komatiite magmas were between 4.5 and 6 wt.%, based on augite thermometry [*Parman et al.*, 1997]. The predicted compositions of mantle melts at 3.0-6.0 GPa with 6 wt.% H₂O are shown in Fig. 14. Also shown are the

composition of Barberton chill margins with less than 29 wt.% MgO. Samples on the low end of the MgO spectrum are consistent with melting at low pressures. The SiO₂ contents imply a pressure of 3.7 GPa, while the FeO contents imply a pressure of 3.0 GPa. The observed ol-opx saturation point for a Barberton komatiite composition with 24 wt.% MgO is 2.4 GPa (Fig. 4). The discrepancy between the modeled and experimentally determined melting conditions implies that the model is not accurate at high pressures, where the hydrous equilibrium data on which the model is based are scarce. Thus we take the experimentally determined multiple saturation point (2.4 GPa, 1440°C) as the melting conditions.

Komatiite compositions at the high MgO end of the spectrum, are not produced by the model at any pressure (Fig. 14). Their low SiO₂ contents imply pressures up to 6.0 GPa, yet their relatively low FeO contents require pressures below 4.5 GPa. In the low MgO komatiites, comparing FeO contents of observed and predicted melt compositions came closest to yielding the correct melting conditions. The TiO₂ and Al₂O₃ contents of the high MgO samples also fall off the predicted melt curves (Fig. 14). We suggest that even the samples with 26-29 wt.% MgO have been affected by metamorphism, which has lowered their SiO₂ contents, raised their MgO contents, and had little effect on TiO₂ or Al₂O₃. The relatively unaffected komatiite samples with 24 to 26 wt.% MgO imply melting conditions of 2.4 to ~3.0 GPa, and 1440 to ~1500 °C with 6 wt.% H₂O. If water contents closer to those of boninites (2-3 wt.%), melting temperatures are 1560 to ~1600°C.

CONCLUSIONS

The partitioning of elements between melt, ol, and opx, can be described by a Toop and Samis type model in which network formers and network modifiers mix on

different pseudo-crystalline sites in the melt structure [*Toop and Samis, 1962a; Toop and Samis, 1962b*]. H_2O affects element partitioning by diluting network modifiers. The relatively simple element partitioning has been exploited to construct a melting model that predicts the composition and mode of melt, olivine, and orthopyroxene in equilibrium with each other at a given P, T, and bulk composition.

The melting model argues that few of the andesites found at Mt. Shasta in the Cascadian arc are near-primary. Only the lowest SiO_2 , highest MgO melts approach the compositions of mantle melts. The melting conditions predicted by the melting model for these high-magnesium andesites are 1.0 GPa and 1250°C with 6-15 wt.% H_2O in the melt. Boninite magmas from the North Tonga trench imply melting conditions of 1.0 GPa and temperatures of 1550°C , with 3 wt.% magmatic H_2O . The predicted melting temperatures are surprisingly high for a subduction zone. Boninite magmas are produced almost exclusively in fore-arcs during the early stages of arc volcanism. This implies that the high mantle temperatures that produce boninites are related to the mantle flow pattern that briefly exists beneath arcs at the onset of subduction [*Stern and Bloomer, 1992*]. Finally, Barberton komatiites can be produced by hydrous melting at low pressures between 2.4 and 3.0 GPa. The predicted mantle melting temperatures are 1440 to 1500°C , for an melt H_2O content of 6 wt.%, and 1560 to 1600°C for a melt H_2O content of 3 wt.%.

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TABLES

Table 1. Starting compositions

	BK	W	W3	A
SiO ₂	49.23	48.12	46.27	57.00
TiO ₂	0.43	0.49	0.37	0.56
Al ₂ O ₃	4.62	13.79	10.32	14.15
Cr ₂ O ₃	0.34	0.25	0.19	0.05
FeO	11.13	8.48	8.80	7.20
MnO	0.2	0.13	0.10	0.07
MgO	23.14	18.72	26.40	9.15
CaO	10.14	8.73	6.53	8.02
Na ₂ O	0.61	1.10	0.82	3.00
K ₂ O	0.02	0.03	0.02	0.69
P ₂ O ₅	0.05	0.23	0.17	0.11
Nio	0.14	0.02	0.01	0.01
Sum	100.1	100.1	100.0	100.0

Table 2. Experimental results

exp. #	P (GPa)	T (°C)	time (hr)	H ₂ O	gl/ quench	ol	opx	cpx	sp(*=gt)	ol Kd	opx Kd	cpx Kd	Fe change	H ₂ O change	sum R ²
BK2.19	2.2	1400	31	6	94.1(24)	9.9(16)	-4.2(30)	-	tr	0.32	0.29	-	0.07	-	0.630
BK2.20	2.2	1350	57	6	74(1)	7(1)	19(2)	-	tr	0.33	0.28	-	0.03	-	-
Bk2.20 remelt					76.3(7)	4.1(6)	19.9(9)	-	-	0.36	0.31	-	0.008	-	0.367
BK2.24	1.5	1300	23	6	82.2(8)	18.1(7)	-	-	-	0.33	-	-	0.06	-	0.525
BK2.27	1.5	1450	26	0	56.5(9)	14.9(4)	-	28.3(10)	-	0.357	-	0.340	0.009	-	0.087
BK2.28	1.5	1500	48	0	90.8(42)	13.6(26)	3.8(53)	-	-	0.360	0.35	-	0.107	-	2.183
BK2.29	2.2	1500	64	0	52.0(21)	10.2(9)	38.1(23)	-	-	0.39	0.37	-	0.027	-	0.469
BK2.30	1.5	1275	28	6	63.9(15)	20.0(9)	4.1(17)	11.6(14)	-	0.33	0.3	0.28	0.021	-	0.214
W7	1.2	1320	23	6.5	93.7(3)	5.84(2)	-	-	0.18(2)	0.34	-	-	-0.03	-0.10	0.068
W9	1.5	1200	33	6.5	81.6(40)	13.5(37)	3.7(58)	-	0.01(1)	0.334	0.34	-	-0.17	-0.04	2.145
W10	1.5	1250	20	6.5	92.6(2)	7.6(2)	-	-	.076(2)	0.355	-	-	0.03	-0.07	0.050
W11	1.5	1175	23	6.5	77.8(5)	14.1(5)	8.0(8)	-	tr	0.345	0.32	-	-0.11	-	0.050
W12	1.5	1175	31	6.5	65.2(4)	10.7(4)	19.5(6)	4.6(4)	tr	0.335	0.32	0.31	-0.05	-0.27	0.020
W13	2	1200	21	6.5	76.3(27)	-	29.9(11)	-	4.2(24)*	-	0.3	-	-0.04	-	0.537
W18	2	1300	28	6.5	91.9(8)	-	7.4(7)	-	-	-	0.320	-	-0.03	-	0.234
W20	1.5	1400	76	0	68.1(8)	tr	31.2(7)	-	0.7(3)	-	0.32	-	-0.044	-	0.202
W21	2	1450	71	0	58.6(13)	-	28.9(9)	12.6(19)	.1(2)	-	0.33	0.38	0.006	-	0.068
W22	2	1250	26	6.5	80.2(18)	1.7(16)	17.6(27)	-	-	0.35	0.33	-	0.030	-	0.698
W3.31	2	1300	24	6.4	72.5(9)	25.6(7)	1.8(1.2)	-	-	0.350	0.323	-	0.016	0.16	0.140
W3.32	2	1450	70	0	57.1(19)	21.3(14)	21.7(26)	-	-	0.336	0.331	-	-0.071	-	0.546
W3.33	2	1275	26	6.4	62.7(10)	23.2(8)	14.0(13)	-	-	0.339	0.319	-	0.040	0.14	0.167
W3.34	2	1425	94	0	38.0(50)	20.2(28)	30.9(64)	11.3(65)	-	0.327	0.307	0.35	0.090	-	1.887
W3.35	1.5	1450	67	0	75.4(29)	29.2(23)	tr	-	-	0.342	0.335	-	-0.120	-	1.340
W3.36	2	1475	72	0	62.3(6)	22.0(4)	15.7(8)	-	-	0.340	0.331	-	0.015	-	0.049
a1.2	1.5	1300	70	0	76.5(13)	-	8.9(15)	13.9(23)	-	-	0.33	0.35	-0.11	-	0.624
a1.7	1	1175	30	4.5	y	y	-	-	-	-	-	-	-	-	-
a1.8	1.3	1200	24	4.5	y	-	y	y	-	-	-	-	-	-	-
a1.9	1.15	1200	21	4.5	y	-	y	y	-	-	-	-	-	-	-
a1.10	1	1175	15	4.5	y	-	y	y	-	-	-	-	-	-	-

Table 3. Experimental products

exp.	phase	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	NiO	H ₂ O
BK2.19	ves. gl	50.48(76) ¹	0.49(1)	5.13(11)	0.36(6)	10.42(29)	0.22(4)	20.9(11)	11.36(53)	0.52(3)	0.02(1)	0.06(3)	0.01(2)	6.38
	ol	41.18(44)	0.0(1)	0.03(1)	0.09(1)	8.08(20)	0.11(1)	50.92(41)	0.19(2)	0	0	0	0.07(1)	0
	opx	57.49(28)	0.01(1)	0.55(4)	0.41(4)	4.96(11)	0.11(2)	34.77(19)	1.52(5)	0	0	0	0.03(1)	0
BK2.20	ves. gl	43.06(49)	0.48(2)	8.2(13)	0.37(2)	11.34(36)	0.21(2)	16.26(3)	11.37(2)	0.56(3)	0.07(1)	0.09(1)	0.06(2)	8.11
	remelt	47.35(44)	0.53(1)	6.15(7)	0.34(2)	11.3(36)	0.22(3)	19.04(14)	12.44(14)	0.79(6)	0.02(1)	0.07(1)	0.06(2)	
	ol	40.83(31)	0.01(1)	0.02(1)	0.11(1)	10.93(18)	0.16(1)	47.37(48)	0.22(2)	0	0	0	0.06(3)	0
	opx	57.33(34)	0.03(1)	0.75(3)	0.48(2)	6.63(10)	0.17(1)	33.23(2)	2.2(3)	0.01(1)	0	0	0.05(1)	0
BK2.24	quench	50.73(21)	0.51(2)	5.55(6)	0.42(4)	12.00(18)	0.21(2)	17.63(10)	12.34(10)	0.43(8)	0.09(2)	0.06(1)	0.03(2)	7.25
	ol	40.82(25)	0(1)	0.02(1)	0.14(2)	10.57(22)	0.15(2)	47.78(48)	0.23(2)	0	0	0	0.07(1)	0
BK2.27	gl	48.66(57)	0.74(5)	7.77(53)	0.32(4)	12.65(46)	0.21(3)	16.03(85)	12.8(21)	0.68(14)	0.05(2)	0.09(2)	0.01(2)	0
	ol	40.16(33)	0.01(1)	0.06(1)	0.17(2)	13.03(11)	0.15(2)	46.25(47)	0.47(2)	0	0	0	0.05(2)	0
	cpx	55.58(18)	0.07(1)	1.35(11)	0.59(4)	6.84(11)	0.18(3)	25.49(49)	9.89(44)	0.17(4)	0	0	0	0
BK2.29	q	46.8(11)	0.82(11)	8.39(56)	0.27(4)	12.9(10)	0.21(2)	17.01(67)	12.24(36)	0.46(12)	0.05(3)	0.07(1)	0.01(1)	0
	ol	40.02(29)	0.01(1)	0.09(2)	0.13(1)	13.42(22)	0.16(1)	45.35(35)	0.4(2)	0	0	0	0.06(2)	0
	opx	54.58(17)	0.08(1)	1.92(22)	0.54(3)	7.13(1)	0.2(2)	25.53(40)	9.3(40)	0.23(2)	0	0	0	0
BK2.30	vg	50.76(89)	0.56(2)	6.47(10)	0.35(2)	12.59(42)	0.22(3)	15.73(23)	12.32(43)	0.87(11)	0.06(1)	0.06(2)	0.00(1)	9.39
	ol	40.24(30)	0.03(1)	0.04(2)	0.10(1)	12.34(12)	0.15(2)	46.49(37)	0.22(1)	0	0	0	0.05(1)	0
	opx	56.99(40)	0.04(1)	0.61(4)	0.6(5)	7.7(16)	0.18(3)	31.77(13)	2.21(13)	0.02(1)	0	0	0	0
	cpx	54.81(47)	0.04(1)	0.74(4)	0.91(9)	4.51(15)	0.12(2)	20.5(22)	18.3(3)	0.18(2)	0	0	0	0

¹ 2-Sigma errors on last digit reported in parentheses.

Table 3(cont.). Experimental products

exp.	phase	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	NiO	H ₂ O
W7	gl	45.17(25)	0.46(2)	13.6(9)	0.16(2)	7.62(16)	0.13(2)	15.6(7)	8.53(9)	1.07(4)	0.03(1)	0.21(3)	0.03(2)	7.40(35)
	ol	41.4(37)	0.01(1)	0.05(2)	0.09(1)	8.17(8)	0.11(2)	49.46(35)	0.15(2)	0	0	0	0.01(1)	0
	sp	0.15(1)	0.23(1)	24.70(30)	43.95(23)	12.94(16)	0.20(1)	17.25(27)	0.06(4)	0	0	0	0.03(2)	0
W9	gl	44.77(28)	0.56(1)	16.01(12)	0.06(1)	6.27(14)	0.13(2)	11.67(9)	10.16(9)	1.02(3)	0.12(1)	0.25(1)	0.02(1)	8.96(47)
	ol	41.11(55)	0.00(1)	0.05(1)	0.05(1)	8.99(16)	0.10(2)	50.02(77)	0.14(2)	0	0	0	0.05(2)	0
	opx	54.81(40)	0.04(1)	4.58(33)	0.87(6)	5.9(12)	0.12(2)	32.79(31)	1.12(2)	0.02(1)	0	0	0	0
	sp	0.23(17)	0.15(2)	40.95(12)	27.9(12)	12.14(27)	0.13(2)	18.65(64)	0.08(3)	0	0	0	0.01(1)	0
W10	gl	44.81(21)	0.47(2)	13.73(5)	0.19(1)	7.96(16)	0.12(2)	14.93(9)	8.68(9)	1.05(5)	0.03(1)	0.24(2)	0.03(2)	7.76(26)
	ol	40.84(22)	0.01(1)	0.06(1)	0.13(3)	9.22(19)	0.10(1)	48.77(45)	0.12(3)	0	0	0	0.02(2)	0
	sp	0.15(1)	0.20(2)	28.49(72)	40.3(66)	13.1(17)	0.17(1)	17.54(27)	0.10(4)	0	0	0	0	0
W11	quench	42.14(88)	0.56(6)	15.00(34)	0.07(1)	7.35(14)	0.11(2)	10.4(32)	9.54(15)	1.06(8)	0.08(1)	0.30(3)	0.04(2)	8.38
	ol	40.21	0	0.04	0.06	11.39	0.14	46.74	0.1	0	0	0	0.04	0
	opx	53.95	0.08	4.49	0.95	7.07	0.09	31.11	1	0	0	0	0	0
W12	glass	43.49(27)	0.65(2)	17.21(1)	0.04(2)	7.67(18)	0.11(2)	9.57(6)	10.62(7)	1.57(8)	0.05(1)	0.31(1)	0.01(1)	8.69(39)
	ol	39.66(23)	0.01(1)	0.06(4)	0.03(1)	12.53(20)	0.14(2)	46.66(16)	0.16(2)	0	0	0	0.05(2)	0
	opx	53.24(45)	0.09(1)	6.38(29)	0.41(8)	7.8(10)	0.13(2)	30.21(27)	1.34(7)	0.02(1)	0	0	0	0
	cpx	51.52(27)	0.18(1)	5.68(32)	0.37(5)	4.36(14)	0.07(2)	17.36(18)	19.62(38)	0.35(4)	0	0	0	0
W13	quench	39.76(90)	0.58(2)	14.63(4)	0.07(2)	8.16(15)	0.10(2)	10.76(51)	9.83(18)	1.04(12)	0.07(1)	0.29(1)	0.02(1)	10.07
	opx	53.85(33)	0.06(1)	5.43(3)	0.52(9)	7.19(13)	0.12(2)	31.29(39)	1.2(7)	0.01(1)	0	0	0	0
	gt	41.29(28)	0.13(1)	22.82(21)	1.38(9)	7.96(14)	0.21(3)	19.09(37)	6.7(11)	0.01(1)	0	0	0	0

Table 3(cont.). Experimental products

exp.	phase	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	NiO	H ₂ O
W18	quench	48.09(17)	0.5(1)	14.55(8)	0.17(2)	8.5(13)	0.11(2)	17.35(9)	9.37(9)	1.00(10)	0.11(2)	0.23(2)	0.01(1)	7.09
	opx	55.25(38)	0.04(1)	3.91(22)	0.96(6)	5.31(10)	0.10(5)	33.82(28)	0.83(1)	0.02(1)	0	0	0	0
W20	gl	46.43(34)	0.69(1)	16.76(9)	0.08(2)	8.83(19)	0.12(2)	13.27(14)	11.85(10)	1.25(7)	0.06(1)	0.35(2)	0	0
	opx	53.03(40)	0.09(1)	6.47(13)	0.50(2)	6.51(6)	0.08(1)	30.44(24)	2.21(5)	0.06(2)	0	0	0	0
	sp	0.28(4)	0.10(2)	61.87(64)	7.43(16)	8.47(21)	0.06(2)	21.64(64)	0.05(1)	0	0	0	0.02(2)	0
W21	gl	45.99(23)	0.77(2)	16.76(10)	0.09(3)	9.78(14)	0.12(2)	13.09(8)	11.29(10)	1.28(9)	0.06(1)	0.40(2)	0.01(1)	0
	opx	51.06(36)	0.09(1)	9.12(26)	0.46(2)	7.09(1)	0.09(2)	29.00(20)	2.27(6)	0.1(1)	0	0	0	0
	cpx	50.78(41)	0.13(2)	9.83(29)	0.50(2)	5.88(17)	0.11(2)	20.9(39)	11.68(49)	0.52(4)	0	0	0	0
	sp	0.35(3)	0.09(1)	62.87(59)	4.74(8)	9.1(10)	0.06(2)	22.07(25)	0.16(1)	0	0	0	0.01(1)	0
W22	gl	46.98(34)	0.57(2)	16.77(38)	0.11(3)	8.96(14)	0.13(2)	15.27(23)	10.00(16)	0.87(10)	0.08(2)	0.26(2)	0.00(1)	8.1(13)
	ol	41.00(25)	0.02(1)	0.05(1)	0.05(1)	10.01(21)	0.09(2)	48.99(21)	0.11(1)	0.01(1)	0	0	0	0
	opx	55.04(53)	0.06(1)	4.72(10)	0.83(1)	6.24(26)	0.12(3)	32.41(23)	0.96(8)	0.02(1)	0	0	0	0
W3.31	gl	44.53(27)	0.46(2)	13.56(15)	0.16(4)	8.32(20)	0.06(6)	16.01(14)	8.10(14)	0.95(6)	0.03(2)	0.3(4)	0.09(4)	7.43(38)
	ol	40.85(59)	0.00(1)	0.05(2)	0.07(1)	9.01(23)	0.08(3)	49.56(42)	0.12(1)	0	0	0	0.1	0
	opx	55.44(53)	0.05(1)	3.63(24)	0.83(1)	5.61(13)	0.08(1)	33.40(5)	0.79(3)	0.02(2)	0	0	0	0
W3.32	vgl	45.47(48)	0.63(2)	15.50(20)	0.11(4)	8.76(17)	0.08(5)	16.03(15)	11.22(11)	1.34(8)	0.02(2)	0.43(4)	0.14(5)	0
	ol	40.71(28)	0.01(1)	0.18(6)	0.08(1)	9.14(16)	0.08(3)	49.72(41)	0.27(1)	0	0	0	0.08(1)	0
	opx	53.45(35)	0.08(1)	6.95(40)	0.43(3)	5.66(19)	0.09(2)	31.28(18)	1.91(5)	0.09(1)	0	0	0	0

Table 3(cont.). Experimental products

exp.	phase	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	NiO	H ₂ O
W3.33	gl	42.49(28)	0.52(2)	14.34(13)	0.10(2)	8.65(19)	0.09(7)	14.24(13)	9.33(12)	1.05(8)	0.03(2)	0.34(4)	0.10(5)	8.73(60)
	ol	40.47(36)	0.01(1)	0.05(1)	0.05(2)	10.03(13)	0.1(2)	48.71(39)	0.13(2)	0	0	0	0	0
	opx	54.47(35)	0.05(1)	4.82(24)	0.76(11)	6.28(21)	0.09(2)	32.42(31)	0.95(3)	0.02(2)	0	0	0	0
W3.36	gl	46.47(37)	0.56(2)	14.68(16)	0.13(2)	9.55(16)	0.08(2)	17.00(18)	10.01(10)	1.13(11)	0.03(1)	0.28(3)	0.01(1)	0
	ol	40.29(36)	0.00(1)	0.18(2)	0.09(2)	9.4(20)	0.07(2)	49.22(30)	0.26(1)	0	0	0	0	0
	opx	53.94(52)	0.08(1)	6.44(62)	0.45(4)	5.83(8)	0.04(4)	31.32(21)	1.6(7)	0.07(1)	0	0	0	0
A1.2	gl	57.8(30)	0.73(1)	17.57(10)	0.00(1)	4.07(16)	0.04(1)	6.16(6)	9.03(11)	3.19(14)	0.58(2)	0.12(2)	0.00(1)	0
	opx	54.26(40)	0.14(2)	4.69(53)	0.24(2)	6.7(14)	0.09(1)	30.87(39)	2.16(8)	0.1(1)	0	0	0	0
	cpx	52.22(45)	0.24(2)	5.84(38)	0.32(2)	4.59(14)	0.10(2)	19.61(34)	15.77(55)	0.62(4)	0	0	0	0

Table 4. Melt reactions

Exp. pair	P (GPa)	T difference (°C)	melt	reaction coefficients			sum
				ol	opx	cpx	
BK2.30-24	1.5	1275-1300	1	-0.11	-0.22	-0.63	-0.97
BK2.19-20	2.2	1350-1400	1	0.16	-1.07	-	-0.90
W12-9	1.5	1175-1200	1	-0.04	-0.61	-0.38	-1.02
W9-10	1.5	1200-1250	1	-0.18	-0.81	-	-0.99
W22-13	2.0	1200-1250	1	-0.15	-0.87	-	-1.02
W33-31	2.0	1275-1300	1	0.24	-1.24	-	-1.00
W32-36	2.0	1450-1475	1	0.13	-1.15	-	-1.02

Table 5a. Linear fits to olivine partition coefficients using full data set

	const	1/T	P	H ₂ O	const	1/T	H ₂ O	const	P	H ₂ O	const	1/T
SiO ₂	-0.230	118.4	0.001	0.483	-0.064	-84.89	0.529	-0.138	0.001	0.516	-0.341	354.0
rel. Error	0.233	0.583	0.272	0.063	0.528	0.571	0.062	0.039	0.270	0.047	0.247	0.331
R ² ,F	0.932	630.1			0.906	667.6		0.927	873.0		0.205	35.78
TiO ₂	-3.045	2095	-0.007	0.353	-3.531	2610	0.249	-1.215	-0.026	0.796	-3.919	3154
rel. Error	1.075	1.777	5.845	2.651	0.454	0.831	2.830	0.312	0.943	0.636	0.296	0.481
R ² ,F	0.296	5.878			0.294	8.940		0.274	8.117		0.285	17.57
Al ₂ O ₃	0.020	-3056	0.003	0.141	0.559	-3726	0.289	-2.383	0.014	-0.606	0.392	-3464
rel. Error	41.201	0.343	1.425	2.453	0.547	0.118	0.960	0.027	0.143	0.444	0.675	0.106
R ² ,F	0.796	124.9			0.792	184.5		0.725	127.8		0.783	353.0
Cr ₂ O ₃	-1.156	1460	-0.002	-0.188	-1.431	1802	-0.264	-0.049	-0.007	0.218	-1.282	1562.6
rel. Error	0.669	0.695	2.386	2.294	0.286	0.334	1.487	1.621	0.389	1.544	0.270	0.312
R ² ,F	0.279	14.30			0.274	21.16		0.226	16.35		0.263	40.28
FeO	-1.512	2064	0.003	0.014	-1.138	1605	0.116	0.078	-0.005	0.586	-1.199	1702
rel. Error	0.105	0.099	0.358	6.552	0.083	0.084	0.780	0.394	0.224	0.235	0.069	0.067
R ² ,F	0.891	374.6			0.867	450.3		0.577	94.27		0.861	860.6
MnO	-1.441	1817	0.002	0.079	-1.196	1517	0.143	-0.042	-0.005	0.564	-1.269	1633
rel. Error	0.346	0.355	1.727	3.543	0.222	0.253	1.798	1.322	0.391	0.435	0.183	0.197
R ² ,F	0.449	34.51			0.443	50.99		0.314	29.32		0.438	100.6
MgO	-1.240	2366	0.003	-0.115	-0.848	1885	-0.007	0.583	-0.006	0.541	-0.844	1879
rel. Error	0.115	0.078	0.307	0.706	0.103	0.067	11.651	0.057	0.203	0.277	0.089	0.055
R ² ,F	0.925	561.1			0.902	634.3		0.570	91.61		0.902	1278
CaO	-1.490	-175	0.000	-0.195	-1.445	-229.2	-0.183	-1.624	0.001	-0.244	-1.350	-381.2
rel. Error	0.173	1.901	4.919	0.750	0.095	0.867	0.728	0.016	0.960	0.466	0.090	0.443
R ² ,F	0.171	9.401			0.170	14.11		0.164	13.55		0.125	19.92
Na ₂ O	-1.490	-175	0.000	-0.195	-1.445	-229.2	-0.183	-1.624	0.001	-0.244	-1.350	-381.2
rel. Error	0.173	1.901	4.919	0.750	0.095	0.867	0.728	0.016	0.960	0.466	0.090	0.443
R ² ,F	0.171	9.401			0.170	14.11		0.164	13.55		0.125	19.92

Table 5b. Linear fits to orthopyroxene partition coefficients using full data set

	const	1/T	P	H ₂ O	const	1/T	H ₂ O	const	P	H ₂ O	const	1/T
SiO ₂	-0.075	-72.42	0.000	0.547	-0.011	-154.9	0.566	-0.128	0.001	0.527	-0.438	567.1
rel. Error	1.476	2.039	1.582	0.095	4.121	0.451	0.076	0.082	0.440	0.058	0.290	0.331
R ² ,F	0.974	478.8			0.973	705.8		0.974	718.0		0.482	37.28
TiO ₂	-0.884	-1392	0.000	1.405	-0.889	-1388	1.405	-1.901	0.003	1.040	-3.455	2446
rel. Error	4.966	4.220	351.4	1.283	3.979	3.671	1.140	0.445	16.13	0.826	0.669	1.241
R ² ,F	0.567	2.624			0.567	4.592		0.543	4.163		0.302	3.455
Al ₂ O ₃	-0.096	-2908			0.641	-3874	0.269	-2.221	0.011	-0.859	0.425	-3509
rel. Error	11.476	0.514	1.368	19.627	0.688	0.184	1.604	0.054	0.225	0.393	0.647	0.116
R ² ,F	0.896	106.6			0.890	154.0		0.853	110.1		0.886	301.7
Cr ₂ O ₃	-2.276	2902	0.003	-0.763	-1.660	2106	-0.581	-0.125	-0.005	0.062	-1.221	1365
rel. Error	0.272	0.286	0.922	0.383	0.154	0.194	0.432	0.712	0.352	4.182	0.173	0.229
R ² ,F	0.807	53.06			0.783	70.30		0.554	24.19		0.661	77.91
FeO	-1.420	1970	0.002	0.004	-1.047	1489	0.114	0.040	-0.004	0.564	-1.133	1635
rel. Error	0.131	0.126	0.457	19.921	0.085	0.095	0.764	1.209	0.269	0.252	0.056	0.058
R ² ,F	0.982	702.8			0.973	706.9		0.863	122.6		0.968	1223
MnO	-1.468	1902	0.001	-0.019	-1.194	1548	0.062	-0.058	-0.004	0.521	-1.240	1627
rel. Error	0.463	0.480	2.275	16.981	0.224	0.276	4.236	1.340	0.400	0.434	0.143	0.161
R ² ,F	0.803	51.48			0.798	77.23		0.710	47.73		0.797	157.3
MgO	-1.044	2110	0.002	-0.039	-0.671	1629	0.071	0.520	-0.004	0.561	-0.725	1720
rel. Error	0.178	0.119	0.459	2.274	0.133	0.087	1.230	0.100	0.259	0.269	0.084	0.052
R ² ,F	0.984	767.3			0.975	774.6		0.859	118.9		0.974	1483
CaO	-0.757	-1211	-0.002	0.118	-1.223	-610.6	-0.019	-1.655	0.001	-0.226	-1.208	-635.2
rel. Error	0.675	0.567	1.010	2.053	0.171	0.548	10.645	0.034	0.944	0.718	0.115	0.323
R ² ,F	0.544	15.11			0.496	19.17		0.391	12.52		0.495	39.244
Na ₂ O	-0.757	-1211	-0.002	0.118	-1.223	-610.6	-0.019	-1.655	0.001	-0.226	-1.208	-635.2
rel. Error	0.675	0.567	1.010	2.053	0.171	0.548	10.645	0.034	0.944	0.718	0.115	0.323
R ² ,F	0.544	15.11			0.496	19.17		0.391	12.52		0.495	39.244

Table 5c. Linear fits to olivine partition coefficients using Parman and Walter data set

	const	1/T	P	H ₂ O	const	1/T	H ₂ O	const	P	H ₂ O	const	1/T
SiO ₂	-0.075	-72.42	0.000	0.547	-0.011	-154.9	0.566	-0.128	0.001	0.527	-0.438	567.1
rel. Error	1.476	2.039	1.582	0.095	4.121	0.451	0.076	0.082	0.440	0.058	0.290	0.331
R ² ,F	0.974	478.8			0.973	705.8		0.974	718.0		0.482	37.28
TiO ₂	-0.884	-1392	0.000	1.405	-0.889	-1388	1.405	-1.901	0.003	1.040	-3.455	2446
rel. Error	4.966	4.220	351.4	1.283	3.979	3.671	1.140	0.445	16.13	0.826	0.669	1.241
R ² ,F	0.567	2.624			0.567	4.592		0.543	4.163		0.302	3.455
Al ₂ O ₃	-0.096	-2908	0.003	0.027	0.641	-3874	0.269	-2.221	0.011	-0.859	0.425	-3509
rel. Error	11.476	0.514	1.368	19.627	0.688	0.184	1.604	0.054	0.225	0.393	0.647	0.116
R ² ,F	0.896	106.6			0.890	154.0		0.853	110.1		0.886	301.7
Cr ₂ O ₃	-2.276	2902	0.003	-0.763	-1.660	2106	-0.581	-0.125	-0.005	0.062	-1.221	1365
rel. Error	0.272	0.286	0.922	0.383	0.154	0.194	0.432	0.712	0.352	4.182	0.173	0.229
R ² ,F	0.807	53.06			0.783	70.30		0.554	24.19		0.661	77.91
FeO	-1.420	1970	0.002	0.004	-1.047	1489	0.114	0.040	-0.004	0.564	-1.133	1635
rel. Error	0.131	0.126	0.457	19.921	0.085	0.095	0.764	1.209	0.269	0.252	0.056	0.058
R ² ,F	0.982	702.8			0.973	706.9		0.863	122.6		0.968	1223
MnO	-1.468	1902	0.001	-0.019	-1.194	1548	0.062	-0.058	-0.004	0.521	-1.240	1627
rel. Error	0.463	0.480	2.275	16.98	0.224	0.276	4.236	1.340	0.400	0.434	0.143	0.161
R ² ,F	0.803	51.48			0.798	77.23		0.710	47.73		0.797	157.3
MgO	-1.044	2110	0.002	-0.039	-0.671	1629	0.071	0.520	-0.004	0.561	-0.725	1720
rel. Error	0.178	0.119	0.459	2.274	0.133	0.087	1.230	0.100	0.259	0.269	0.084	0.052
R ² ,F	0.984	767.3			0.975	774.6		0.859	118.9		0.974	1483
CaO	-0.757	-1211	-0.002	0.118	-1.223	-610.6	-0.019	-1.655	0.001	-0.226	-1.208	-635.2
rel. Error	0.675	0.567	1.010	2.053	0.171	0.548	10.65	0.034	0.944	0.718	0.115	0.323
R ² ,F	0.544	15.11			0.496	19.17		0.391	12.52		0.495	39.24
Na ₂ O	-0.757	-1211	-0.002	0.118	-1.223	-610.6	-0.019	-1.655	0.001	-0.226	-1.208	-635.2
rel. Error	0.675	0.567	1.010	2.053	0.171	0.548	10.65	0.034	0.944	0.718	0.115	0.323
R ² ,F	0.544	15.11			0.496	19.17		0.391	12.52		0.495	39.24

Table 5d. Linear fits to orthopyroxene partition coefficients using Parman and Walter data set

	const	1/T	P	H ₂ O	const	1/T	H ₂ O	const	P	H ₂ O	const	1/T
SiO ₂	0.258	-325	0.000	0.652	0.238	-299	0.646	0.012	0.001	0.561	-0.349	641
rel. Error	0.545	0.568	6.022	0.097	0.279	0.332	0.078	1.421	0.501	0.078	0.683	0.520
R ² ,F	0.975	347			0.975	537		0.962	359		0.348	15.49
TiO ₂	-3.081	3013	0.001	-0.775	-2.873	2753	-0.713	-0.794	-0.009	0.067	-2.225	1715
rel. Error	0.385	0.516	4.999	0.686	0.194	0.304	0.595	0.179	0.476	5.647	0.212	0.386
R ² ,F	0.646	16.4			0.644	25.27		0.438	10.91		0.493	28.15
Al ₂ O ₃	-2.185	2161	0.010	-0.655	-0.433	-29.57	-0.132	-0.545	0.003	-0.052	-0.313	-222
rel. Error	0.787	1.044	0.862	1.178	2.055	45.08	5.115	0.322	1.598	9.050	2.025	3.988
R ² ,F	0.186	2.052			0.015	0.208		0.069	1.041		0.009	0.263
Cr ₂ O ₃	-4.436	6956	0.007	-1.010	-3.290	5508	-0.645	0.794	-0.016	1.025	-2.682	4531
rel. Error	0.369	0.312	1.257	0.747	0.244	0.221	0.955	0.315	0.460	0.637	0.220	0.182
R ² ,F	0.860	53.0			0.845	73.64		0.625	22.49		0.819	126
FeO	-1.981	2509	0.003	-0.189	-1.473	1873	-0.037	-0.077	-0.005	0.512	-1.439	1819
rel. Error	0.217	0.225	0.742	1.020	0.155	0.183	4.662	1.077	0.457	0.431	0.113	0.125
R ² ,F	0.924	110			0.903	130		0.690	31.10		0.902	267
MnO	-2.174	2851	0.005	-0.228	-1.376	1853	0.010	-0.010	-0.005	0.568	-1.385	1868
rel. Error	0.493	0.493	1.179	2.106	0.386	0.430	40.578	13.23	0.811	0.613	0.272	0.282
R ² ,F	0.680	19.1			0.644	25.35		0.475	12.66		0.644	52.5
MgO	-1.430	2441	0.002	-0.136	-1.030	1942	-0.017	0.423	-0.006	0.546	-1.015	1917
rel. Error	0.286	0.219	0.898	1.344	0.203	0.162	9.266	0.190	0.410	0.391	0.147	0.109
R ² ,F	0.937	133			0.924	171		0.732	38.21		0.924	354
CaO	-0.405	-527	0.002	0.031	-0.114	-890	0.117	-0.805	0.003	-0.117	-0.221	-719
rel. Error	2.150	2.168	2.630	12.749	3.618	0.697	2.676	0.105	0.713	1.926	1.342	0.577
R ² ,F	0.332	4.466			0.317	6.485		0.309	6.274		0.302	12.56
Na ₂ O	1.041	-3413	0.007	-0.143	2.194	-4865	0.213	-1.548	0.018	-1.097	2.003	-4560
rel. Error	1.257	0.503	1.009	4.052	0.289	0.195	2.267	0.096	0.246	0.377	0.229	0.142
R ² ,F	0.905	79.4			0.889	104		0.841	68.94		0.886	209

Table 6. Comparison of predicted and observed melt compositions

experiment	30.14 ¹	model	60.03 ¹	model	BK2.20	model	W3.31	model	W3.33	model	T4243 ²	model	T4330 ²	model
P(GPa)	3.0	3.0	6.0	6.0	2.2	2.2	2.0	2.0	2.0	2.0	1.0	1.0	1.0	1.0
T(C)	1540	1540	1770	1800	1350	1400	1300	1350	1275	1310	1400	1500	1440	1540
phase percent														
gl	24.4	22.6	49.7	51.8	76.3	76.2	72.5	67.5	62.7	62.9	-	26.2	-	30.5
ol	50.5	58.5	41.6	40.8	4.1	17.7	25.6	30.5	23.2	31.0	-	63.9	-	63.9
opx	25.1	18.9	8.7	7.4	19.9	6.2	1.8	2.0	14	6.1	-	9.9	-	5.6
melt composition														
SiO ₂	46.91	46.25	46.9	46.4	43.06	46.78	44.53	44.28	42.49	43.46	51.4	49.88	51.6	50.79
TiO ₂	0.64	0.63	0.36	0.3	0.48	0.54	0.46	0.50	0.52	0.54	0.49	0.37	0.45	0.32
Al ₂ O ₃	12.46	12.68	8.79	6.96	8.19	5.62	13.56	14.17	14.34	14.98	12.04	12.22	10.98	10.97
FeO	8.86	8.94	9.87	9.96	11.34	10.69	8.32	7.92	8.65	7.77	7.23	7.22	7.64	7.49
MgO	18.22	17.16	26.48	28.74	16.26	15.09	16.01	13.71	14.24	12.41	16.23	16.09	17.9	17.65
CaO	10.86	11.02	6.8	6.07	11.37	12.36	8.10	8.94	9.33	9.53	10.59	10.50	9.44	9.52
Na ₂ O	0.82	0.86	0.43	0.41	0.56	0.76	0.95	1.14	1.05	1.23	1.05	1.03	0.84	0.90
K ₂ O	0.34	0.35	0.18	0.17	0.07	0.02	0.03	0.03	0.03	0.03	-	0.00	-	0.00
H ₂ O	0	0	0	0	8.11	7.47	7.43	8.90	8.73	9.61	-	0.00	-	0.00

¹ Experiment from Walter (1998)

² Experiment from Falloon and Danushevsky (2000)

Table 7. Wallrock reaction calculations

	85-41c	85-44	ol	opx	85-44 -0.31ol + 0.50opx
SiO ₂	56.19	51.60	40.32	54.80	56.16
TiO ₂	0.63	0.59	0.06	0.12	0.60
Al ₂ O ₃	14.82	15.95	0.02	4.70	15.21
Cr ₂ O ₃	0.00	0.16	0.08	0.37	0.37
FeO	4.91	8.08	9.80	6.39	6.69
MnO	0.00	0.11	0.12	0.10	0.18
MgO	10.29	11.30	49.80	32.80	9.96
CaO	9.40	9.43	0.06	0.71	7.98
Na ₂ O	3.02	2.59	0.00	0.10	2.21
K ₂ O	0.44	0.31	0.00	0.00	0.33

FIGURE CAPTIONS

Figure 1. Backscattered electron image of hydrous experiment W7 containing melt (now glass) and olivine. The melt has almost completely quenched to glass. A few quench crystals have nucleated on the walls of the capsule and on the olivine crystal. The experiment is 2mm across.

Figure 2. Backscattered electron image of hydrous experiment BK19 containing melt, olivine, and orthopyroxene. The melt has quenched to a mixture of pyroxene lathes and patches of vesiculated glass. Because the crystals and melt have segregated, the melt could be cut out and remelted (see text). The experiment is 2mm across.

Figure 3. Compositions of experimental melts and inferred phase boundaries plotted using the mineral components of Grove [Grove, 1993]. Projection is from plagioclase and H₂O. The ol-opx boundary shifts towards ol as pressure increases from 1.5 GPa (gray filled circles), to 2.0 and 2.2 GPa (open circles). The letters w and d after pressure labels refer to H₂O bearing, and anhydrous experiments, respectively. The upper four boundaries are for composition BK. The boundary farthest to the right is for composition A. All others are for composition W and its modified derivative, W3. H₂O shifts the ol-opx boundary away from ol, but the effect decreases as the ol content of the melt increases. Bulk compositions BK, W, and A are shown by filled circles.

Figure 4. Phase diagram for composition BK, with and without H₂O. Anhydrous results are shown by black lines and triangles. H₂O-undersaturated results are shown by

gray lines and squares. H_2O depresses the crystallization point of opx more than ol, and therefore shifts the liquidus ol-opx saturation point to higher pressures and lower temperatures.

Figure 5. Phase diagram for composition W, with and without H_2O . Anhydrous results are shown by black lines and triangles. H_2O -undersaturated results are shown by gray lines and squares.

Figure 6. Molar cation partition coefficients for ol-melt equilibrium versus $1/T$. a) SiO_2 , b) MgO and FeO, c) Al_2O_3 , d) Cr_2O_3 , e) CaO. Anhydrous data are shown as circles and hydrous data are shown as squares. Filled symbols are from experiments on composition BK and open symbols are for experiments on composition W and W3. FeO and MgO show excellent linear correlations. There is no evidence that H_2O or other bulk compositional parameters have much effect on FeO and MgO partitioning in high degree melts. In contrast, there is a clear break between the hydrous and anhydrous experiments for SiO_2 partitioning.

Figure 7. Molar cation partition coefficients for opx-melt equilibrium. a) SiO_2 , b) MgO and FeO, c) Al_2O_3 , d) Cr_2O_3 , e) CaO. Symbols are the same as for Fig. 6. Like ol, FeO and MgO D values for linear trends versus $1/T$, but SiO_2 does not.

Figure 8. SiO_2 mineral/melt partition coefficients plotted versus melt H_2O content for a) olivine and b) orthopyroxene. The data indicate that H_2O is the main control on SiO_2 partitioning. Symbols are the same as for Fig. 6.

Figure 9. SiO_2 mineral/melt partition coefficients recalculated leaving H_2O out of the melt composition for a) olivine and b) orthopyroxene. Here, SiO_2 partitioning shows little dependence on H_2O content or bulk composition. This supports a Toop and Samis type model in which SiO_2 and H_2O occupy different sites in the melt structure.

Figure 10. Predicted phase fractions for melt (solid line), ol (long dashed line), and opx (short dashed line) using fertile mantle composition. Calculations were performed for a) 3.0, b) 4.0, c) 5.0, and d) 6.0 GPa. Observed phase fractions for melt (solid circle), ol (open square), and opx (open circle) from experiments of Walter are shown for comparison [Walter, 1998].

Figure 11. Predicted phase fractions for a) composition BK and b) composition W3. Symbols are same as for Fig. 10.

Figure 12. Effect of H_2O on phase fractions and melt compositions. Predicted phase fractions for melting of fertile mantle at 1.0 GPa with a) 0 wt.% H_2O , b) 1.5 wt.% H_2O , c) 2.9 wt.% H_2O , and d) 5.9 wt.% H_2O . Symbols are same as for Fig. 10. e-j) Compositions of predicted melts (lines) and high magnesian andesites from Mt. Shasta (filled squares). Sample analyses from Baker et al. (1994). The H_2O contents of the highest and lowest degree melt along each melting curve is labeled on either side of the lines. Gray arrows show the effect of 10 wt.% fractionation of olivine and orthopyroxene. Sample 85-44 could be produced at 1.0 GPa by hydrous melting, while 85-41c cannot be produced by mantle melting. Neither can 85-41c be related to 85-44

by ol or opx fractionation alone. Melt/wallrock reaction could be responsible for the high SiO₂ in a magma as magnesian as 85-41c (see text).

Figure 13. Effect of source depletion on phase fractions and melt compositions.

Predicted phase fractions for hydrous mantle melting at 1.0 GPa using a) fertile lherzolite from the West River Kettle [Walter, 1998], b) depleted harzburgite from the Troodos ophiolite [Falloon and Danyushevsky, 2000], and c) moderately depleted composition which was estimated as a 50/50 mixture of the lherzolite and harzburgite compositions. Symbols are same as for Fig. 10. d-i) Predicted compositions of melts (lines) and of boninite samples from the North Tonga Trench (filled circles). Boninite analyses from Cameron et al. (1983). Gray arrow shows the effect of 10 wt.% ol fractionation. The most magnesian boninite could be produced at 1.0 GPa by hydrous melting at higher temperatures and from a more depleted source than Shasta HMA. H₂O content of highest and lowest extent melt are labeled on highly depleted mantle melting curve. Melt H₂O contents along other curves are similar.

Figure 14. Effect of pressure on phase fractions and melt compositions. Predicted phase fractions for hydrous mantle melting at a) 1.0 GPa and b) 6.0 GPa. Mantle composition is a depleted harzburgite. Symbols are same as for Fig. 10. c-h) Predicted compositions of melts (lines) and of komatiite chill margins from Barberton komatiites (filled diamonds). Data from Dann (unpub.). Gray arrow shows the effect of 20 wt.% ol fractionation. Melt H₂O contents vary from 3 to 7 wt.% along the melting curves. Low MgO compositions can be produced by hydrous melting at 3.0 to 3.7 GPa, while high MgO compositions cannot be produced by melting at any pressure.

FIGURES

Figure 1. Backscattered electron image of hydrous experiment W7

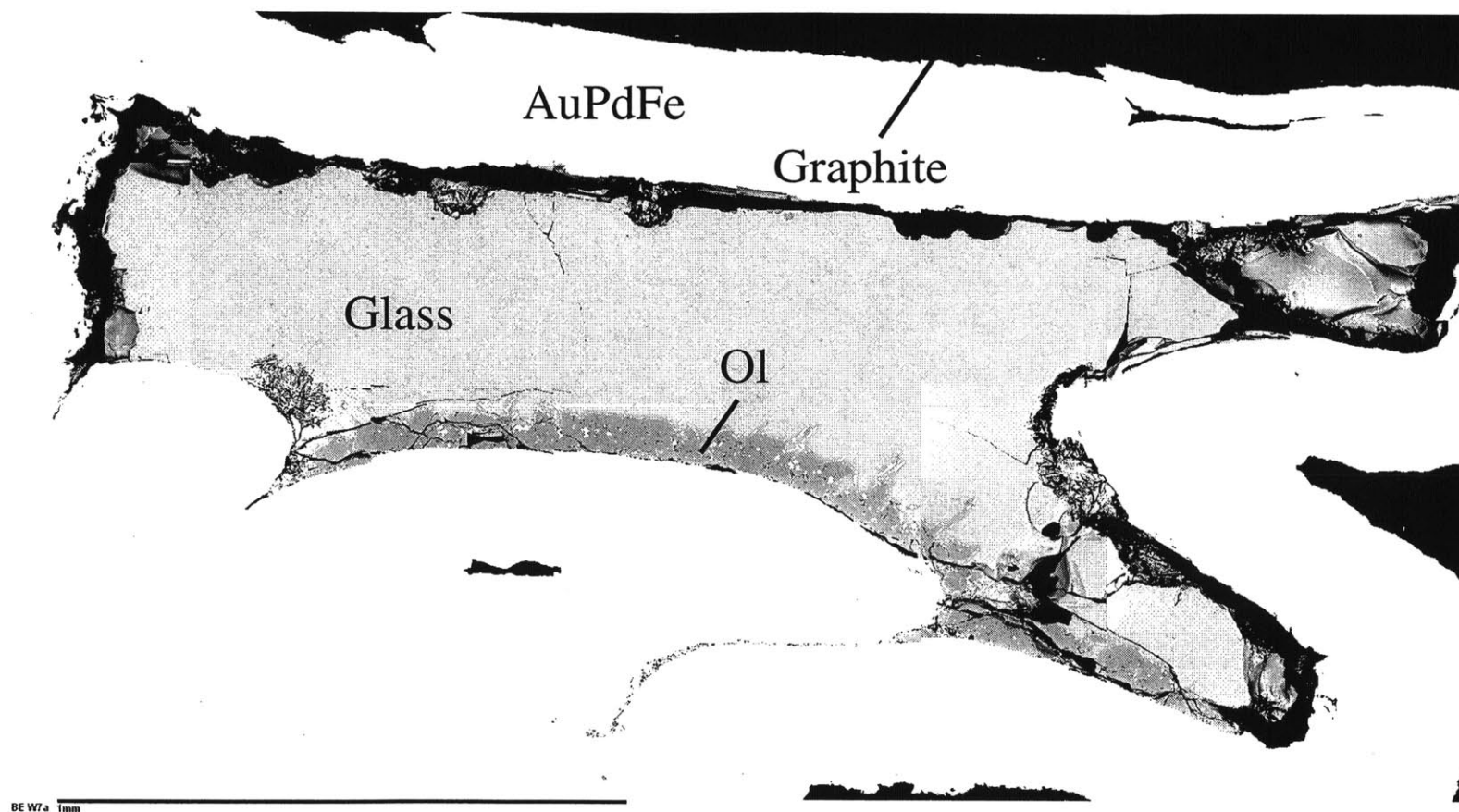


Figure 2. Backscattered electron image of unquenched melt in hydrous experiment BK19

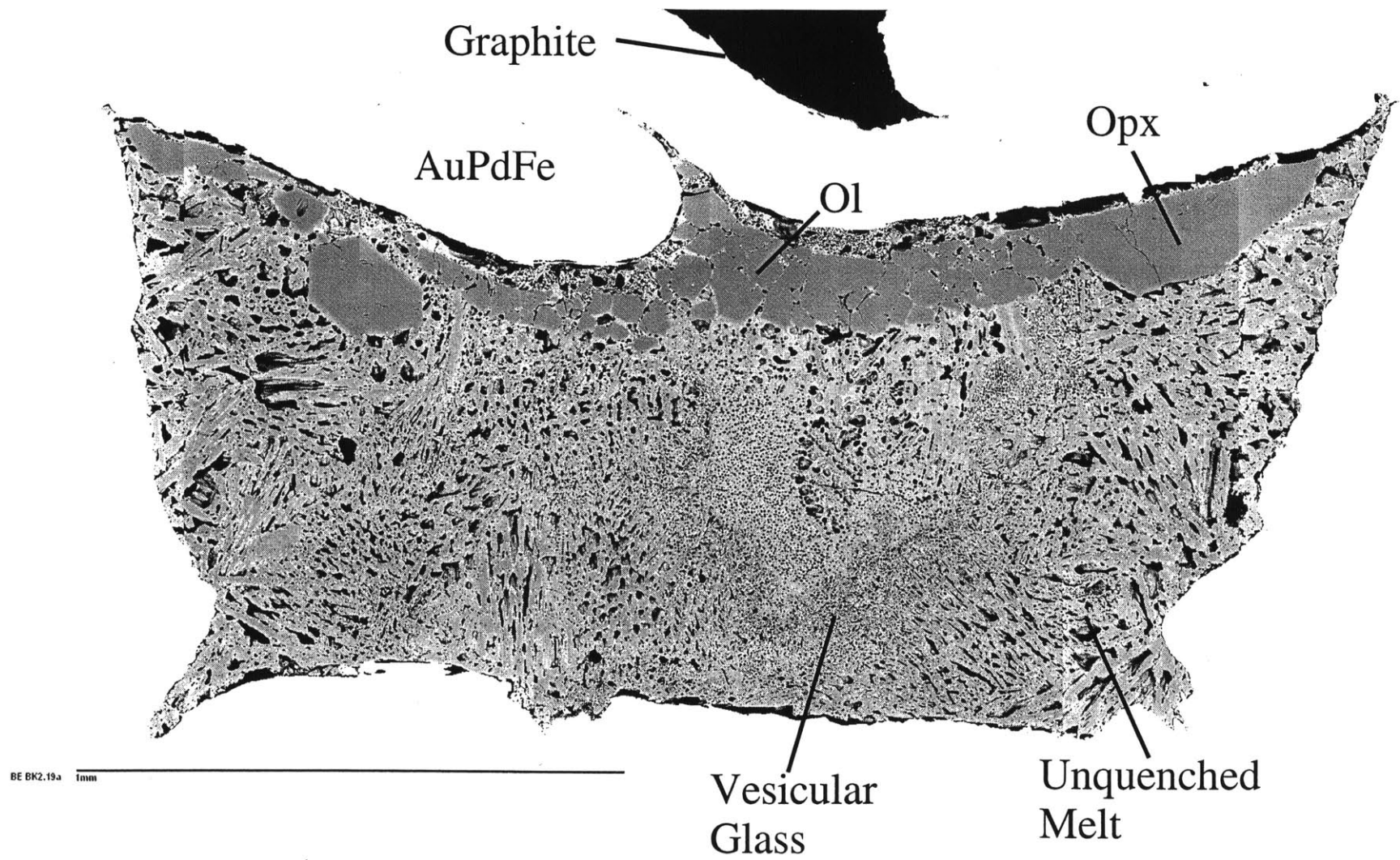


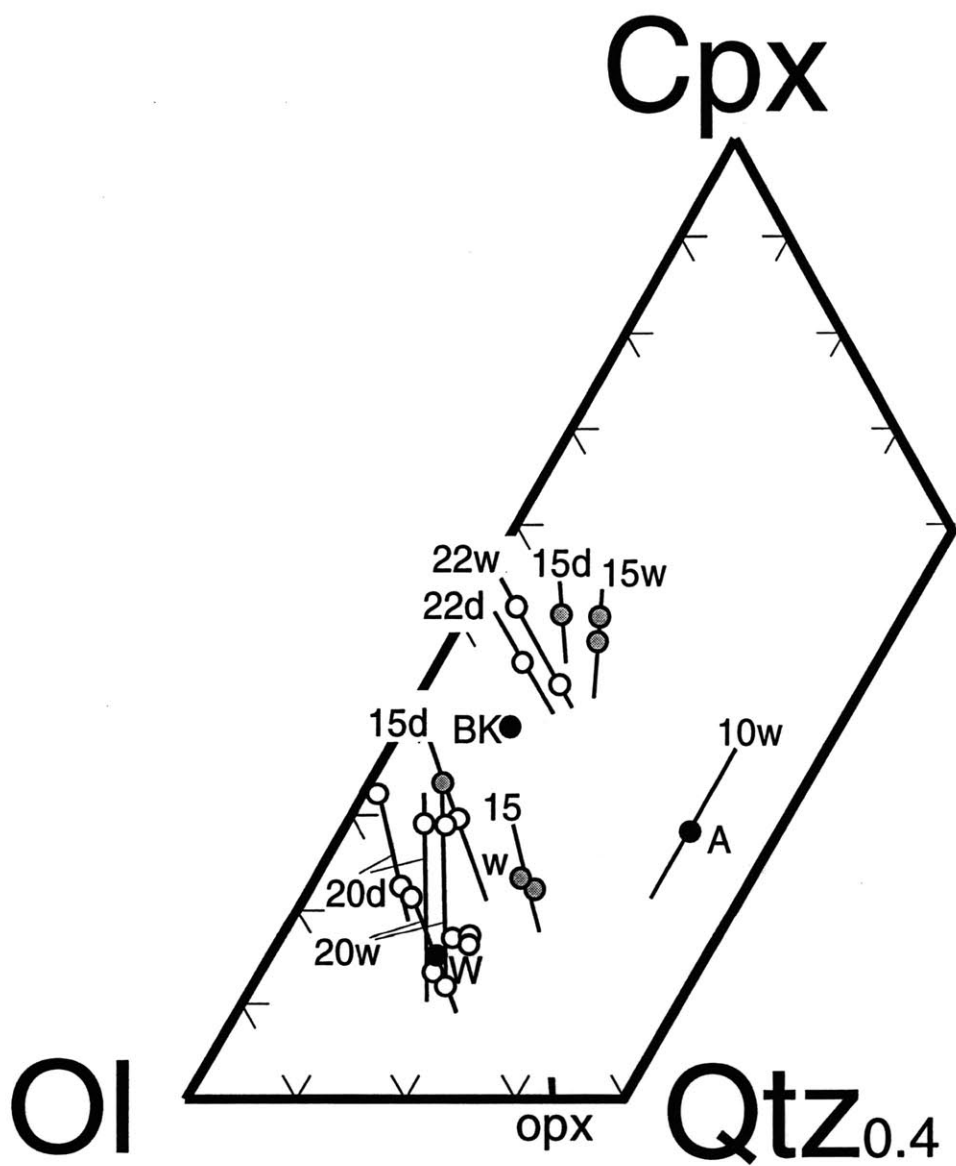
Figure 3. Experimental melt compositions

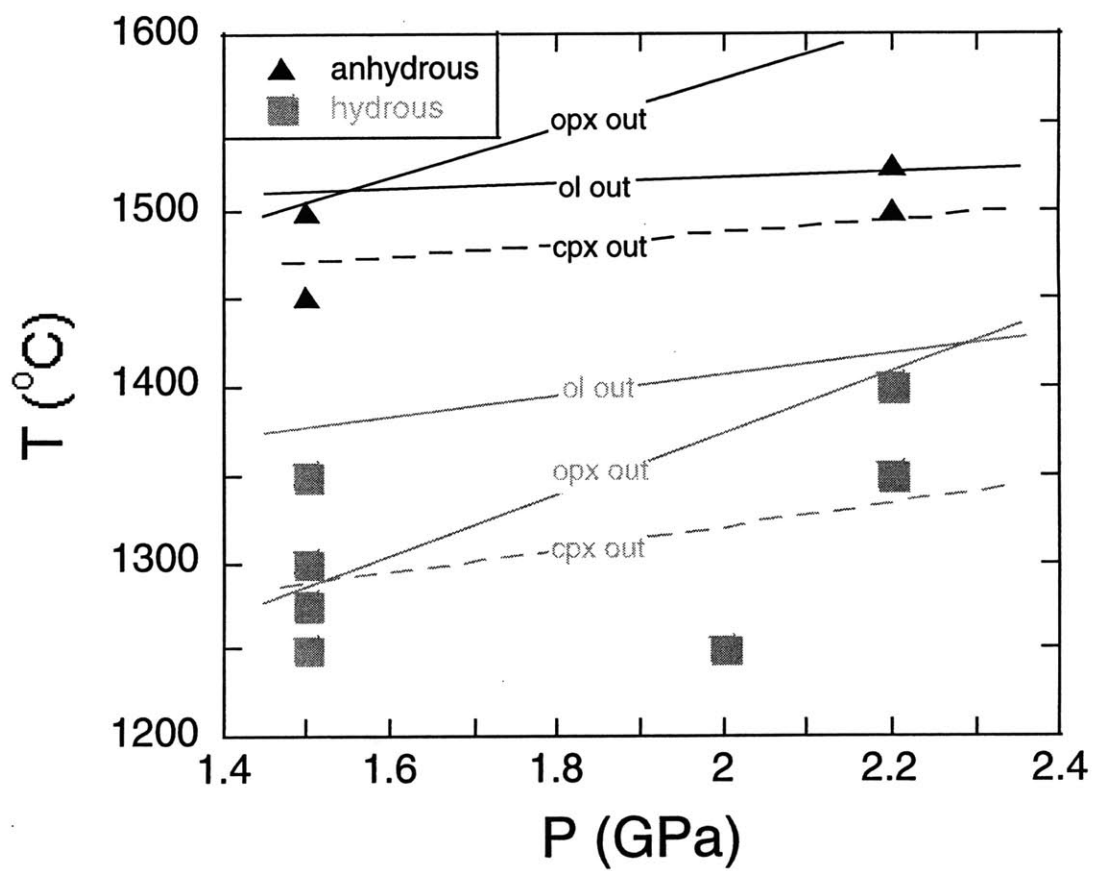
Figure 4. Anhydrous and hydrous phase diagram for composition BK

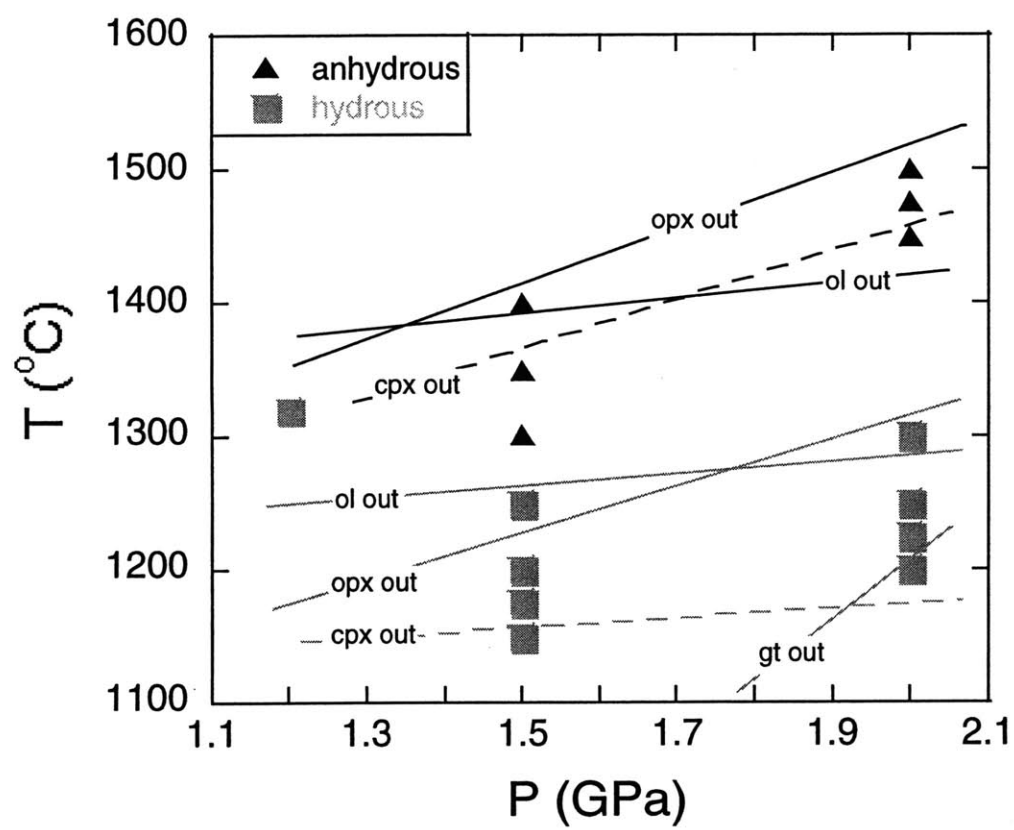
Figure 5. Anhydrous and hydrous phase diagram for composition W

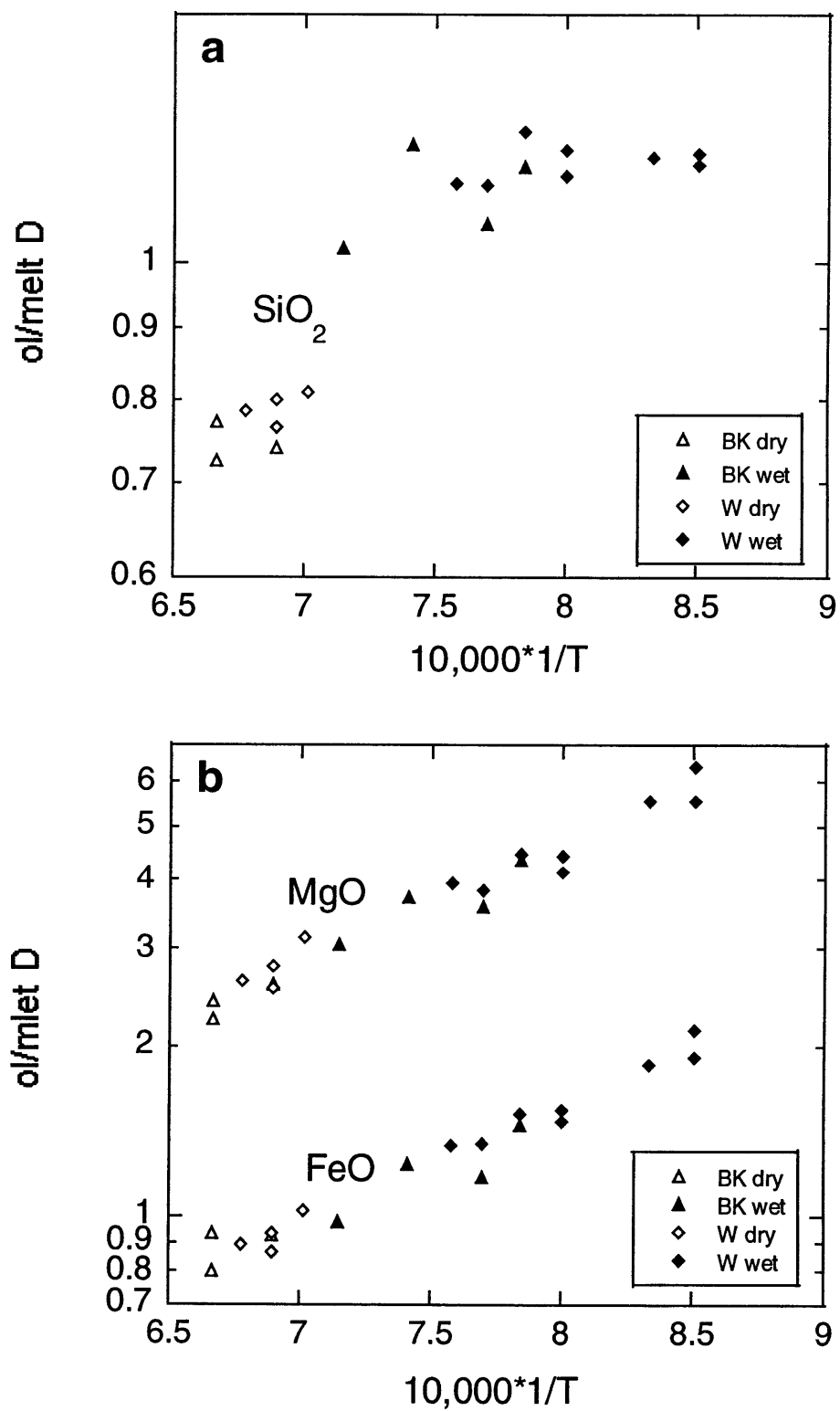
Figure 6. Anhydrous and hydrous ol/melt partition coefficients

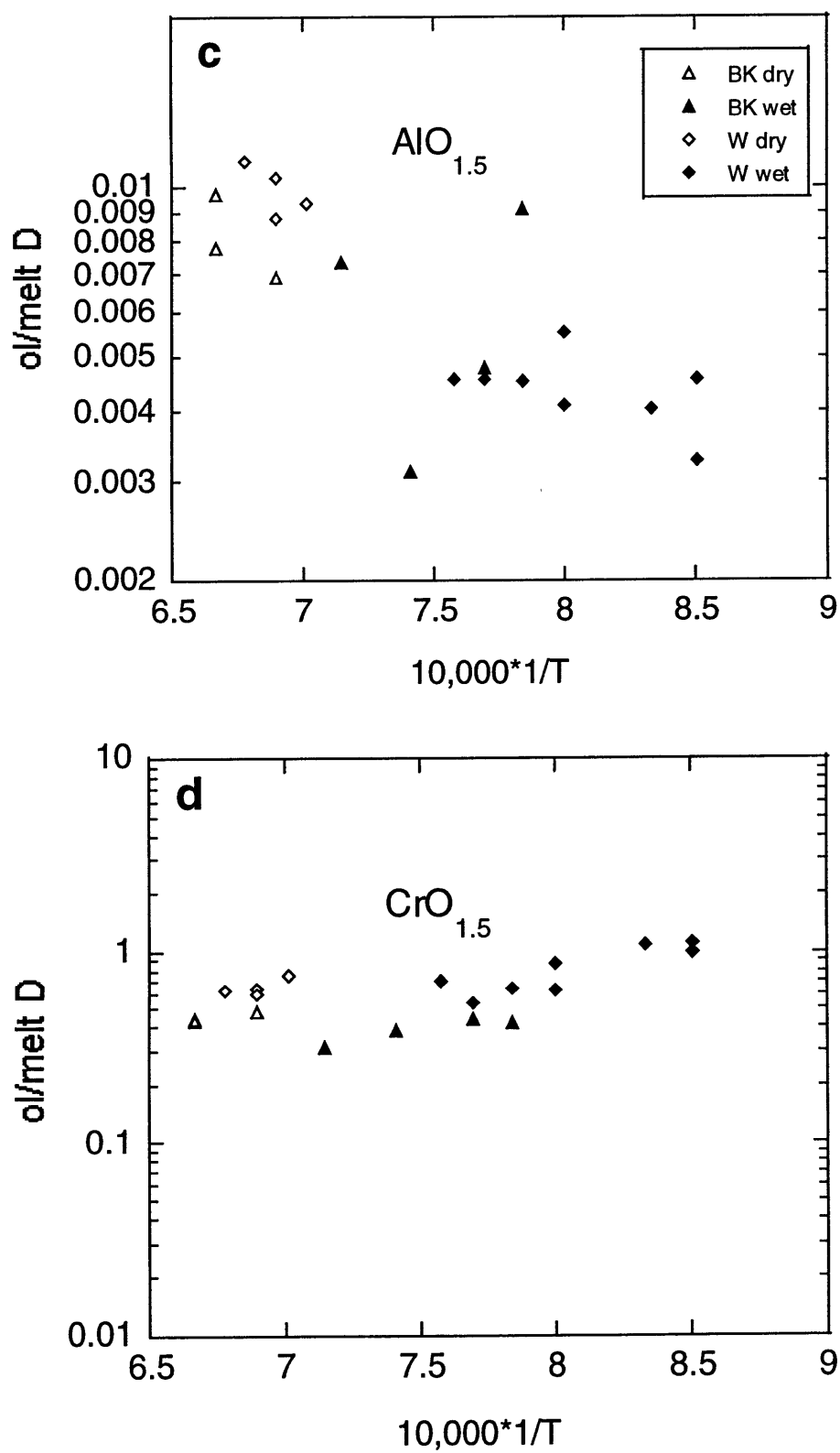
Figure 6(cont.). Anhydrous and hydrous ol/melt partition coefficients

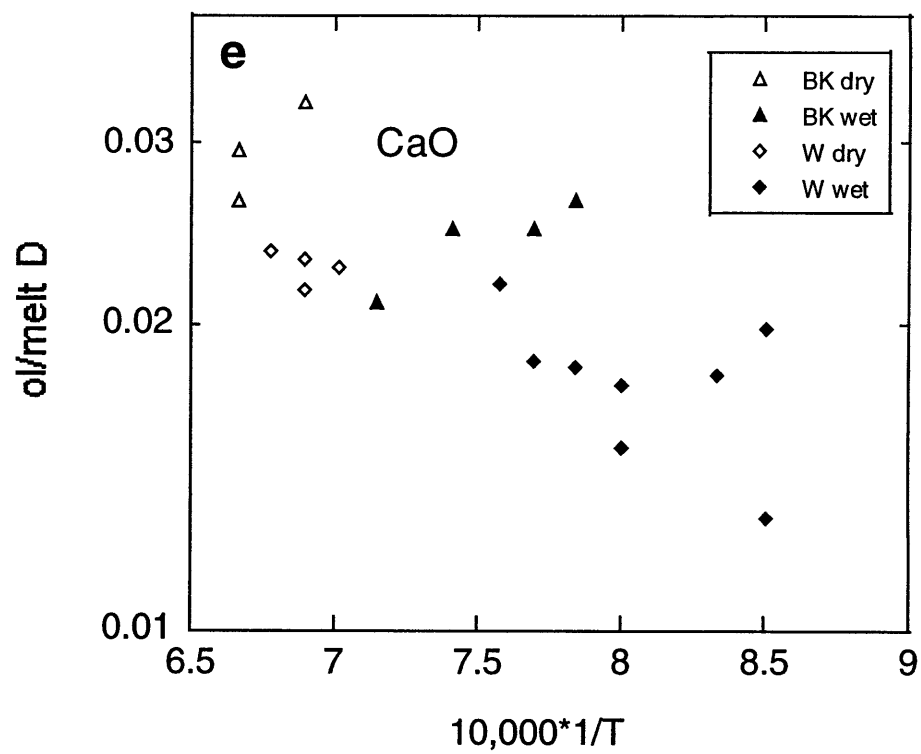
Figure 6(cont.). Anhydrous and hydrous ol/melt partition coefficients

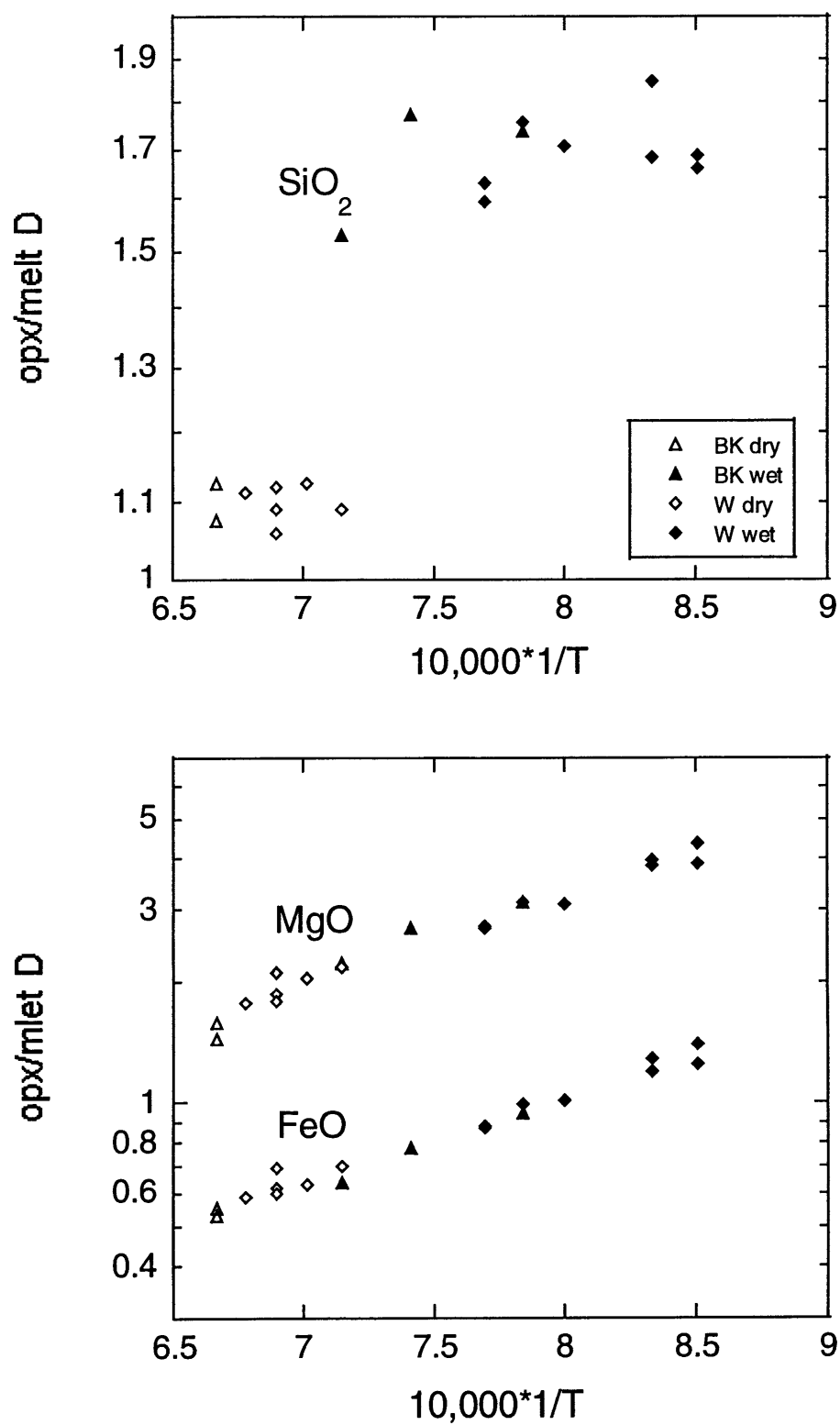
Figure 7. Anhydrous and hydrous opx /melt partition coefficients

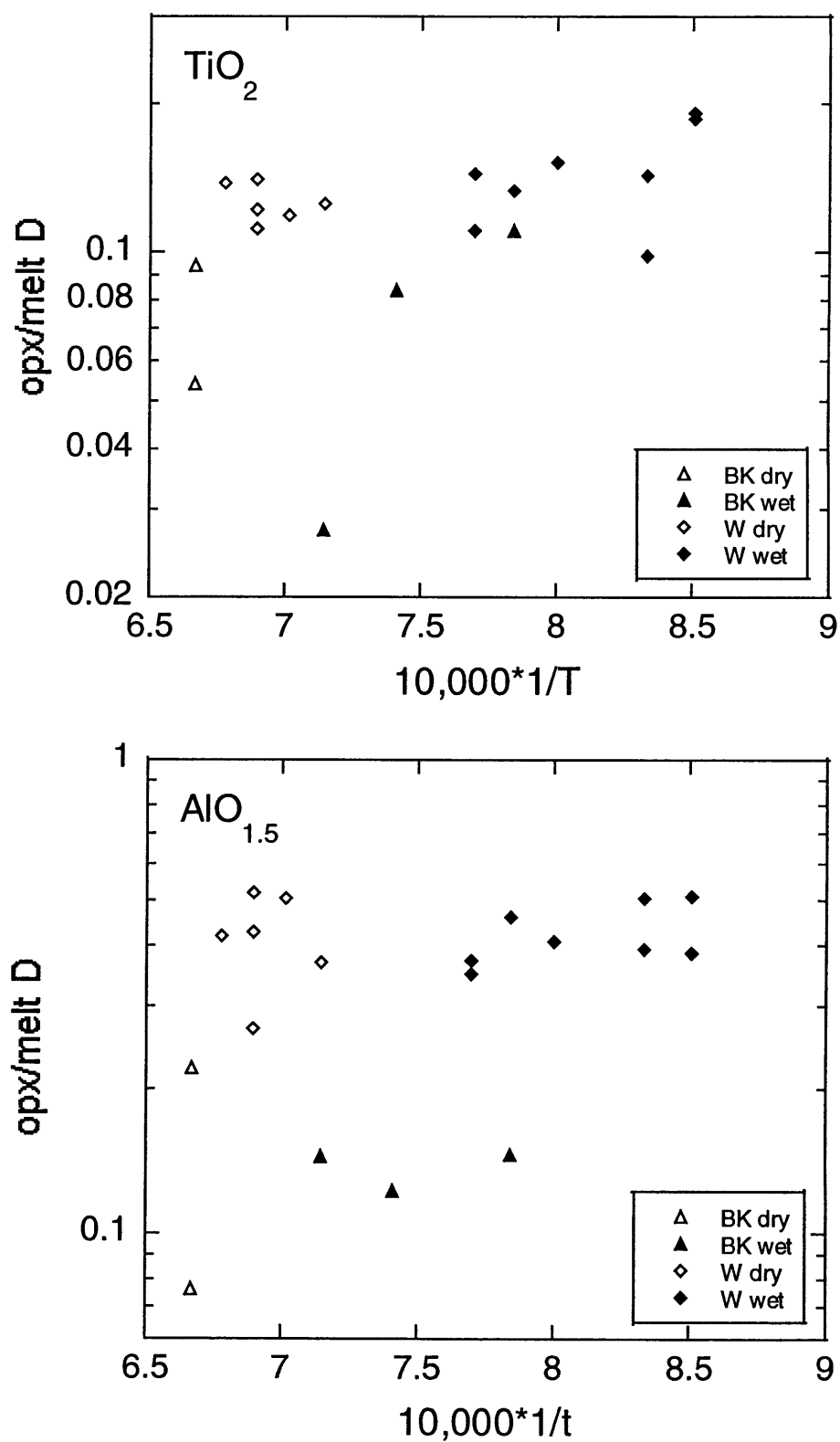
Figure 7(cont.). Anhydrous and hydrous opx /melt partition coefficients

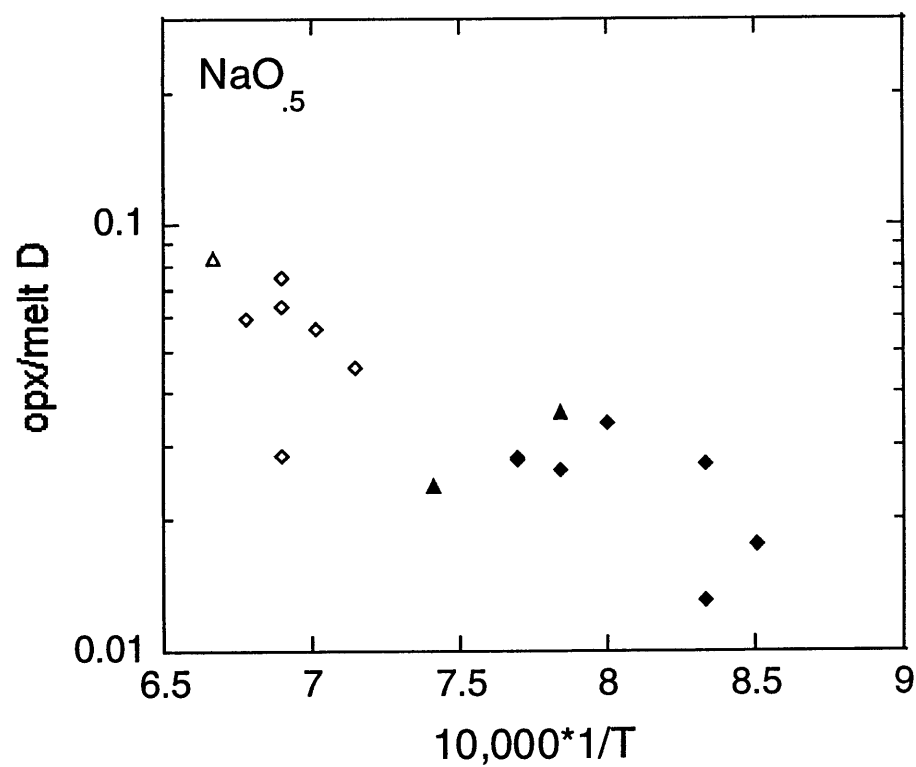
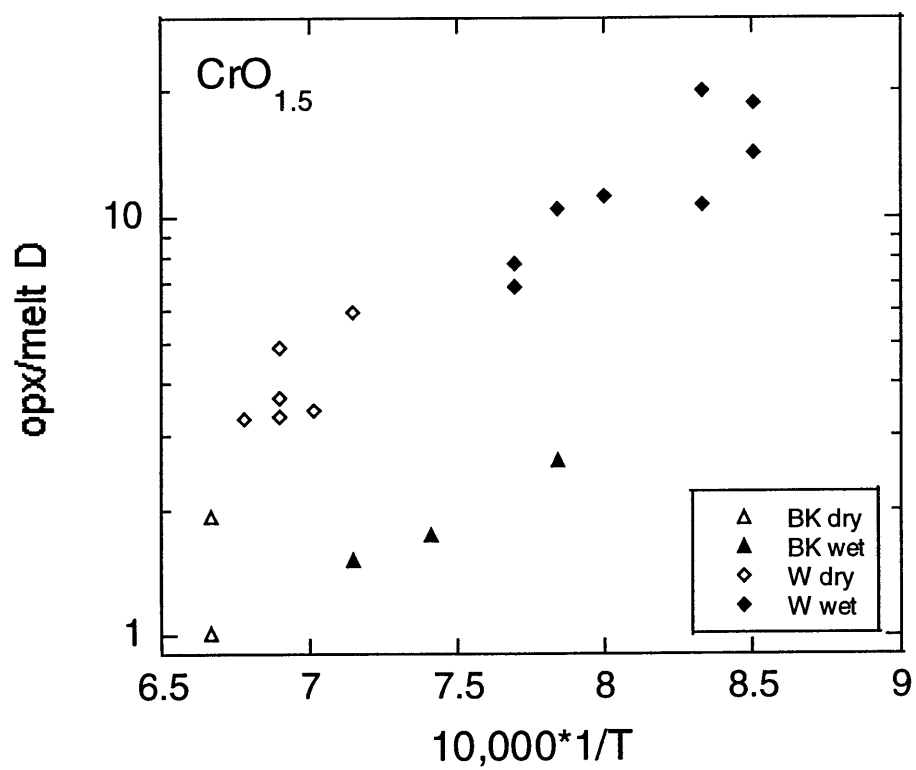
Figure 7(cont.). Anhydrous and hydrous opx/melt partition coefficients

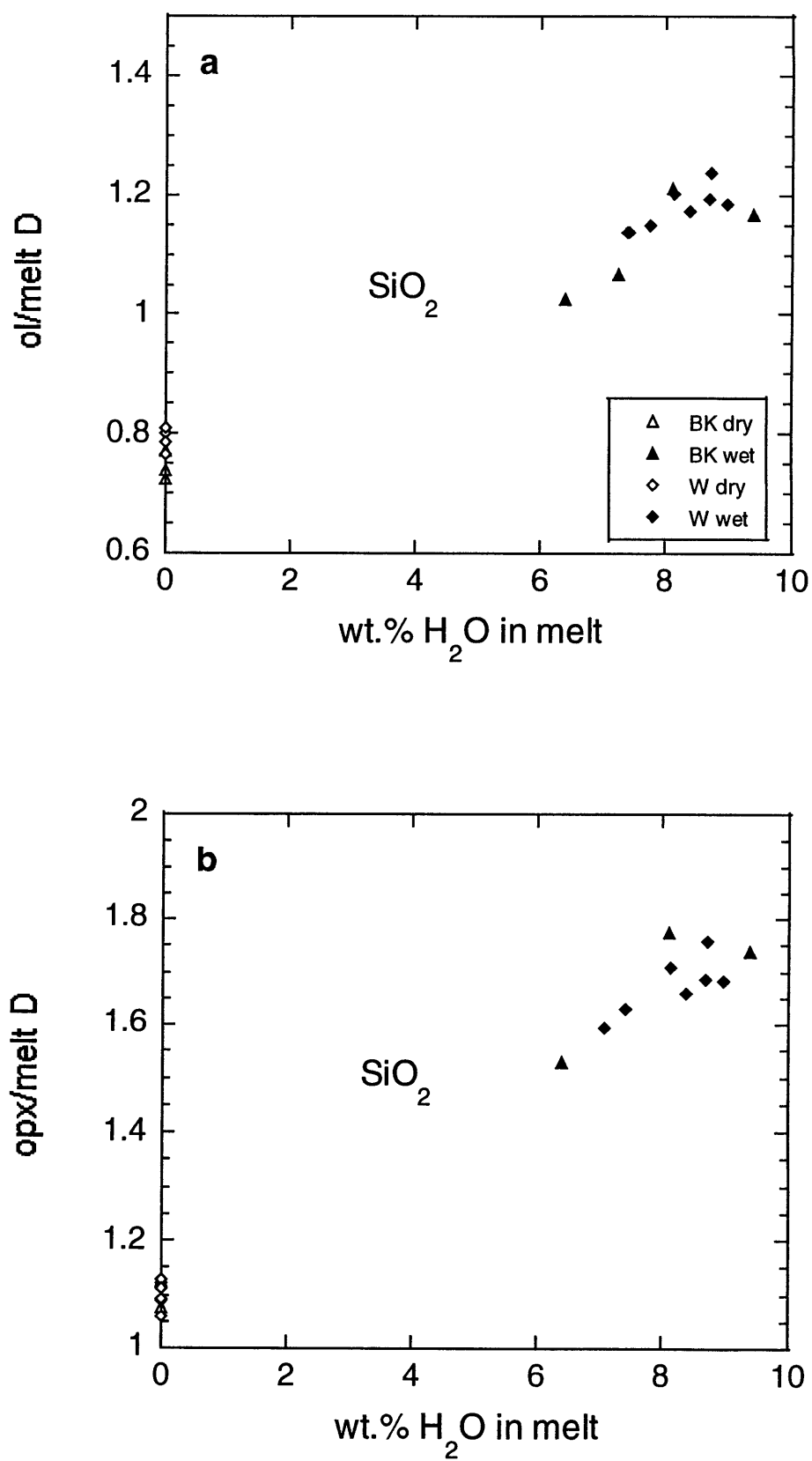
Figure 8. SiO₂ partition coefficients versus melt H₂O content

Figure 9. SiO₂ partition coefficients calculated with H₂O removed from the melt

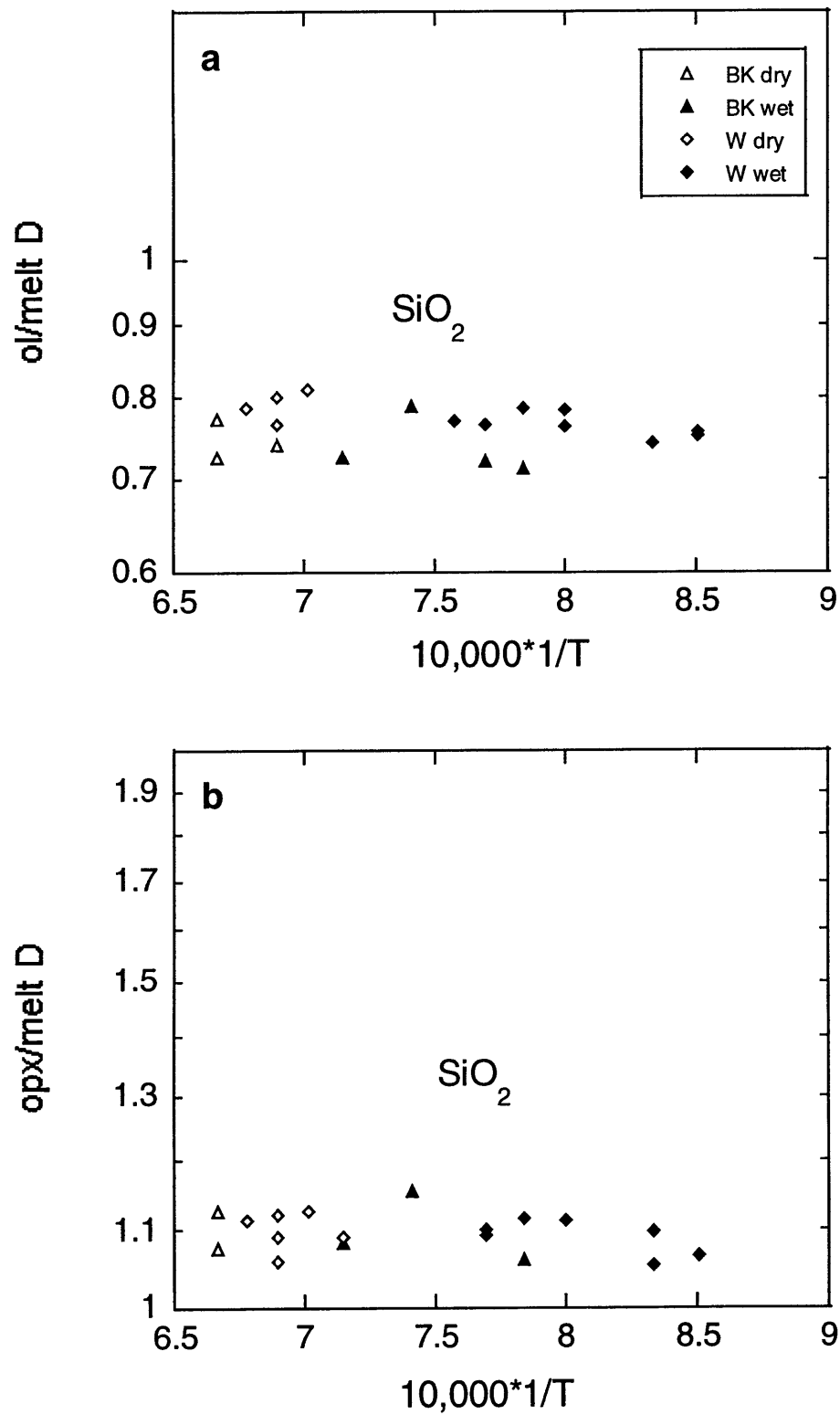


Figure 10. Observed and predicted phase fractions for fertile mantle melting

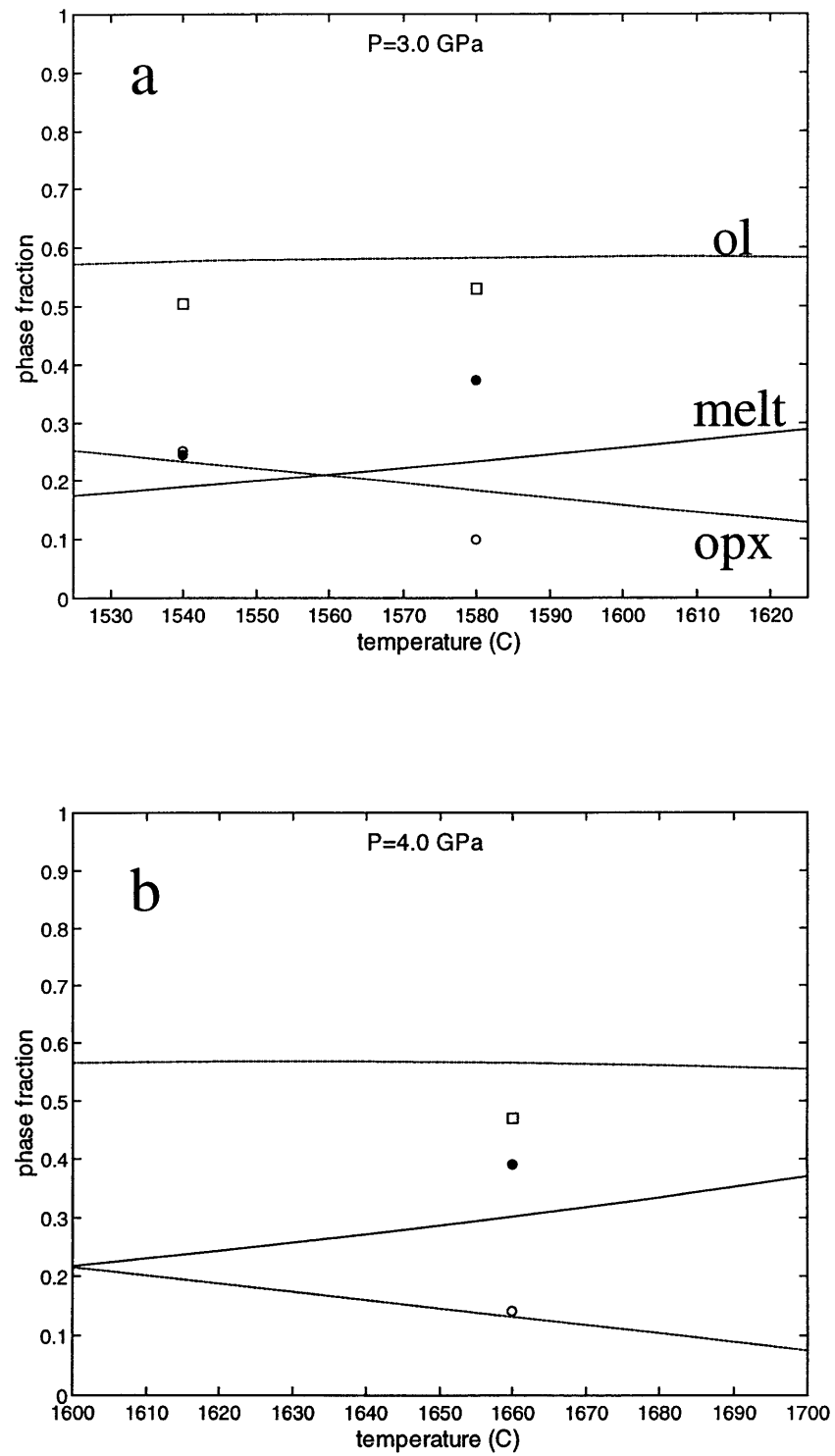


Figure 10(cont.). Observed and predicted phase fractions for fertile mantle melting

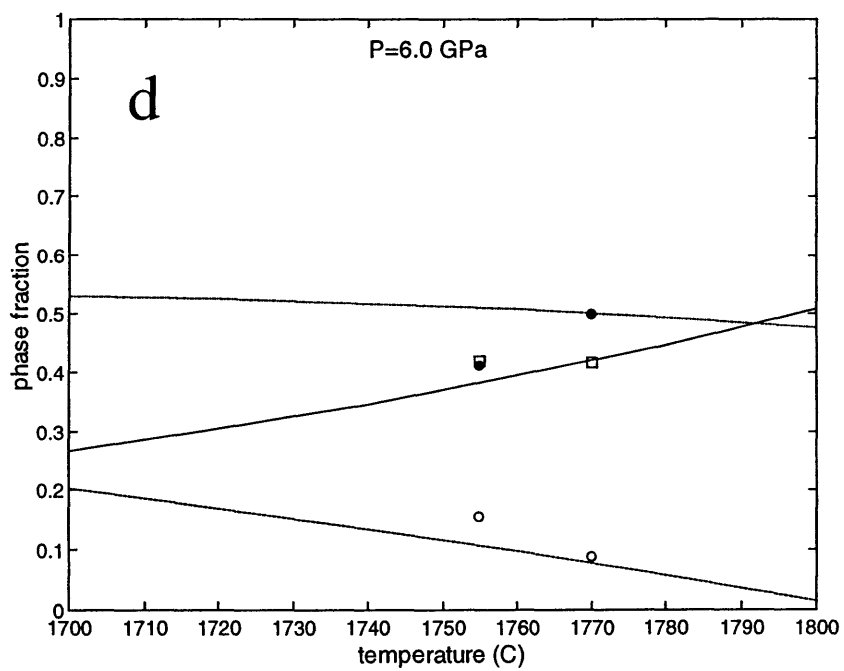
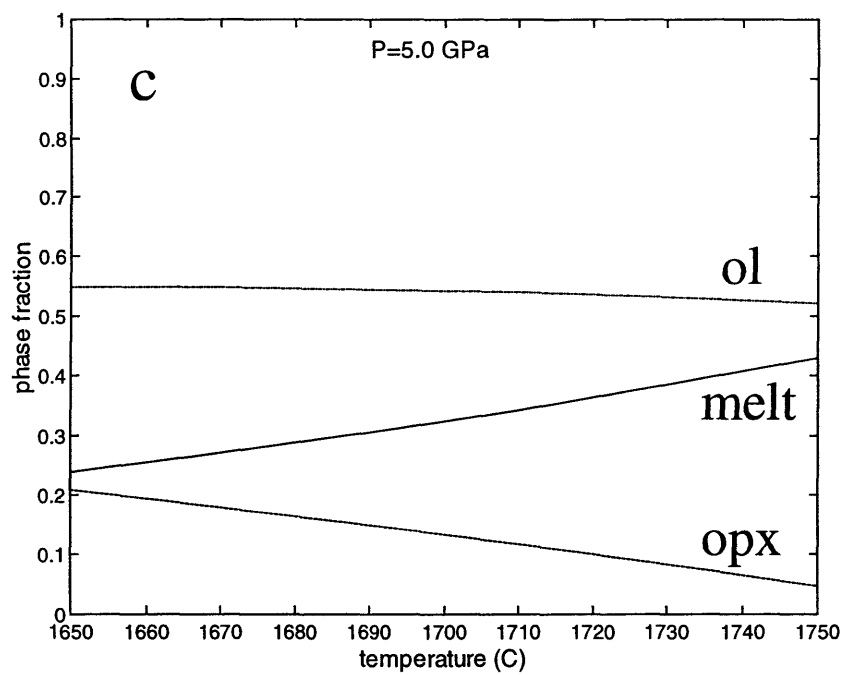


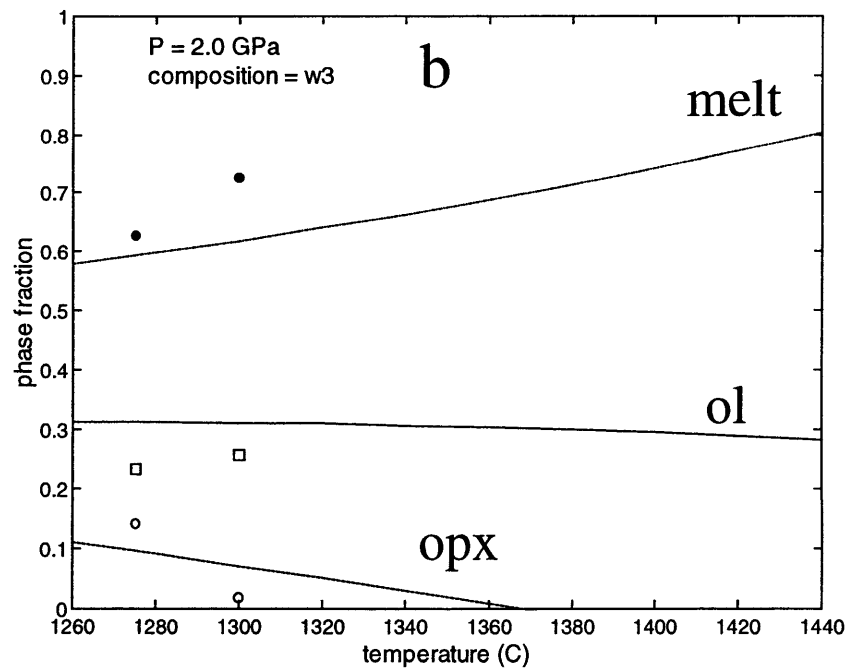
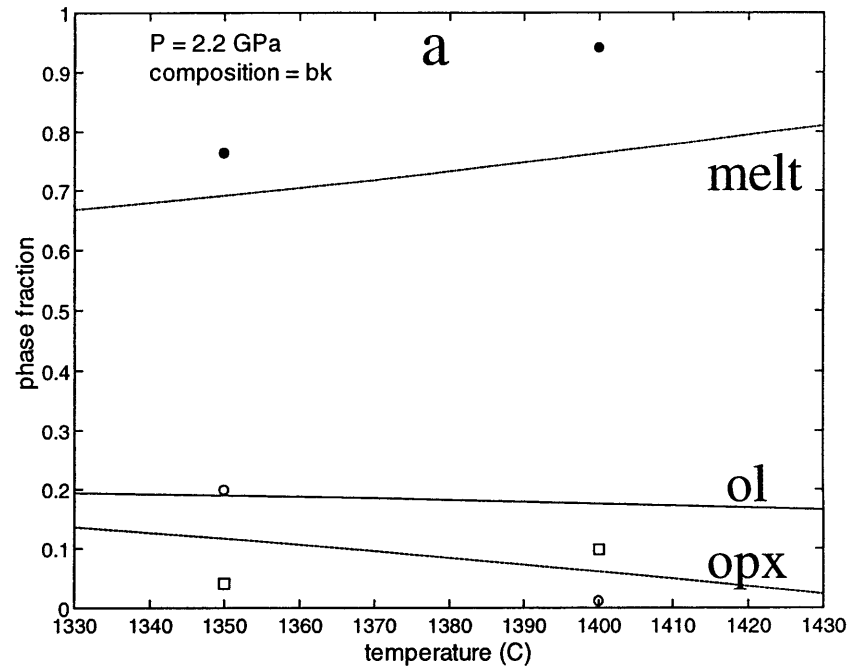
Figure 11. Observed and predicted phase fractions for BK and W3

Figure 12. Predicted phase proportions and melt compositions for fertile mantle with variable amounts of H₂O

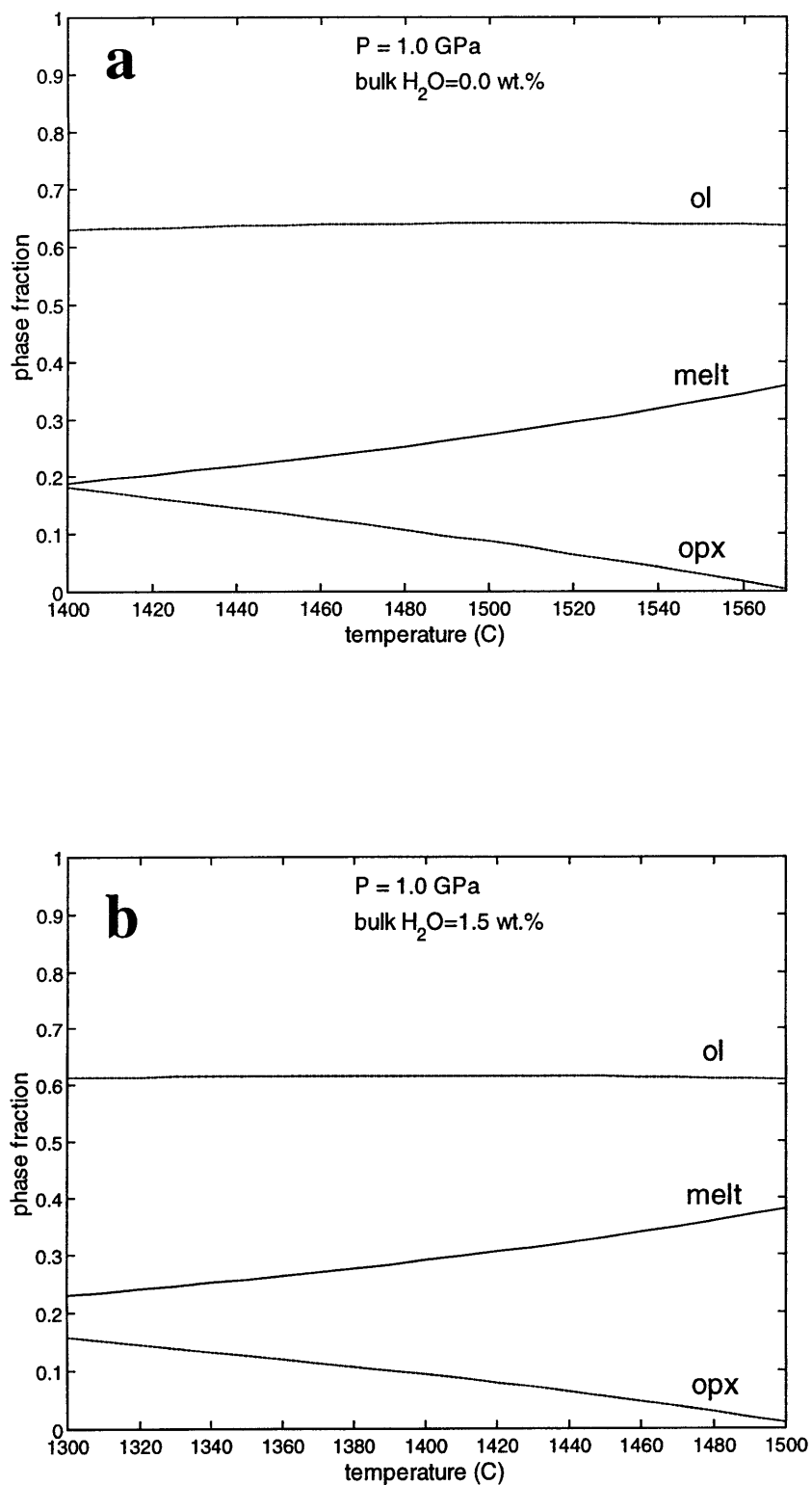


Figure 12(cont.). Predicted phase proportions and melt compositions for fertile mantle with variable amounts of H₂O

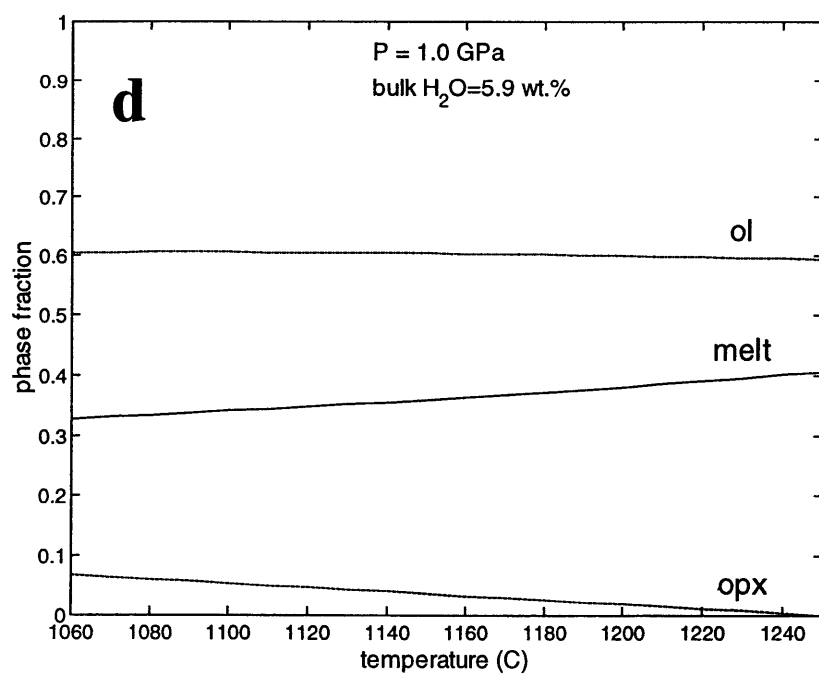
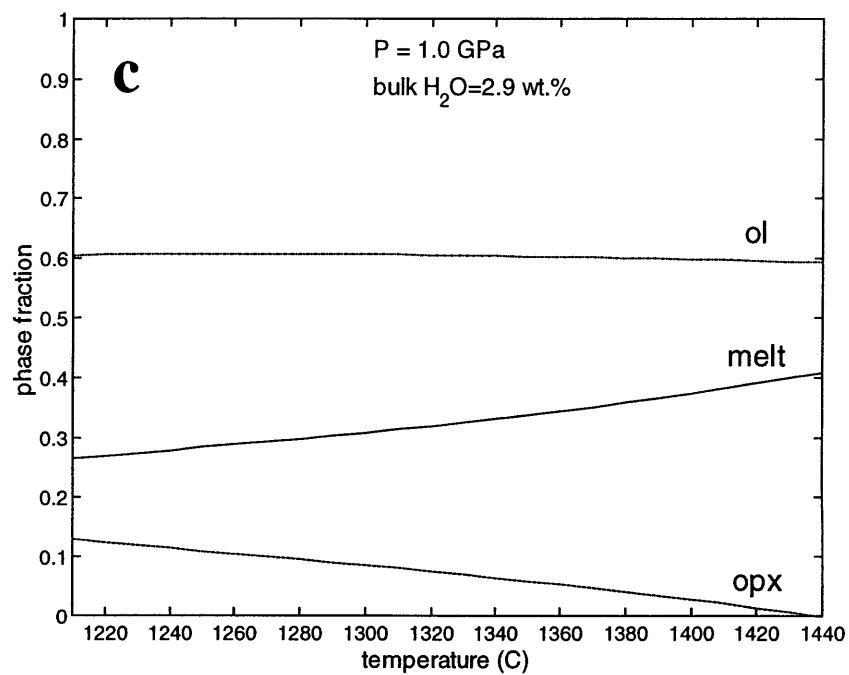


Figure 12(cont.). Predicted phase proportions and melt compositions for fertile mantle with variable amounts of H₂O

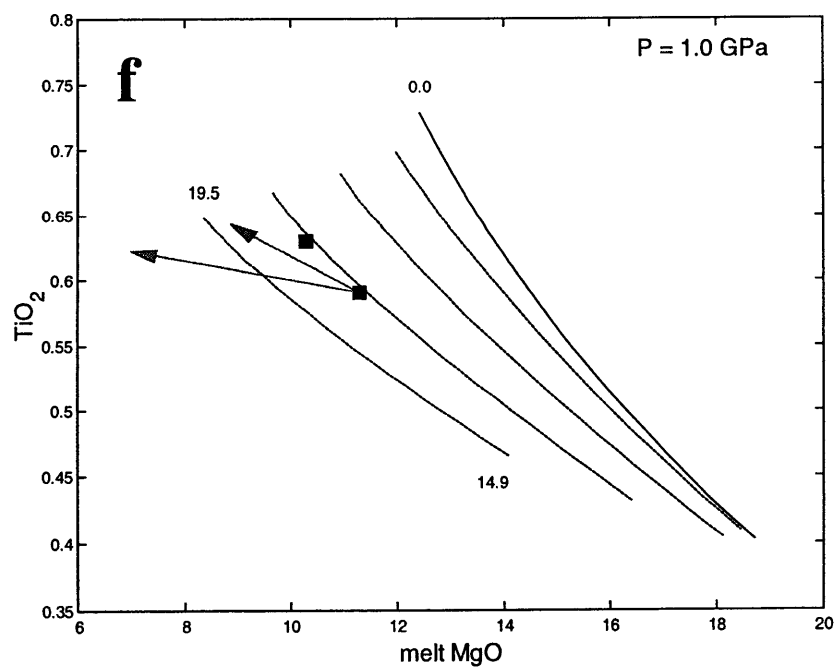
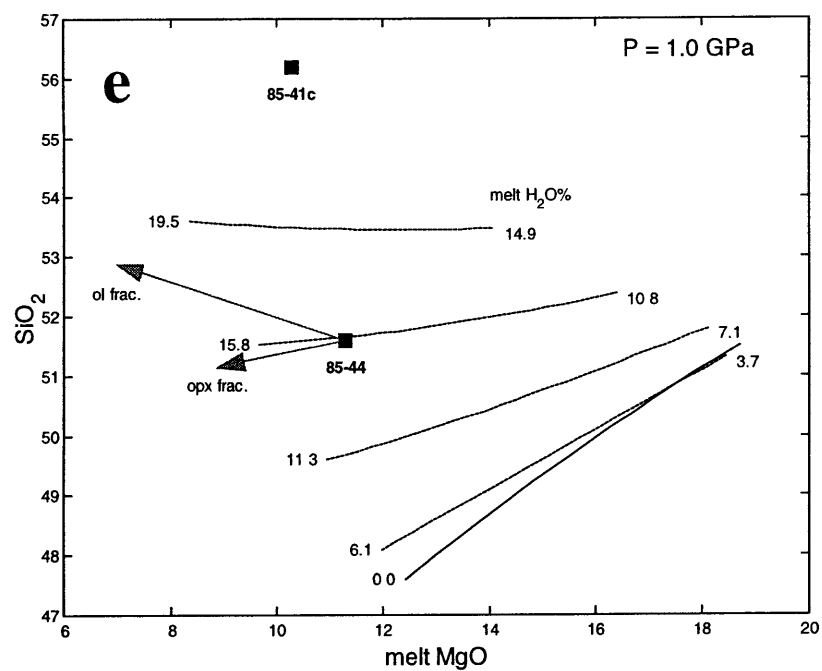


Figure 12(cont.). Predicted phase proportions and melt compositions for fertile mantle with variable amounts of H₂O

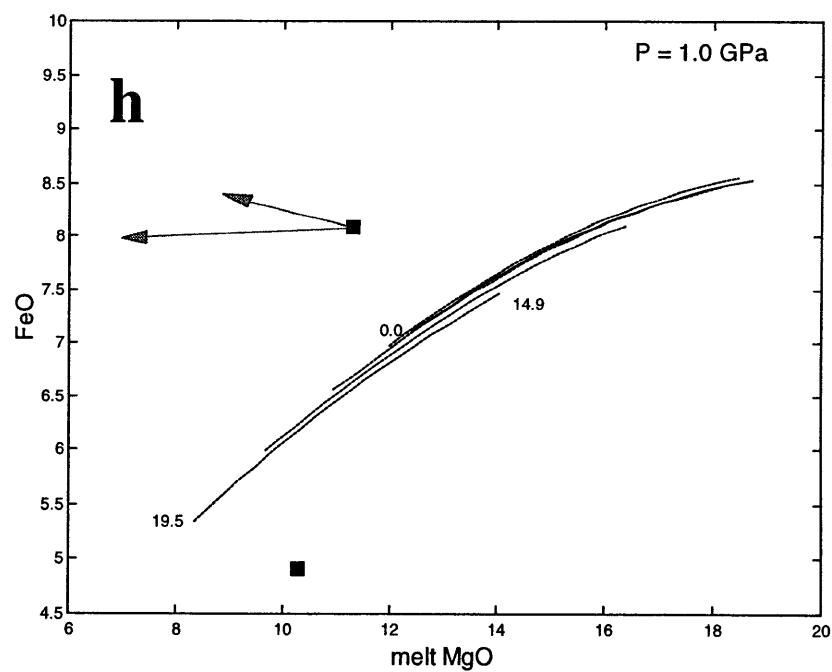
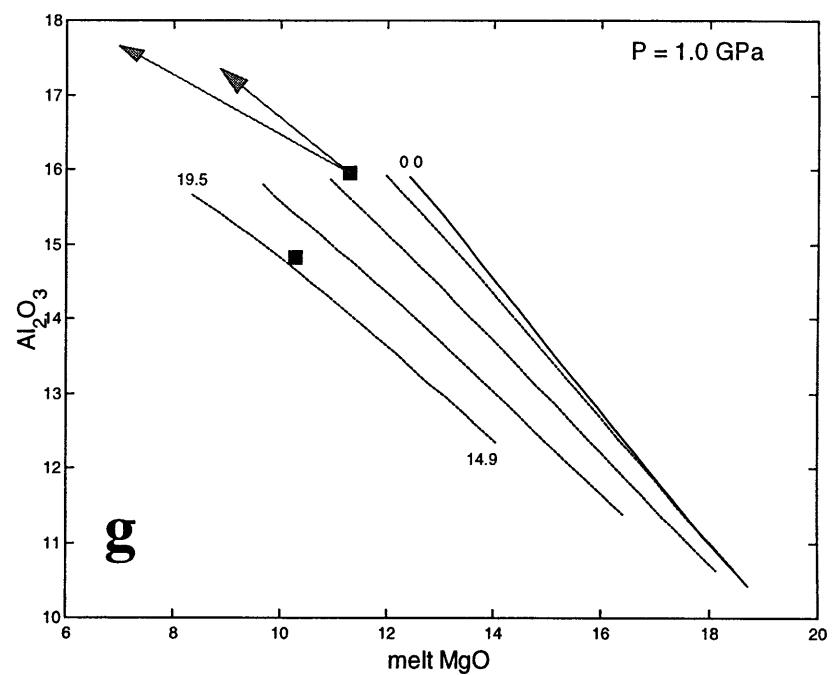


Figure 12(cont.). Predicted phase proportions and melt compositions for fertile mantle with variable amounts of H₂O

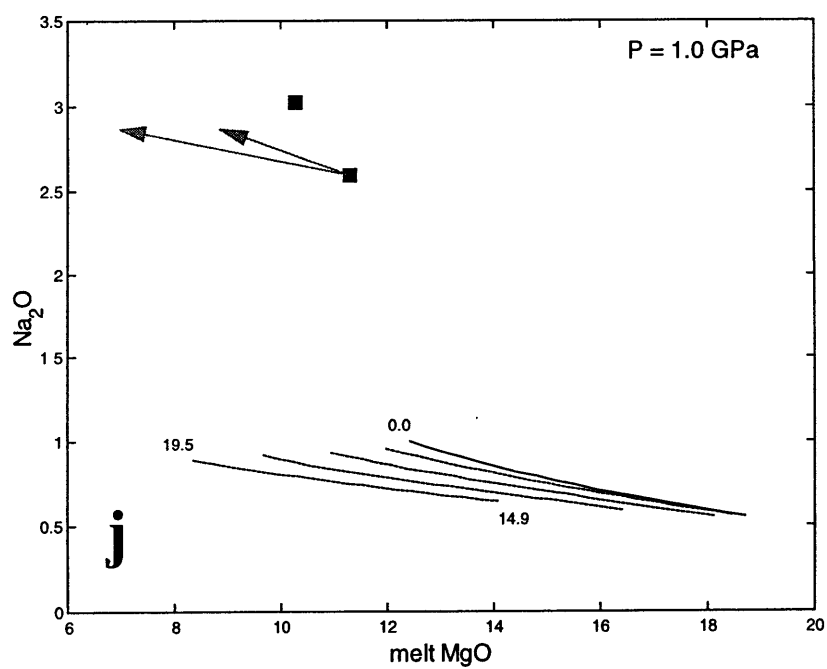
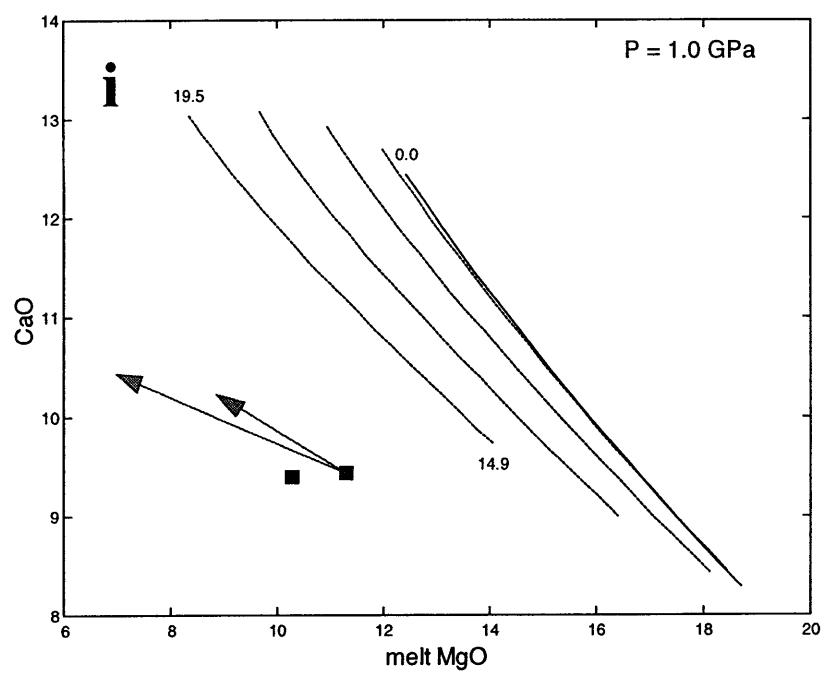


Figure 12(cont.). Predicted phase proportions and melt compositions for fertile mantle with variable amounts of H₂O

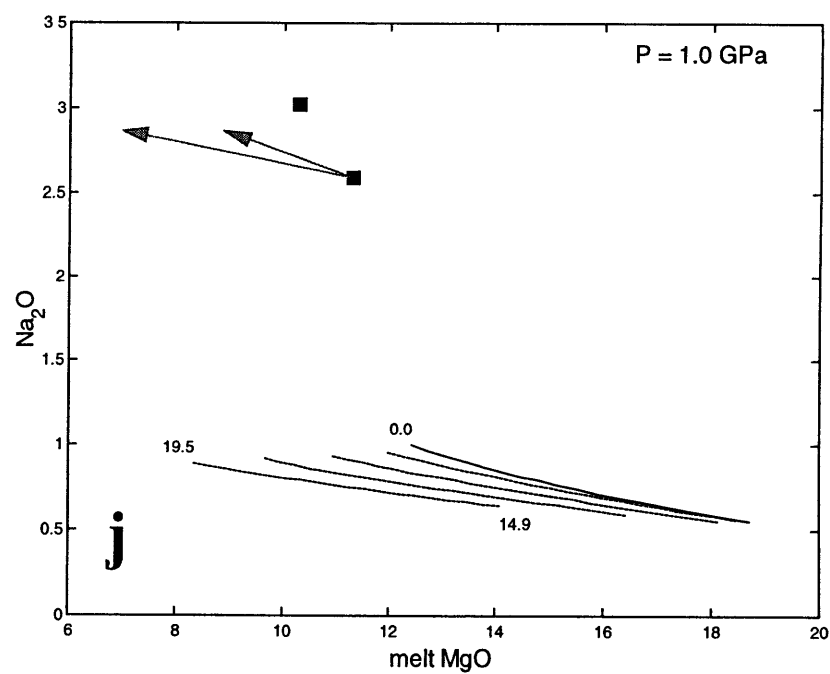
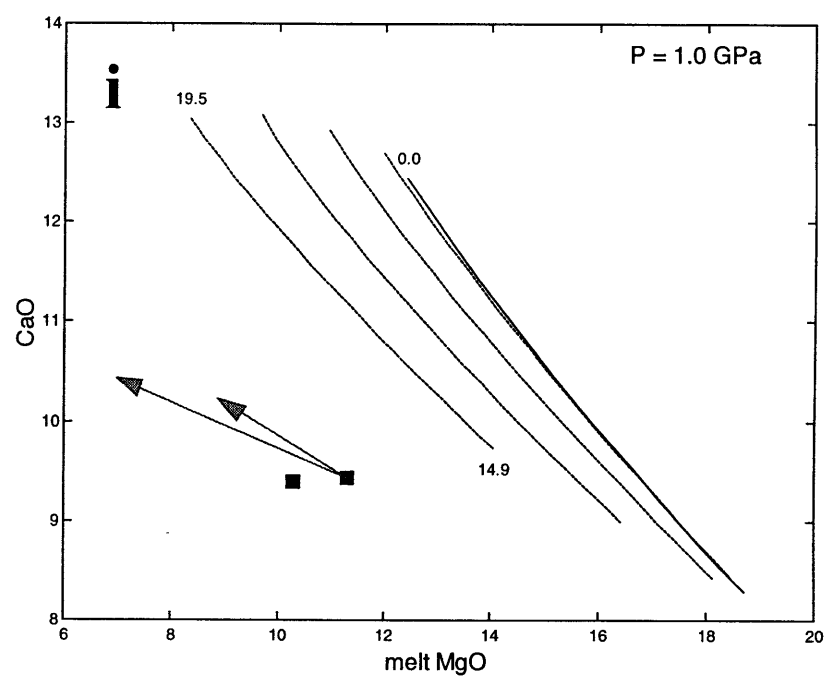


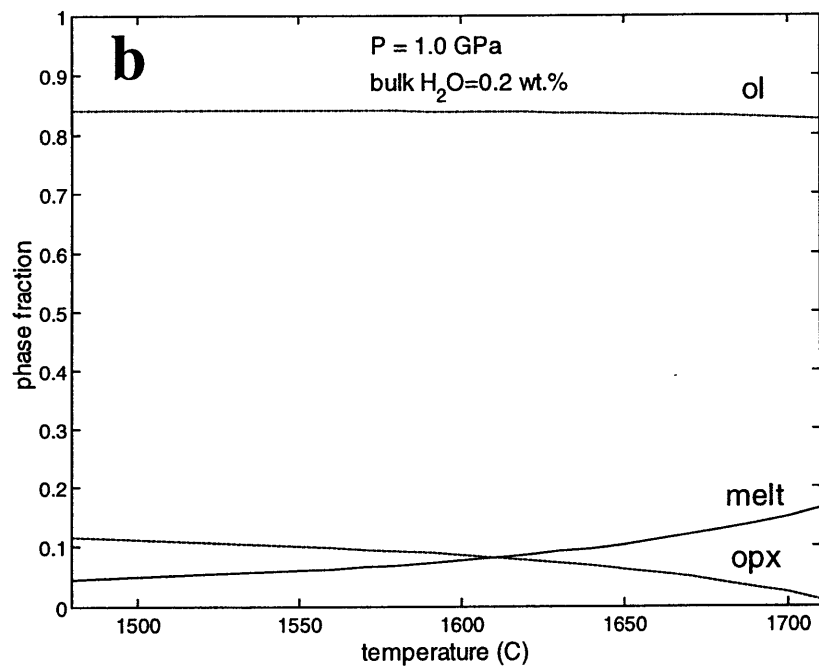
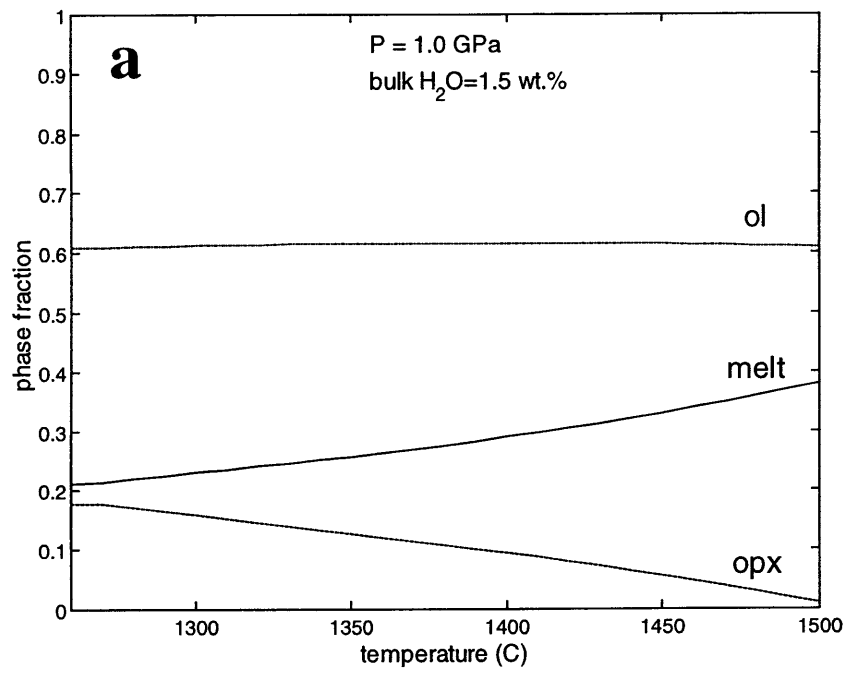
Figure 13. Melting of fertile and depleted mantle at 1.0 GPa

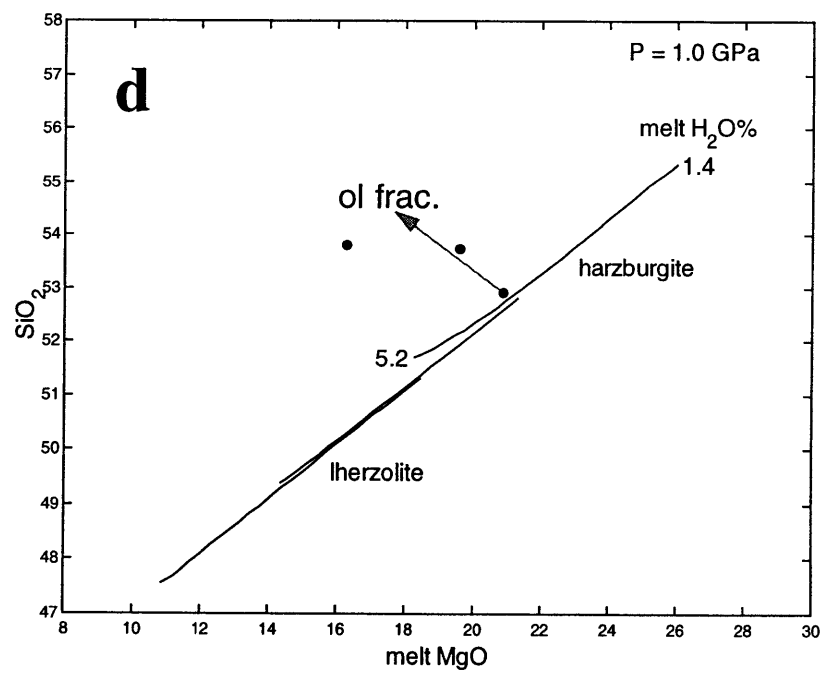
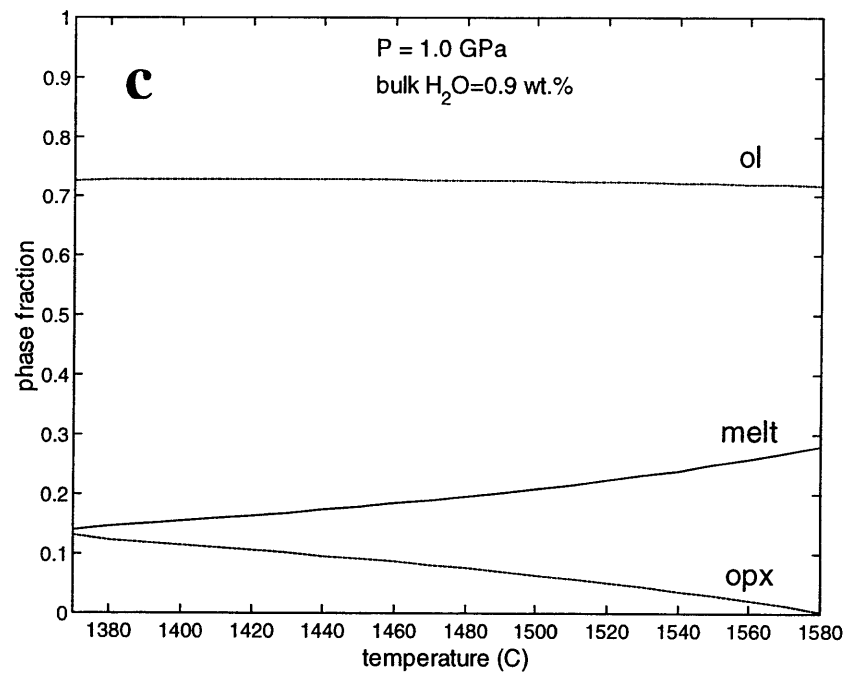
Figure 13(cont.). Melting of fertile and depleted mantle at 1.0 GPa

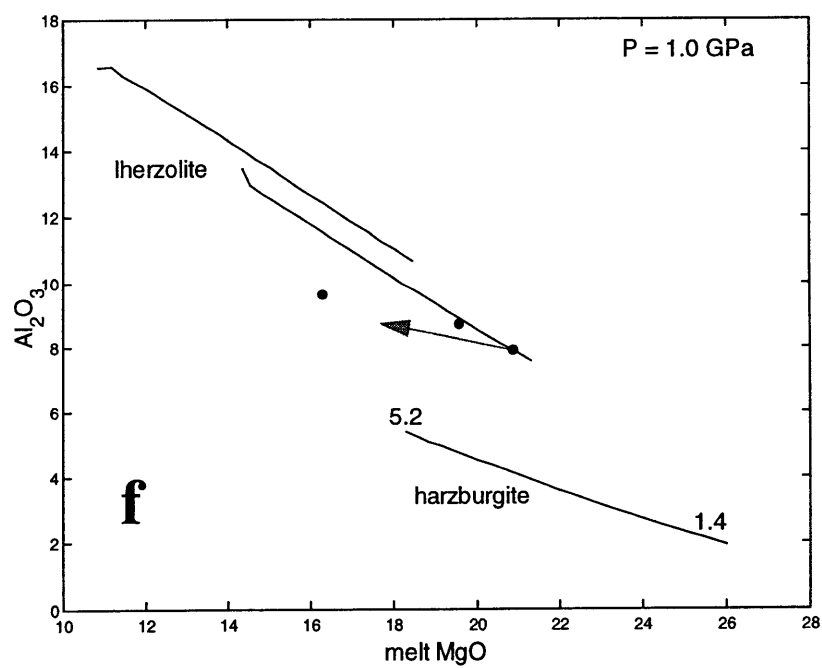
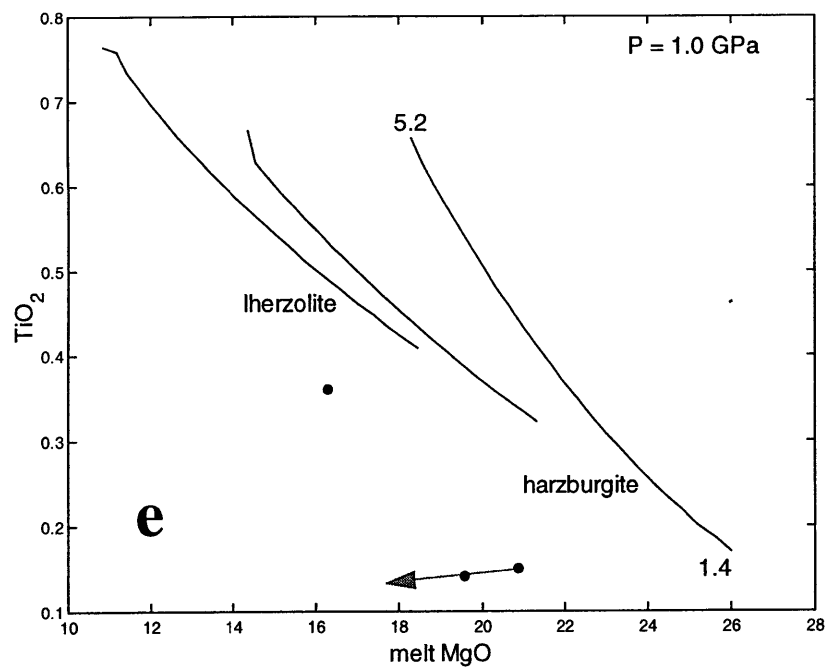
Figure 13(cont.). Melting of fertile and depleted mantle at 1.0 GPa

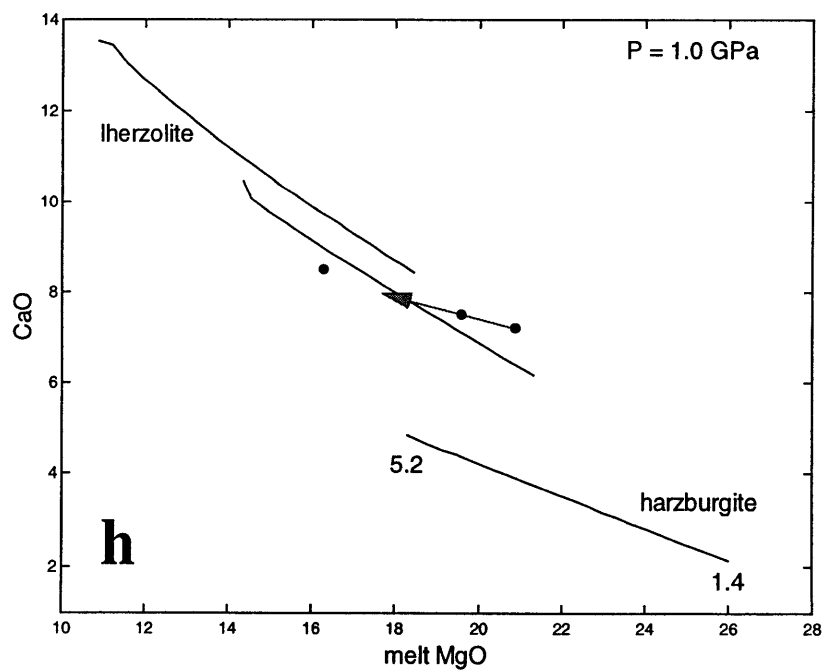
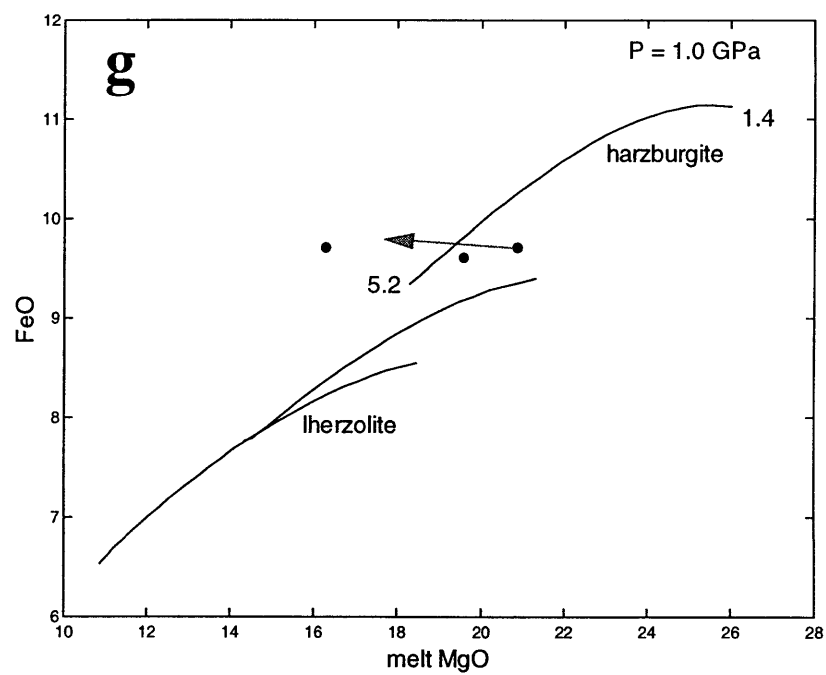
Figure 13(cont.). Melting of fertile and depleted mantle at 1.0 GP

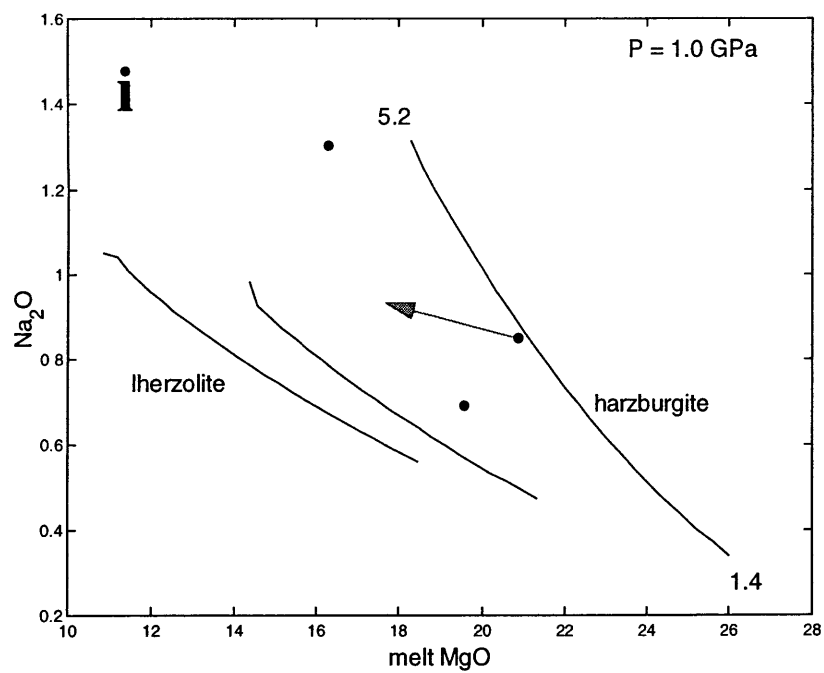
Figure 13(cont.). Melting of fertile and depleted mantle at 1.0 GPa

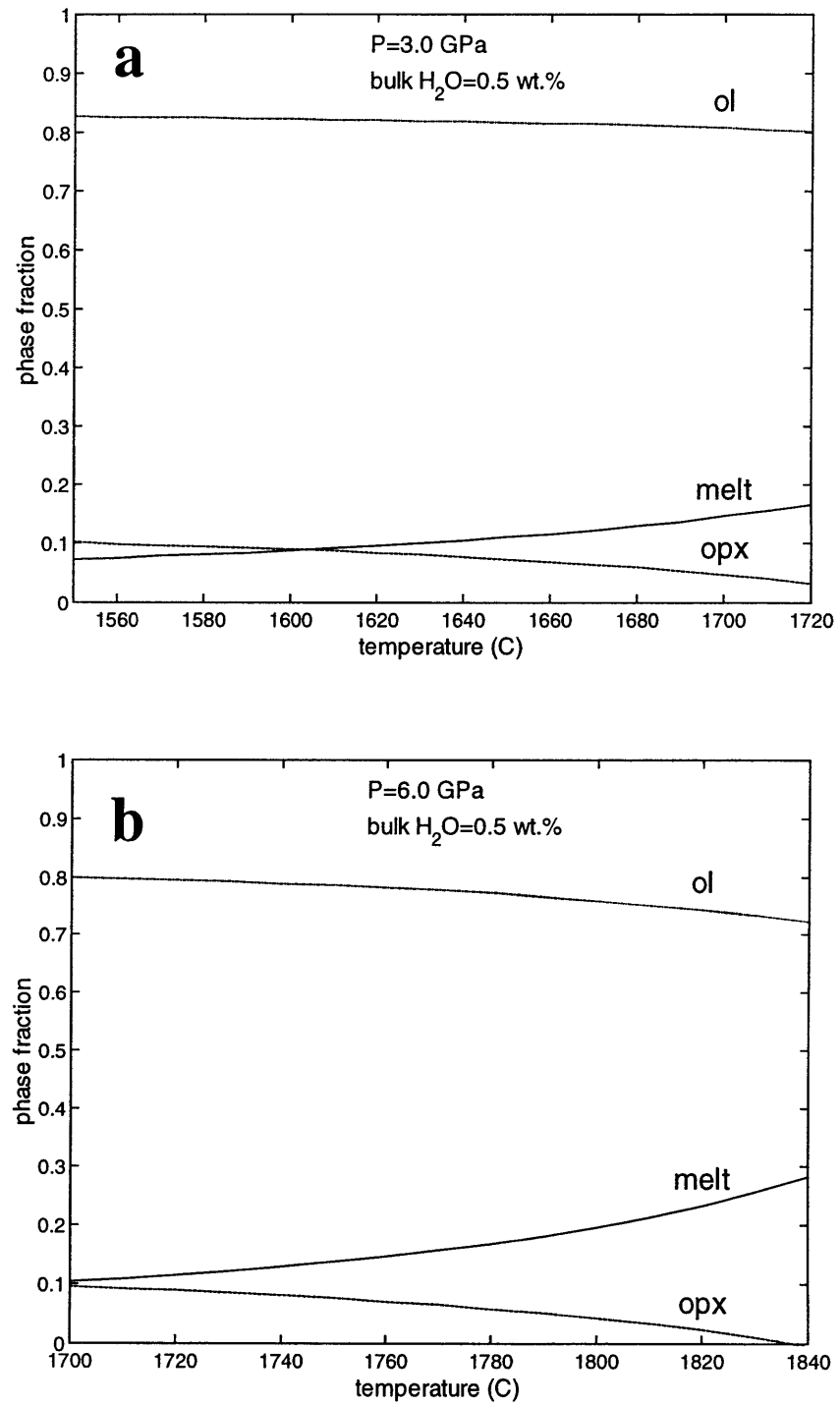
Figure 14. High pressure, hydrous melting of depleted mantle

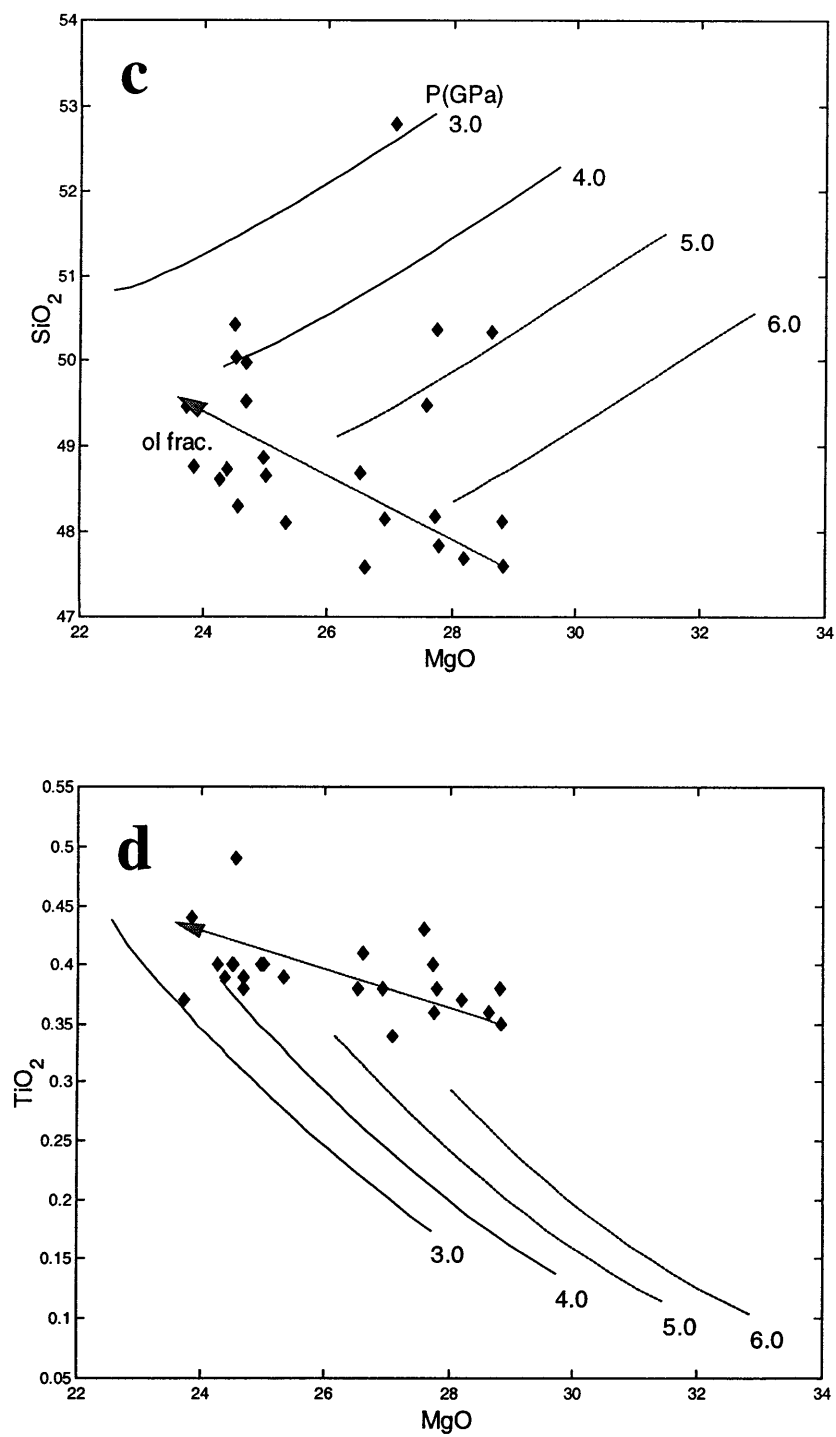
Figure 14(cont). High pressure, hydrous melting of depleted mantle

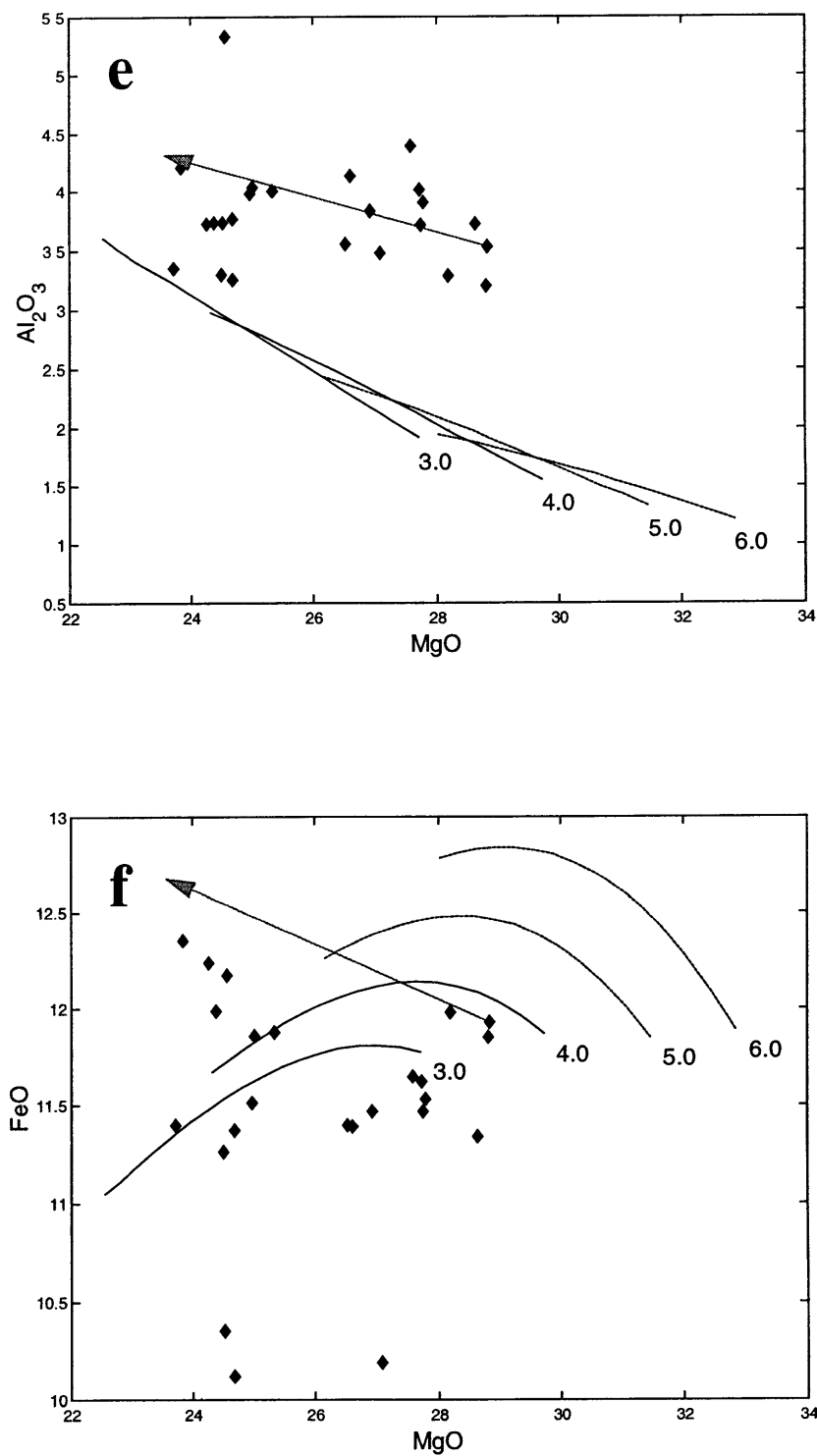
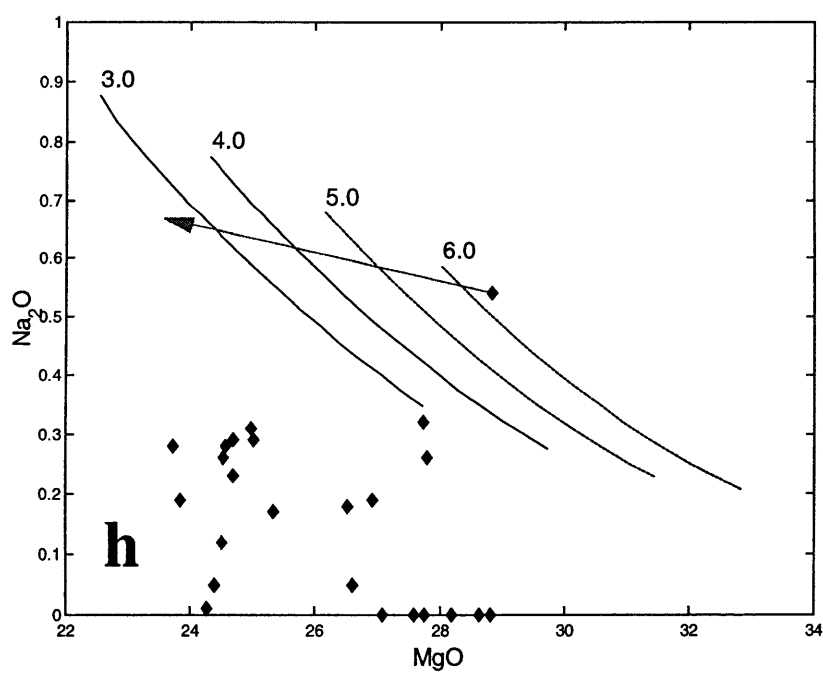
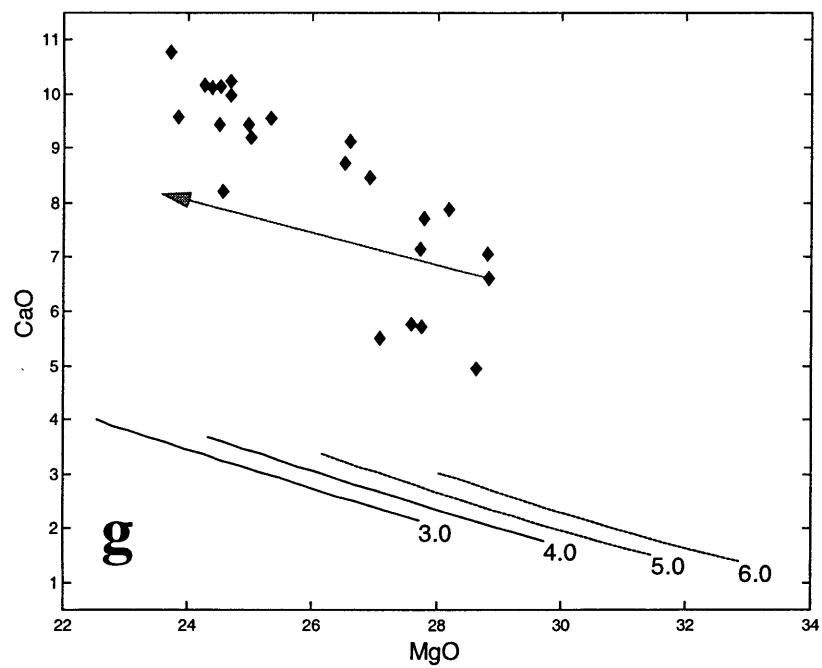
Figure 14(cont). High pressure, hydrous melting of depleted mantle

Figure 14(cont). High pressure, hydrous melting of depleted mantle

CHAPTER 4. THE PRODUCTION OF BARBERTON KOMATIITES IN AN ARCHEAN SUBDUCTION ZONE

The 3.5 Ga komatiites and basaltic komatiites of the Barberton Mountainland, South Africa, share a number of major and trace element characteristics with modern subduction-related boninites. The similarities include high SiO_2 for a given MgO content, high $\text{Mg\#}$, high $\text{CaO/Al}_2\text{O}_3$, low TiO_2 , variable LREE, U-shaped trace element patterns, and low Ti/Zr . Many of the Archean basaltic komatiites are chemically indistinguishable from modern boninites. On this basis, we propose that Barberton basaltic komatiites are the Archean equivalent of boninites, and were produced by similar melting conditions in a 3.5 Ga subduction zone. In this model, komatiites are higher temperature, higher pressure analogs of boninites, and are the result of hotter ($\sim 100^\circ\text{C}$) arc mantle in the Archean. Boninites and komatiites are also interlayered in greenstone belts in the Superior Province and in Central Africa, and basaltic komatiites worldwide display the same chemical similarity to boninites as seen in Barberton, implying that the subduction model may be applicable to all komatiite occurrences. If so, estimated Archean mantle temperatures are not as high as required by the plume model for komatiite generation (up to 2000°C). The proposed melting process produces a depleted, metasomatised, and cold mantle residue that may be the material from which the Kaapvaal cratonic keel was formed.

INTRODUCTION

It has been proposed that komatiites were produced by mantle plumes like those responsible for volcanism in Hawaii or Iceland today [Arndt *et al.*, 1998; Herzberg, 1995; Walter, 1998]. In this model, the high MgO (up to 29wt.%) and FeO contents of komatiites imply high mantle temperatures and extremely deep melting in the Archean. Yet boninites are amongst the highest MgO magmas produced in recent geologic history, and are produced exclusively in subduction zones by hydrous melting at shallow depths [Crawford *et al.*, 1989]. The high concentrations of H₂O in boninites allows them to be produced at moderate mantle temperatures (1400-1500°C). If komatiite were produced in subduction zones, it would have profound implications for models of Earth evolution as the high temperatures of the Archean mantle implied by plume models could be greatly reduced [Allegre, 1982]. Boninites are chemically and petrographically very similar to basaltic komatiites [Cameron *et al.*, 1979; Sun *et al.*, 1989], which are a ubiquitous component of komatiite sequences. In addition, boninites have been found interlayered with Archean komatiites in the Superior province and in Central Africa [Kerrick *et al.*, 1998; Poidevin, 1994]. The high SiO₂ komatiites of Nondweni also are similar to boninites and it has been proposed that they were formed in a subduction zone [Wilson and Versfeld, 1994].

The similarity of basaltic komatiites and boninites is not the only observation that links komatiites with subduction zones. A subduction origin was first proposed on the basis that komatiites are often found within a sequence of more typical subduction related volcanic units [Brooks and Hart, 1974]. Petrologic evidence for high H₂O contents comes from the composition of augite preserved in Barberton komatiites [Parman *et al.*, 1997], and from the presence of hydrous igneous amphibole in komatiites from the

Abitibi greenstone belt [Stone, 1997]. Tuffs of komatiite composition are also fairly common in komatiite sequences, and may provide further evidence of high magmatic H₂O contents [Echeverria and Aitken, 1986; Hollings and Wyman, 1999; Tomlinson *et al.*, 1999].

In this contribution, we first focus on Barberton komatiites. Barberton is one of the oldest komatiite sequences, has amongst the highest MgO contents, and therefore implies the most extreme Archean mantle conditions [Herzberg, 1995]. We demonstrate that Barberton komatiites and, in particular, basaltic komatiites are closely related to boninites geochemically. After examining the compositions of Barberton samples, we examine a global database of komatiite and basaltic komatiite geochemical analyses and show that they possess the same compositional affinities for boninites that are seen in Barberton komatiites. Finally, we propose a melting model based upon the inferred equilibration conditions of hydrous komatiitic magmas, the TE constraints on the composition of the mantle source, and geodynamic models of mantle flow in modern subduction zones.

MAJOR ELEMENT COMPOSITION OF BARBERTON KOMATIITES AND BASALTIC KOMATIITES

The most striking chemical feature of Barberton komatiites is their high MgO, 23-33wt.% (Fig. 1, Table 1). It is likely that the highest MgO values have been increased somewhat by serpentinization [de Wit *et al.*, 1987; Parman *et al.*, 1997]. Based upon olivine compositions, the maximum MgO of the komatiite magmas was 26-29 wt.% [Nisbet *et al.*, 1993]. Nevertheless, their MgO contents are far above that of any modern magma. Basaltic komatiite samples have MgO contents between 10 and 18 wt.%, and

fall along an extension of the compositional trends seen in the komatiites (Fig. 1a). Though there is a notable gap in compositions with MgO between 18 and 23 wt.% MgO. The trend defined by komatiites and basaltic komatiites is broadly along an olivine control line, but the SiO₂ content of many samples is too high to be produced by olivine fractionation alone. The serpentinization that has affected the samples will lower SiO₂ contents, and there is no petrographic evidence for silicification in the samples. So we interpret the high SiO₂ to be a compositional feature of the magma.

The relatively high SiO₂ contents of the komatiites and basaltic komatiites are similar to hydrous magmas found in modern subduction zones [Gill, 1981]. In particular, the basaltic komatiites overlap the compositional field for boninites (Fig. 1a). While there are no modern magmas with MgO contents as high as komatiites, the compositional trends in boninites point towards the komatiite compositions. In contrast, the SiO₂ contents of the Barberton samples are distinct from anhydrous magmas produced at modern mid-ocean ridges and ocean islands.

Another distinctive feature of the komatiitic samples is their low TiO₂. Only one sample has greater than 1 wt.% TiO₂ (Fig. 1b). Low TiO₂ is a common feature of modern arc magmas, and boninites are particularly TiO₂ poor [Gill, 1981; Hickey and Frey, 1982]. Many of the basaltic komatiites fall within the boninite field, though most have slightly higher TiO₂. The MgO-TiO₂ trend in the komatiitic samples is lower than that seen in MORB or OIB, even when compared to olivine phyric picrites. Interestingly, boninites often have lower TiO₂ than komatiites with much higher MgO contents. If boninites and komatiites were produced from the same source, the higher MgO of komatiites would imply that they should have lower TiO₂. The extremely low TiO₂ in

boninites implies that they were produced from a more depleted source than either basaltic komatiites or komatiites.

One of the most notable chemical features of Barberton komatiites is their high CaO/Al₂O₃ ratios (1.2-3.3; Fig. 1d). This has been used as evidence for melting within the garnet stability field, as melting within the spinel stability field can only produce magmas with CaO/Al₂O₃ ratios equal to or lower than that of the mantle (0.82) [Herzberg, 1992; Walter, 1998]. By sequestering Al₂O₃, garnet could produce high CaO/Al₂O₃. If so, it should correlate with Al₂O₃. This is not the case for the Barberton komatiites. Their CaO/Al₂O₃ varies widely at a constant Al₂O₃. There is abundant evidence that CaO was mobilized in the komatiites during metamorphism, and this is likely the cause of much of the CaO variation [Parman *et al.*, 1997]. In contrast, CaO/Al₂O₃ in the basaltic komatiites shows much less scatter, and correlates well with Al₂O₃ (Fig. 1d). The trend in basaltic komatiite compositions points towards komatiite compositions with CaO/Al₂O₃=2.5. The CaO/Al₂O₃ versus Al₂O₃ trend in the basaltic komatiites closely parallels the trend observed in boninites. The basaltic komatiites and boninites are distinctive not only for the high CaO/Al₂O₃ present in some samples, but also for low CaO/Al₂O₃ in other samples. Such low values are equally difficult to produce by melting in the spinel facies. In contrast, modern MORB and OIB vary little from the mantle CaO/Al₂O₃ value of the mantle, which is taken as evidence that they are primarily produced within the spinel field.

Like the other major elements, boninite FeO contents overlap those of basaltic komatiites and form a trend versus MgO that points towards komatiites (Fig. 1c). MORB have a similar range of FeO to the komatiitic samples, while OIB FeO contents are higher. The low FeO of basaltic komatiites relative to OIB implies a lower pressure of

melting [*Klein and Langmuir, 1987*]. Yet if garnet was the cause of their high $\text{CaO}/\text{Al}_2\text{O}_3$, it would imply a higher pressure origin than OIB. This apparent paradox can be resolved if basaltic komatiites are the product of hydrous melting. Experimental studies have shown that the addition of H_2O to the mantle stabilizes garnet to lower pressures (1.4 GPa) and temperatures [*Gaetani and Grove, 1998*]. Thus garnet could be present at shallow depths in an arc, and absent at greater depths within a plume.

TRACE ELEMENT COMPOSITION OF BARBERTON KOMATIITES AND BASALTIC KOMATIITES

The chemical similarities seen in the major elements are paralleled by the trace elements. Boninites and basaltic komatiites display wide variations in LILE and LREE, and low overall concentrations of incompatible elements (Fig. 2). Boninites often display a distinctive U-shaped REE pattern [*Hickey and Frey, 1982*]. Strikingly similar REE patterns are found in the Barberton basaltic komatiites (Fig. 2). As is typical for arc magmas, HFSE depletions are common in both rock types. What distinguishes boninites and basaltic komatiites from more typical arc magmas is that they often show enrichments in Zr and Hf, even when the other HFSE such as Ti are depleted. This gives rise to distinctly low Ti/Zr ratios (Fig.3). In addition, the HFSE depletions and fractionation between Ti and Zr are largest in the samples with the strongest LREE enrichment, another typical feature of arc volcanics (Fig.3). In boninites, the correlation between Ti/Zr and La/Sm is interpreted as the variable enrichment of LREE depleted, high Ti/Zr magmas with LREE enriched, low Ti/Zr hydrous slab-derived fluids [*Hickey and Frey, 1982*].

It has been argued that the LREE enrichment in komatiites and basaltic komatiites is due to crustal contamination [Arndt and Jenner, 1986; Barley, 1986; Cattell, 1987]. The geochemical effects of crustal contamination, or fluids that have equilibrated with crust, are quite similar to the effects of addition of slab fluids. LREE will be enriched and HFSE depleted. This is not a coincidence, but simply points out that slab fluids have equilibrated with the subducting crust. Thus there is no doubt that basaltic komatiite magmas are crustally contaminated, the question is where the contamination occurred; in the mantle overlying a subducting slab or in the crust during emplacement. We prefer the former explanation for three reasons: 1) A number of studies have argued for an arc setting for komatiites, 2) The chemical similarity between boninites and basaltic komatiites is too extensive to be a coincidence, 3) No crustal xenoliths have been found in the Barberton komatiites or basaltic komatiites.

Barberton komatiites show similarities with boninites, and significant differences. Like boninites, they vary from LREE depleted to enriched. Unlike boninites, the LREE variations are much lower in amplitude and the majority of samples are LREE depleted (Fig. 4). HFSE depletions also occur in the komatiites. As in boninites, Zr and Hf are sometimes enriched relative to the other HFSE (sample B94-4), though these are much less common in komatiites than in boninites. The range of La/Sm ratios in the komatiites is too small to observe a correlation between La/Sm and Ti/Zr, though the trend does overlap the fields for basaltic komatiites and boninites.

COMPOSITIONS OF KOMATIITES AND BASALTIC KOMATIITES FROM OTHER GREENSTONE BELTS

The compositional overlap between Barberton basaltic komatiites and boninites is also present in basaltic komatiites from greenstone belts worldwide (Fig. 5). These include high SiO_2 , low TiO_2 , and high $\text{CaO}/\text{Al}_2\text{O}_3$. The dataset includes analyses from Kaapvaal, Belingwe, Superior, Yilgarn, and Baltic cratons (see Fig. 5 caption for references). An additional similarity can be seen that is not apparent in the Barberton data. Many komatiites are inter-layered with low-Ti tholeiites as well as basaltic komatiites. These tholeiites are similar to MORB and OIB in most major element concentrations, with the exception of having lower TiO_2 . Nearly identical low-Ti tholeiites are found inter-layered with modern boninites. Typically there is a complete continuum of compositions between boninite and low-Ti tholeiite, and the range of compositions is generally referred to as the 'boninite series' [Bedard, 1999; Kerrich *et al.*, 1998].

Globally the TE compositions of komatiites and basaltic komatiites are more varied than in Barberton. The La/Sm values show a greater range (Fig. 5c). LREE enriched komatiites are still rare, but the La/Sm ratios of those samples extend to much higher values than seen in Barberton (Fig. 3 and 5). While obscure in Barberton, the greater range of La/Sm in the global dataset of komatiites clearly shows that the HFSE depletions correlate with the LREE enrichments. This trend is also well displayed by the global dataset of basaltic komatiites, and to a lesser extent by the low-Ti tholeiites (Fig. 5).

A SUBDUCTION MODEL FOR THE FORMATION OF KOMATIITES AND BASALTIC KOMATIITES

Based upon the extensive similarity between boninites and basaltic komatiites, and the boninite-like chemical signatures in many komatiites (HFSE depletions, LREE enrichments, high SiO₂), we propose that komatiites were produced in Archean subduction zones. In the following section, we construct a model for the production of komatiites and related magmas by hydrous melting in a subduction zone. The basis of the model is to use petrologic estimates of the melting conditions for the various magmas to locate their source regions within the sub-arc mantle by combining them with numerical models of the PT conditions with the sub-arc mantle wedge. Melting conditions for komatiites and boninites are estimated to be 2.5-3.0 GPa and 1500-1550°C, 1.0 GPa and 1400-1500°C, respectively (Ch. 3). Basaltic komatiites with compositions similar to boninites are produced at the same conditions as boninites, while basaltic komatiite compositions intermediate to boninites and komatiites were produced at intermediate conditions. The numerical models of mantle flow and temperature structure we have used are those which include realistic temperature and stress dependent rheologies [Andrews and Sleep, 1974; Furukawa, 1993]. A schematic representation of these models, altered to reflect ~100°C hotter ambient mantle in the Archean, is shown in Fig. 7. The essential feature of such models is that the mantle upwells as it is drawn into the arc. The upwelling of mantle advects high temperatures into the arc, as well as produces the opportunity for decompression melting.

As it ascends into the wedge, mantle on the outside of the corner flow (path A-D) crosses the dry peridotite solidus at ~100 km depth (point A). Along path A-D, the mantle produces anhydrous, tholeiitic melts by decompression melting. At point D, the

depleted mantle approaches the slab and cools below the anhydrous solidus, ending the decompression melting. After it turns the corner and descends, the depleted mantle encounters hydrous fluids rising from the slab. The H_2O allows the depleted mantle to remelt at a lower temperature. These H_2O saturated melts rise into hotter overlying mantle. The increasing temperature causes additional melting, which dilutes the amount of H_2O in the melt. At point D, the temperature gradient reverses and the melt encounters decreasing temperatures. This brings a halt to hydrous melting. Point D represents the last equilibration point of the melt with the mantle. The low pressure, hydrous melts of depleted mantle that segregate at point D are boninites. The anhydrous melts produced along the upwelling limb of the corner flow (thick gray line) are the low-Ti tholeiites that are commonly interlayered with boninites.

Paths on the inside of the corner flow (C-F) are hotter, and will begin melting deeper. But they also do not upwell as much as the exterior paths. Therefore, the amount of anhydrous melting that occurs along the interior path C-F is less than the amount of melting that occurs along the exterior path A-D. As before, hydrous melts will be produced by flux melting and will rise through the inverted thermal gradient. The last equilibration point of these melts (point F) will be deeper and hotter than exterior paths (point D). These deep hydrous melts will be komatiites. The higher P and T results in melts with lower SiO_2 , and higher FeO and MgO than boninites. The low TiO_2 of boninites relative to komatiites results from the greater amount of prior depletion (path A-D) seen by the boninite source mantle. Paths such as B-E, will produce basaltic komatiites and high SiO_2 komatiites, which are intermediate in composition between boninites and komatiites (Figure 1).

The proposed model has a number of appealing aspects. 1) The entire range of melt compositions present in Barberton and other greenstone belts (komatiites, basaltic komatiites, boninites, and low-Ti tholeiites) is produced with a single melting process. In contrast, the plume model must call upon the coincidental juxtaposition of an arc and a plume [Kerrick *et al.*, 1998] to explain the interlayering of boninites and komatiites. 2) The simultaneous production of hydrous (boninites, basaltic komatiites, and komatiites) and anhydrous magmas (tholeiites) at the same time is explained. Essentially, there are two melting processes operating. One that produces anhydrous melting as the mantle rises into the arc system, and one that produces hydrous melting as mantle nears the descending slab and encounters hydrous fluids. 3) The greater depletion of boninites in Ti and MREE compared to komatiites is explained by the greater amount of melting that occurred prior to the production of boninites. This is a natural consequence of the generation of boninites at lower pressures than komatiites. For the mantle to be at shallow depths to produce boninites, it must have risen further than the komatiite source, and therefore undergone more decompression melting. 4) The boninite-like geochemical features present in many komatiites and basaltic komatiites (high SiO₂, low TiO₂, high LREE, HFSE depletion) are the simple result of being produced in an arc, rather than by crustal contamination.

DISCUSSION

Phanerozoic boninites are found in either a) fore-arc crust or b) ophiolites [Crawford *et al.*, 1989]. The presence of boninites in an ophiolite is often used as evidence that the ophiolite is a piece of fore-arc crust. Thus a direct corollary to our arc model is that komatiites were formed in fore-arcs, and are the volcanic portions of

Archean fore-arc crust that was obducted onto continental crust. If so, komatiites do not represent typical arc magmatism in the Archean, but rather they are produced under rare circumstances when the upwelling mantle rises to shallow levels during the initiation of subduction. As the subduction zone matures, the fore-arc will be cooled by the slab and melting there will cease. The cooling of the fore-arc marks the end of the high temperature regime that produces boninites and komatiites, and the beginning of more typical calc-alkaline arc volcanism [*Stern and Bloomer, 1992*].

The arc model predicts that ultra-mafic assemblages intermediate between modern boninite bearing sequences and Archean komatiite bearing sequences should be present in the Proterozoic and Phanerozoic rock record. Such an intermediate case may be preserved in the 1.92 to 2.04 Ga Cape Smith fold belt, northern Ontario. The ultramafic sequences at Cape Smith contain basaltic komatiites and low-Ti tholeiites (a boninite related magma), but do not contain komatiites [*van Staal et al., 1997*]. Consistent with a model for their formation in a young subduction zone's fore-arc, the basaltic komatiites are contemporaneous with the spatially associated Watts Group ophiolite (2.00 Ga), and are followed by the calc-alkaline sequences of the Narsajuaq arc (1.83-1.80 Ga). The younger (480 Ma) Betts Cove ophiolite (Newfoundland) preserves a cooler fore-arc assemblage in which boninites and low Ti tholeiite predominate, interlayered with lesser amounts of basaltic komatiite [*Bedard, 1999; Upadhyay, 1982*]. These intermediate cases represent a link between Phanerozoic fore-arc magmatism and komatiite sequences in Archean greenstone belts and track the cooling of the Earth's mantle.

A hydrous origin for komatiites has been argued against previously on the basis that such ultramafic magmas would devolatilize and crystallize as they ascended, and therefore could not preserve their high Mg#s or would explode violently at low pressures

[Arndt *et al.*, 1998]. Yet, boninites are high Mg# hydrous magmas. They erupt on the ocean floor, and preserve extremely high H₂O contents in their glasses, much higher than predicted by equilibrium studies of H₂O solubility [Ohnenstetter and Brown, 1996]. Thus, while it is clear that our understanding of devolatilization is incomplete, the submarine eruption of komatiites could allow them to preserve high H₂O contents without fractionation or vesiculation. Komatiites that ascend to the surface would vesiculate, and may be represented by the komatiite tuffs that are often observed and by the vesiculated komatiites observed by Dann (in prep.). Both boninites and komatiites are extremely glass rich [Ohnenstetter and Brown, 1992], much more so than other mafic extrusive or intrusive rocks. This could be the result of high magmatic H₂O, which would suppress crystal nucleation. At the same time, high H₂O contents would increase crystal growth rates and could help explain the unusual spinifex textures seen in komatiites [Grove *et al.*, 1997].

The mantle residue left by the production of Barberton komatiites is an excellent candidate for producing the cratonic lithosphere [Boyd, 1989]. The melting events that produced the Kaapvaal lithosphere and Barberton komatiites coincide in age [Pearson *et al.*, 1995], and record similarly high degrees of melting. Komatiites and cratonic lithosphere should not mass balance with fertile peridotite as envisioned by Herzberg [Herzberg, 1993], because a variety of melts are extracted throughout the melting process and an unknown amount of mobile major elements (SiO₂, CaO, Na₂O, K₂O) may be added to the mantle by the metasomatising fluids. In our model the initially fertile mantle is depleted by a combination of anhydrous and hydrous melting processes. As the depleted residue resides in the fore-arc, the depleted mantle will be cooled by conduction and metasomatized by slab fluids. The buoyant (low FeO and Al₂O₃) and viscous (cold)

fore-arc plug could be accreted under the cratons when continent-continent collision ends subduction. Thus it will have both the chemical (depleted, metasomatised) and physical (cold, chemically buoyant) features of the Kaapvaal cratonic keel [*Jordan, 1979*].

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TABLES

Table 1. Siliceous high magnesium basalts (SHMB) and high SiO₂ komatiites

Sample #	SHMB												Komati ⁶	
	Negri ¹		Nondweni ²		Belingwe ³		Venters-dorp ⁴		Welte-vreden ⁵		Ball ⁷	G.L. ⁷		
	331/ 338	331/ 339	Au 824	Au 821	NG 220	NG 137	5	bw/1b	SA412 -8	SA412 -9	NDC87 -12B	RC96 -5	AB9	5085
SiO ₂	55.4	54.7	52.7	53.7	53.5	52.7	52.9	49.5	55.2	53.9	52.1	52.8	52.4	55.0
TiO ₂	0.43	0.39	0.82	0.62	0.54	0.54	0.50	1.03	0.44	0.44	0.32	0.28	0.72	0.49
Al ₂ O ₃	11.7	11.9	8.3	6.5	11.1	10.7	8.1	8.7	10.4	10.2	8.8	9.1	8.6	7.14
Cr ₂ O ₃			0.18	0.30										
FeO*	9.2	9.6	12.7	11.8	10.6	11.2	10.8	11.3	9.4	10.8	10.6	12.3	10.8	9.0
MnO	0.22	0.19	0.23	0.22	0.17	0.16	0.19	0.16	0.18	0.19	0.22	0.19	0.23	0.14
MgO	12.3	11.7	13.4	13.9	16.2	13.3	11.8	14.3	13.1	10.7	14.8	13.6	11.4	13.7
CaO	7.9	7.5	9.8	11.4	6.6	8.9	11.5	8.0	7.2	9.0	10.4	8.0	10.6	8.2
Na ₂ O	1.92	2.72	2.19	1.36	1.19	2.14	2.29	0.89	2.91	3.61	0.67	2.36	2.88	1.55
K ₂ O	0.48	0.07	0.15	0.34	0.02	0.24	0.04	0.31	0.06	0.06	0.94	0.05	0.06	0.22
P ₂ O ₅	0.04	0.04	0.09	0.06	0.06	0.03	0.67	0.31	0.05	0.04	0.03	0.00	0.07	0.06
LOI	1.76	2.47			4.95	3.51		4.99	3.19	1.87	1.78	2.72	1.69	2.75
Total	99.5	98.8	101	100	99.9	99.9	98.9	94.7	98.9	98.8	98.8	98.6	97.9	95.5
Mg#	0.70	0.69	0.65	0.68	0.73	0.68	0.66	0.69	0.71	0.64	0.71	0.66	0.65	0.73
CaO/Al ₂ O ₃	0.67	0.63	1.18	1.76	0.59	0.83	1.42	0.92	0.69	0.88	1.18	0.88	1.23	1.15

¹ Sun *et al.*, 1989; ² Riganti and Wilson, 1995 ³ Nisbet *et al.*, 1977; ⁴ McIver *et al.*, 1982⁵ Lahaye *et al.*, 1995; ⁶ Jahn *et al.*, 1982; ⁷ Hollings *et al.*, 1999⁸ J. Dann (unpub. Data) ; ⁹ Fan and Kerrich, 1997; ¹⁰ Hollings and Kerrich, 1999; ¹¹ Smith, 1987

Table 1(cont.). Siliceous high magnesium basalts (SHMB) and high SiO₂ komatiites

Sample #	SHMB													
	Negri ¹		Nondweni ²		Belingwe ³		Venters-dorp ⁴		Welte-vreden ⁵		Ball ⁷	G.L. ⁷	Komati ⁶	
	331/ 338	331/ 339	Au 824	Au 821	NG 220	NG 137	5	bw/1b	SA412 -8	SA412 -9	NDC87 -12B	RC96 -5	AB9	5085
Ni	172	191	102	374	567		138	773						273
Cr			1203	2024	1528		904	1876	935	567				1220
Zr	49.0	50.0	63.0	44.0			44.0	89.0			31.7	10.7		23.0
Nb	3	3.2	2.4	1.6			2.5	4			1.28	0.35		2
Y			19	14			17	15	12.7	8.74				8
Sr	111	140	62	45			33	67	41.3	25.3				24.3
Rb	13	4	0.5	5.8			1	3	0.92	0.76				1.43
Ba	222	46	22	21			28	192	22.5	12				
Ti	2580	2340									3542	3545		
Ta											0.1	0.03		
Hf											0.91	0.37		
La	8.68	8.28	4.51	7.74					2.59	0.84	2.21	0.42	3.27	
Ce	17.5	15.9	11.3	10.1					6.49	2.52	5.57	1.23	8.89	
Pr			1.6	1.43					0.88	0.4	0.68	0.22		
Nd	6.43	6.5	7.76	6.5					4.14	2.14	2.92	1.16	6.4	
Sm	1.5	1.52	2.49	1.86					1.21	0.83	0.84	0.48	1.86	
Eu	0.47	0.42	0.83	0.61					0.45	0.33	0.32	0.17	0.65	
Gd	1.65	1.66	3.01	2.21					1.58	1.19	1.09	0.86	2.27	
Tb			0.5	0.38					0.28	0.19	0.17	0.16		
Dy	1.9	1.81	3.21	2.33					1.89	1.54	1.24	1.21	2.65	
Ho									0.43	0.33	0.26	0.29		
Er	1.24	1.15	1.85	1.31					1.24	1.04	0.8	0.8	1.65	
Tm									0.18	0.15	0.12	0.12		
Yb	1.2	1.1							1.23	0.97	0.73	0.83	1.53	
Lu	0.19								0.2	0.14	0.12	0.13	0.24	

Table 1.(cont.) Siliceous high magnesium basalts (SHMB) and high SiO₂ komatiites

Sample #	Komatiites													
	Tisdale ⁹		Ball ⁷		N. Caribou ¹⁰				Commondale ¹¹				Barberton ⁸	
	B4	T6	O9D	O9E	O1C	MU95 -23	MU95 -30	SP3	SP9	SP11	SP5	K5- 22 B	K5- 3 1	C-13
SiO ₂	50.8	52.1	50.2	52.8	51.9	49.7	52.2	50.3	52.1	52.4	52.8	52.1	51.0	51.1
TiO ₂	0.40	0.40	0.28	0.17	0.21	0.41	0.27	0.40	0.39	0.32	0.28	0.33	0.52	0.51
Al ₂ O ₃	6.02	4.68	7.78	5.05	5.55	8.68	5.65	7.36	4.66	3.52	3.26	3.43	5.10	5.36
Cr ₂ O ₃												0.34	0.39	0.42
FeO*	10.8	8.8	11.7	9.4	10.2	11.6	10.2	11.5	11.1	10.7	11.4	10.1	11.9	10.5
MnO	0.18	0.14	0.21	0.16	0.13	0.29	0.23	0.19	0.25	0.15	0.14	0.13	0.20	0.13
MgO	26.3	28.5	21.1	23.4	25.3	20.3	23.1	21.3	21.5	24.1	24.9	26.7	19.0	23.0
CaO	5.17	4.07	7.20	7.87	5.47	7.31	6.87	9.25	10.0	9.30	7.06	5.44	9.46	7.62
Na ₂ O	0.01	0.12	0.23	0.11	0.12	0.33	0.25					0.00	0.96	0.00
K ₂ O	0.01	0.01	0.02	0.00	0.00	0.05	0.03	0.02	0.02			0.13	0.04	0.01
P ₂ O ₅	0.03	0.03	0.02	0.02	0.00	0.04	0.02	0.03	0.02	0.01	0.02	0.03	0.04	0.05
LOI	6.40	7.68	3.47	3.41	5.94	3.15	3.84	2.83	1.89	2.40	3.27	4.73	3.17	5.01
Total	99.7	98.8	98.7	99.0	98.9	98.7	98.9	100	100	101	99.8	98.9	98.7	98.8
Mg#	0.81	0.85	0.76	0.82	0.82	0.76	0.80	0.77	0.78	0.80	0.80	0.83	0.74	0.80
CaO/Al ₂ O ₃	0.86	0.87	0.93	1.56	0.99	0.84	1.22	1.26	2.15	2.64	2.17	1.58	1.86	1.42

Table 1.(cont.) Siliceous high magnesium basalts (SHMB) and high SiO₂ komatiites

Sample #	Tisdale ⁹		Ball ⁷		Komatiites N. Caribou ¹⁰			Commondale ¹¹				Barberton ⁸		
	B4	T6	O9D	O9E	O1C	MU95	MU95	SP3	SP9	SP11	SP5	K5-	K5-	C-13
						-23	-30					22	3	
												B	1	
Ni														
Cr														
Zr	18.4	17.4	23.7	14.8	12.1	45.0	31.0	28.4	28.6	23.6	25.2			
Nb	0.32	0.88	1.06	0.72	0.51	3.02	1.45	2.2	2.5	1.9	0.2			
Y														
Sr														
Rb														
Ba	11.5	2.69						7.1	29.4	32.1	19.8			
Ti	3575	3578	3540	3538	3539	3547	3549	3635	3637	3638	3636			
Ta			0.08	0.06	0.04	0.22	0.14							
Hf	0.51	0.52	0.7	0.35	0.39	1.31	0.76						0.73	
La	0.41	0.59	1.37	0.95	1.58	5.85	2.4						2.22	
Ce	1.78	1.56	3.47	2.47	3.56	12.3	5.24						5.49	
Pr	0.38	0.29	0.5	0.34	0.43	1.34	0.59						0.89	
Nd	2.24	1.82	2.2	1.59	2.05	5.48	2.58						4.7	
Sm	0.92	0.88	0.61	0.52	0.66	1.5	0.72						1.42	
Eu	0.16	0.16	0.28	0.14	0.23	0.46	0.27						0.45	
Gd	1.36	1.29	0.97	0.61	0.82	1.72	0.88						1.8	
Tb	0.23	0.24	0.17	0.12	0.14	0.28	0.15						0.3	
Dy	1.6	1.6	1.18	0.81	1.01	1.86	1						1.97	
Ho	0.33	0.33	0.27	0.18	0.2	0.39	0.22						0.4	
Er	0.93	0.91	0.78	0.5	0.58	1.23	0.61						1.18	
Tm	0.13	0.12	0.11	0.07	0.08	0.19	0.09						0.16	
Yb	0.75	0.73	0.77	0.49	0.65	1.21	0.62						1.08	
Lu	0.1	0.1	0.13	0.07	0.1	0.18	0.08						0.16	

FIGURE CAPTIONS

Figure 1. Major element compositions of Barberton komatiite chill margins (filled circles, this study) and basaltic komatiites (filled squares, this study) compared to boninites. a) MgO versus SiO₂. Thin solid line shows effect of olivine fractionation. Only the lowest SiO₂ basaltic komatiites can be related to komatiites by olivine fractionation. b) MgO versus TiO₂. Hatched field are phenocryst bearing picrite samples which may not represent liquid compositions. The boninites, komatiites, and basaltic komatiites have lower TiO₂ than the picrites at all MgO contents. c) MgO versus FeO. d) Al₂O₃ versus CaO/Al₂O₃. Field labeled OIB are glass compositions downloaded from the GeoRoc online database (georoc.mpch-mainz.gwdg.de). Barberton samples analyzed by XRF at Univ. Cape Town.. Field of boninites taken from Marianas, North Tonga, and Bonin island [*Bloomer and Hawkins, 1987; Brown and Jenner, 1989; Crawford et al., 1989; Falloon et al., 1989; Hickey and Frey, 1982, and Brown and Jenner, 1982*].

Figure 2. Comparison of the trace element composition of Barberton basaltic komatiites with Phanerozoic boninites. Nearly identical TE patterns are observed in boninite and basaltic komatiites. a) low La/Sm samples, b) high La/Sm samples with positive Zr and negative Ti anomalies, c) high La/Sm samples with negative Zr and Ti anomalies. Elements arranged in order of compatibility [*Sun and McDonough, 1989*]. CI composition of McDonough and Sun [*1995*]. References for samples are: HOL2 [*Kerr et al., 1999*], 2981 and 46-1 [*Hickey and Frey, 1982*], 5092 [*Jahn et al., 1982*], S-1C,C-9.8,BC-3-12 (this study, analyzed at MIT by ICP-MS).

Figure 3. Ti/Zr versus chondrite normalized $(La/Sm)_n$ (CI composition from *McDonough and Sun, 1995*) for Barberton komatiites (solid squares) and basaltic komatiites (solid circles) compared to boninite (shaded field), MORB (unshaded field), and OIB fields (unshaded field). The negative correlation between Ti/Zr and $(La/Sm)_n$ is a distinctive chemical characteristic of boninites and basaltic komatiites not observed in MORB or OIB.

Figure 4. Trace element composition of selected Barberton komatiites showing range of patterns: LREE depleted with HFSE depletions (B96-7), LREE enriched with HFSE depletions (B95-18), and slightly LREE enriched with positive Zr anomaly. Same element ordering and normalizing procedure as in Fig. 2. Data from Ch. 2.

Figure 5. Major element compositions of komatiites (crosses) and basaltic komatiites (filled triangles) compared to modern boninites (light shaded field). Also shown are composition of low-Ti tholeiites that are interlayered with komatiites (open triangles) and with modern boninites (dark shaded field). a) MgO versus SiO_2 . b) MgO versus TiO_2 . c) Ti/Zr versus $[La/Sm]_n$. Data for komatiites, basaltic komatiites, and interlayered low-Ti tholeiites from Kaapvaal, Belingwe, Yilgarn, Superior, and Baltic cratons [*Arndt and Jenner, 1986; Arndt and Lesher, 1992; Barnes et al., 1995; Cameron and Nisbet, 1982; Cattell, 1987; Echeverria, 1982; Fan and Kerrich, 1997; Hollings and Kerrich, 1999; Hollings and Wyman, 1999; Hollings et al., 1999; Jahn et al., 1982; Jochum et al., 1991; Kerr et al., 1999; Kerrich et al., 1998; Lahaye et al., 1995; Ludden and Gelinas, 1982; McIver et al., 1982; Nisbet et al., 1977; Nisbet et al., 1987; Polat et al., 1999; Puchtel et al., 1999; Pyke et al., 1973; Redman and Keays, 1985; Riganti and Wilson, 1995; Smith*

and Erlank, 1982; Smith, 1987; Sun and Nesbitt, 1978; Sun *et al.*, 1989; Xie and Kerrich, 1994; Xie *et al.*, 1995]. Data for boninite and low-Ti tholeiite field from same references as in Fig. 1.

Figure 6. Trace element composition of komatiites with arc-like TE signatures from the Ball (ND) [Hollings *et al.*, 1999] and Caribou (MU)[Hollings and Kerrich, 1999] greenstone belts. The Zr variation present in the boninite data can also be seen in these komatiites.

Figure 7. a) Cross section of the corner flow in an Archean subduction zone. The slanted upwelling is caused by the temperature dependence of mantle viscosity [Furukawa, 1993]. The penetration of isotherms deep into the wedge in young arcs is predicted from geologic observations [Stern and Bloomer, 1992] and from geodynamic computer models [Kincaid and Sacks, 1997]. Thin dashed lines are isotherms. Thick solid line is the dry peridotite solidus. A, B, and C are points at which the upwelling mantle begins to melt. Gray arrows show anhydrous melting paths that produce low-Ti tholeiite. Thick dashed line is the last equilibration point of rising hydrous melts due to the thermal structure of the wedge. Melting ceases when flow paths rise above this line. Ovals D, E, and F are the regions in which boninites, basaltic komatiites, and komatiites are produced, respectively. Thin gray arrows show the downward limb of the corner flow. Thin black arrows show the ascent of hydrous melts from the water-saturated harzburgite solidus to the point of melt segregation. Melt extent increases along this path as the melts encounter rising temperatures. b) Pressure versus temperature diagram of mantle flow shown in 4a). Symbols and lines are the same. Anhydrous melting paths fall

off the adiabat because of the heat of fusion needed to melt as well as the cooling effects of the slab.

FIGURES

Figure 1

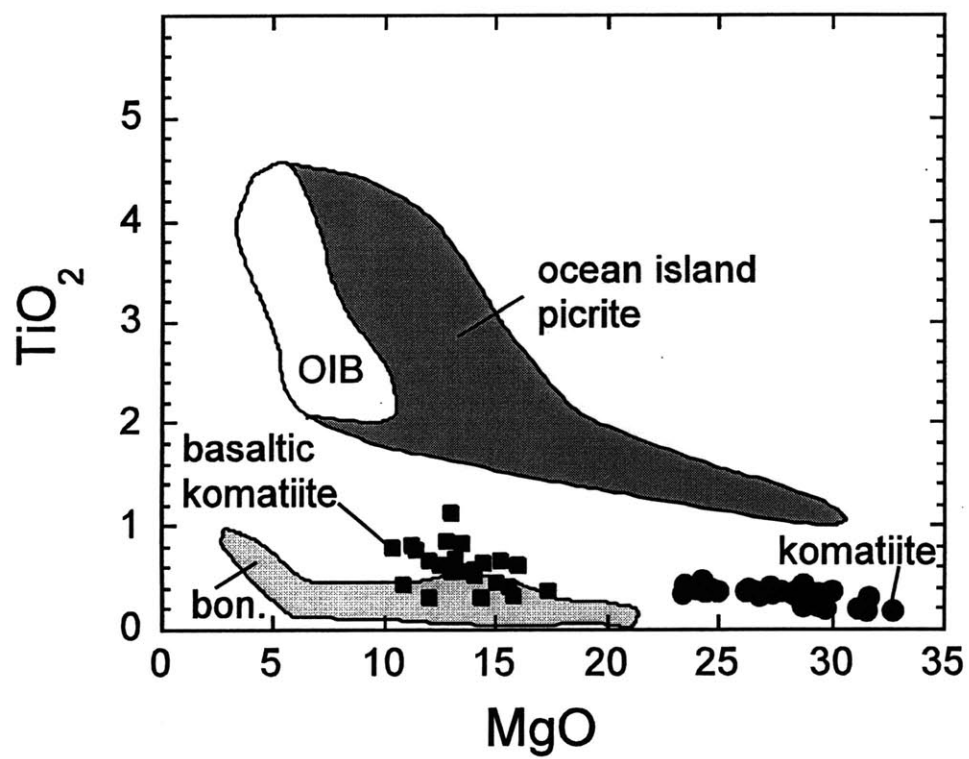
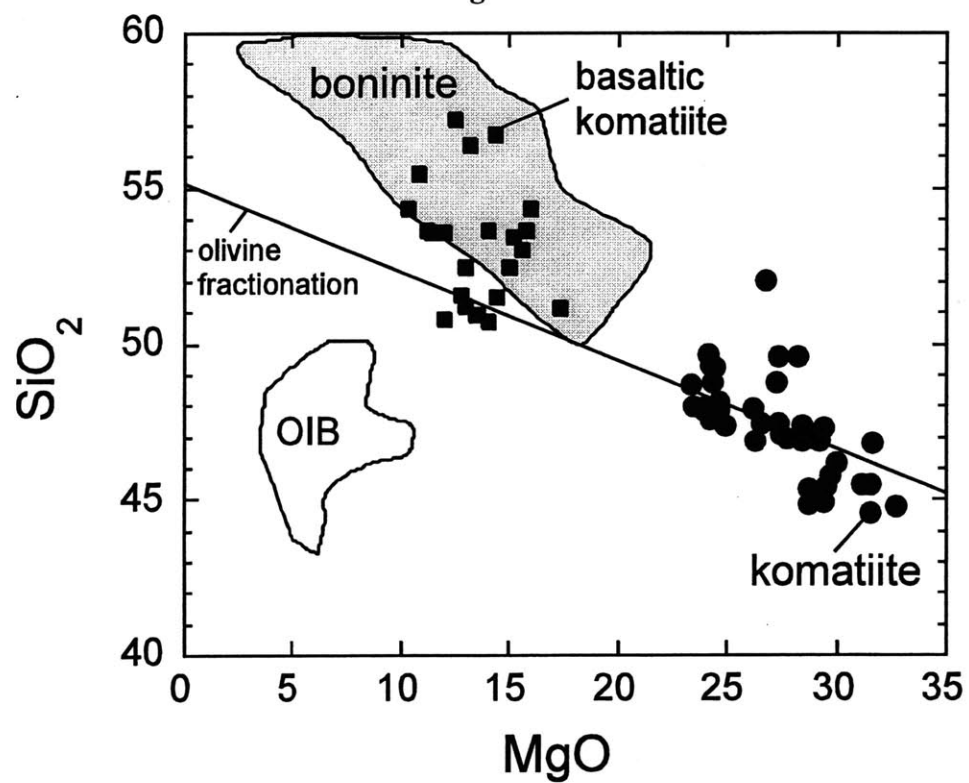


Figure 1(cont.)

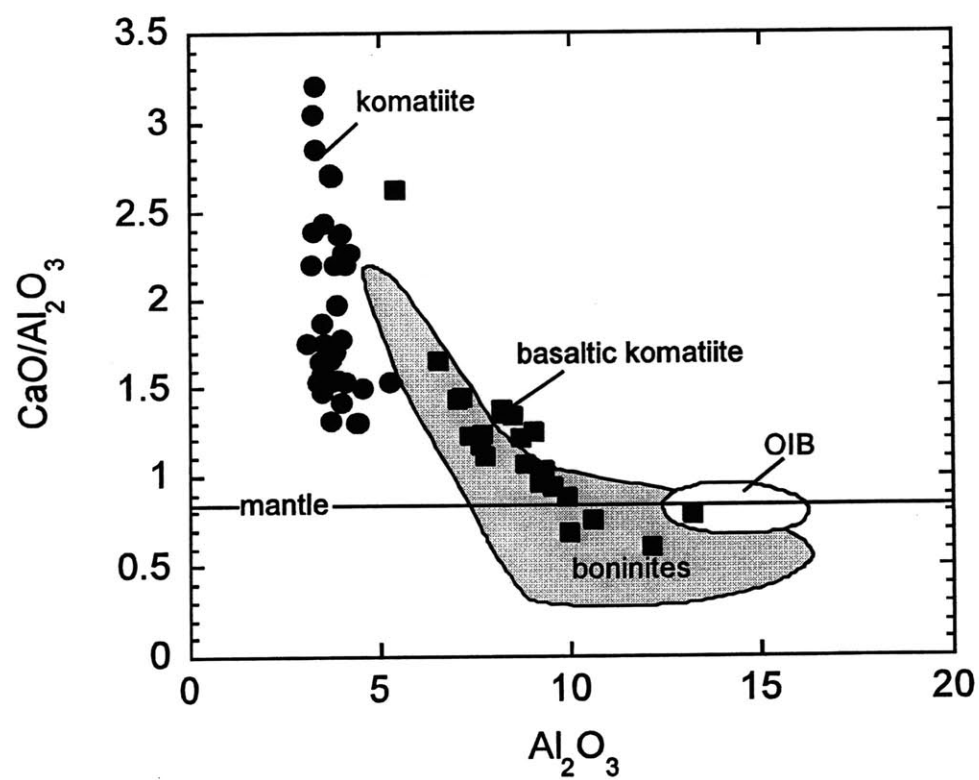
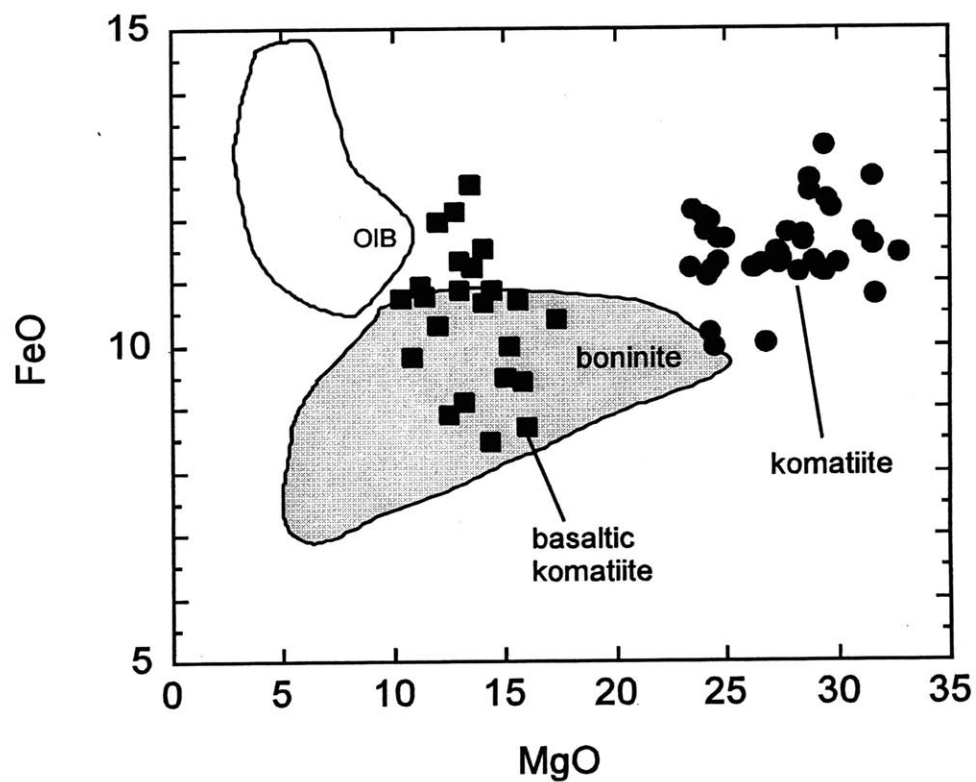


Figure 2

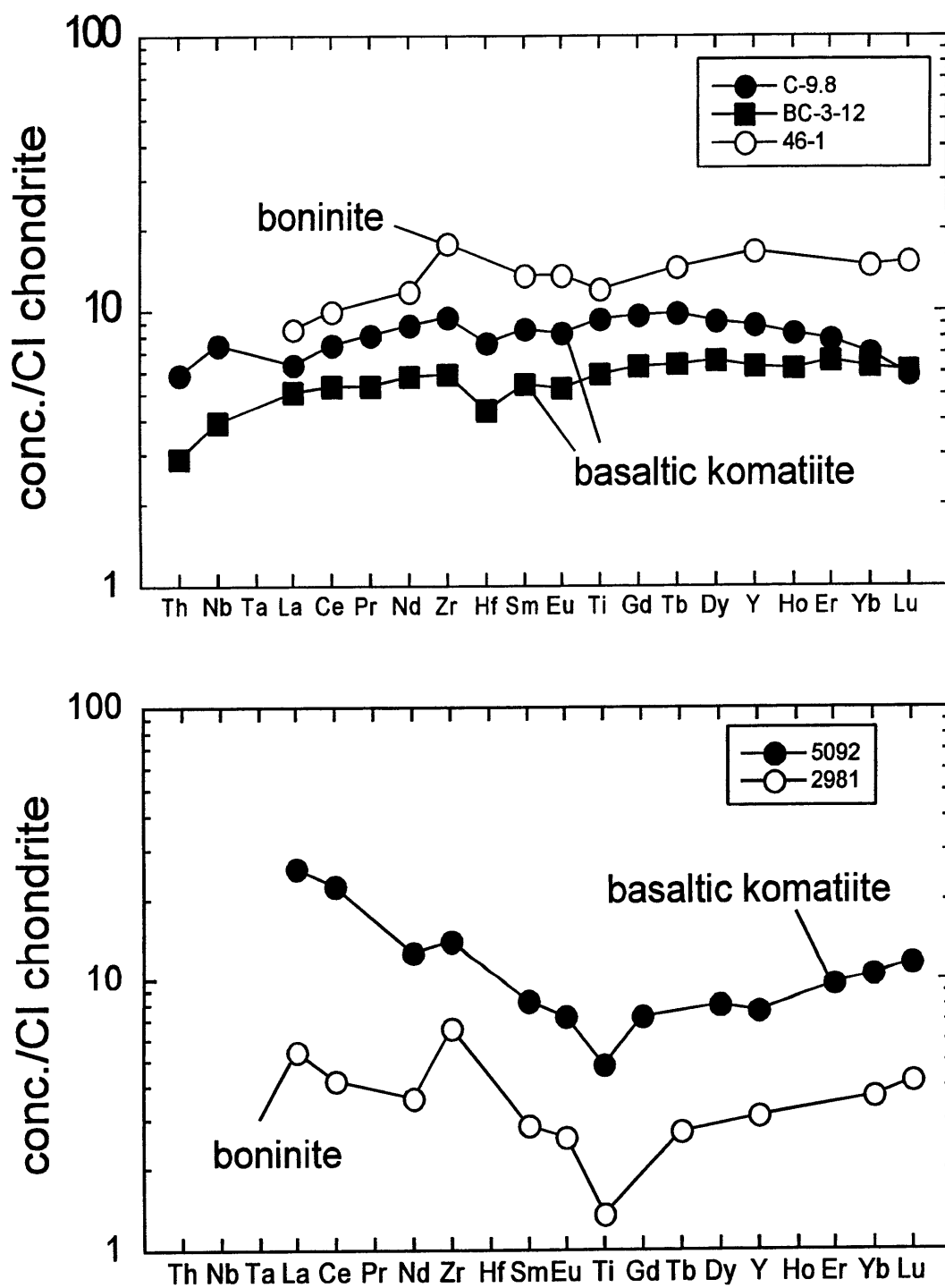


Figure 2(cont.)

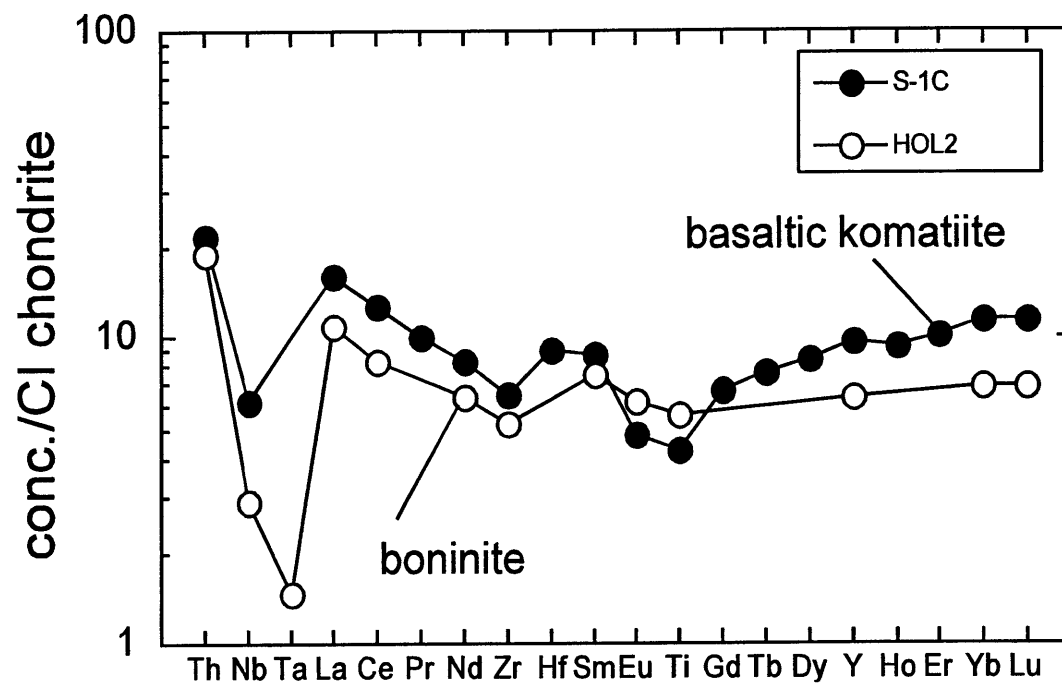


Figure 3

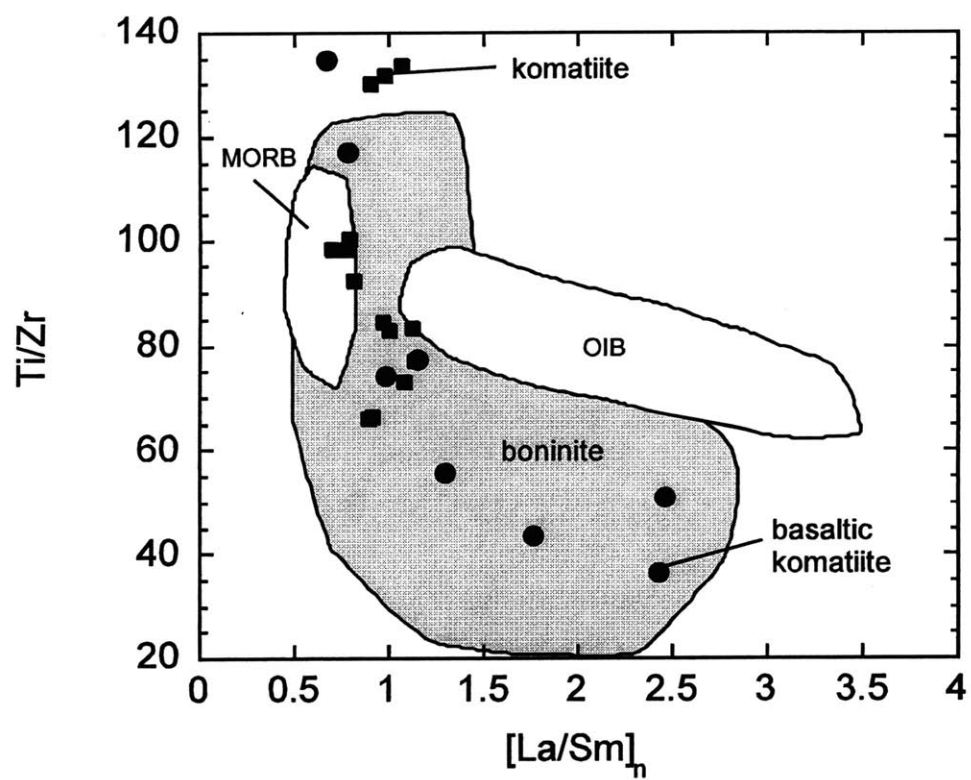


Figure 4

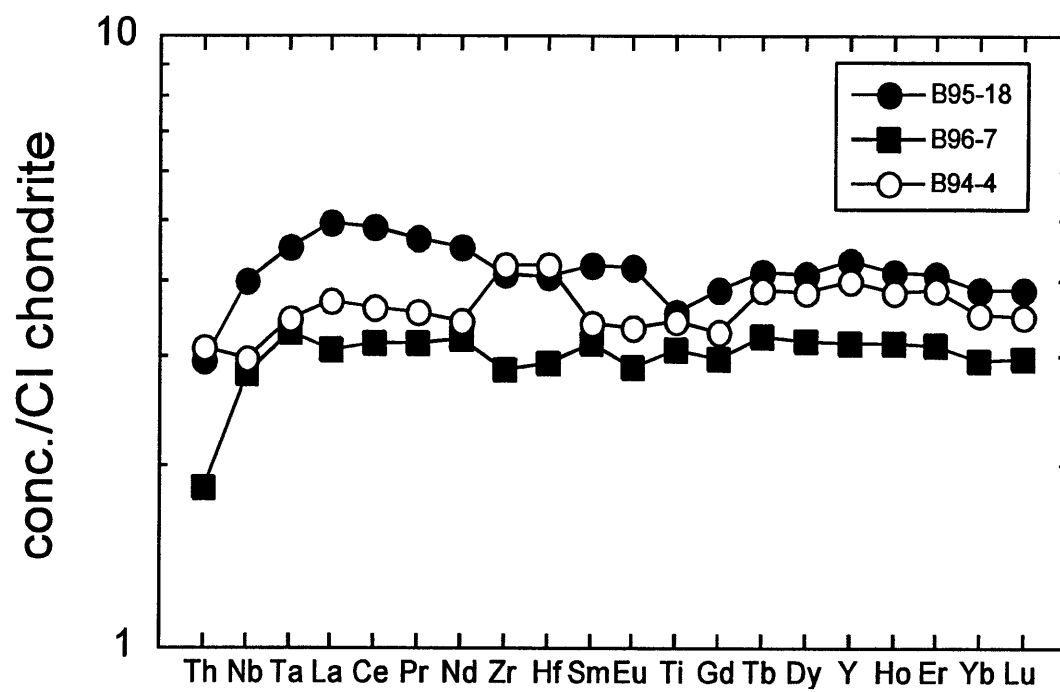


Figure 5

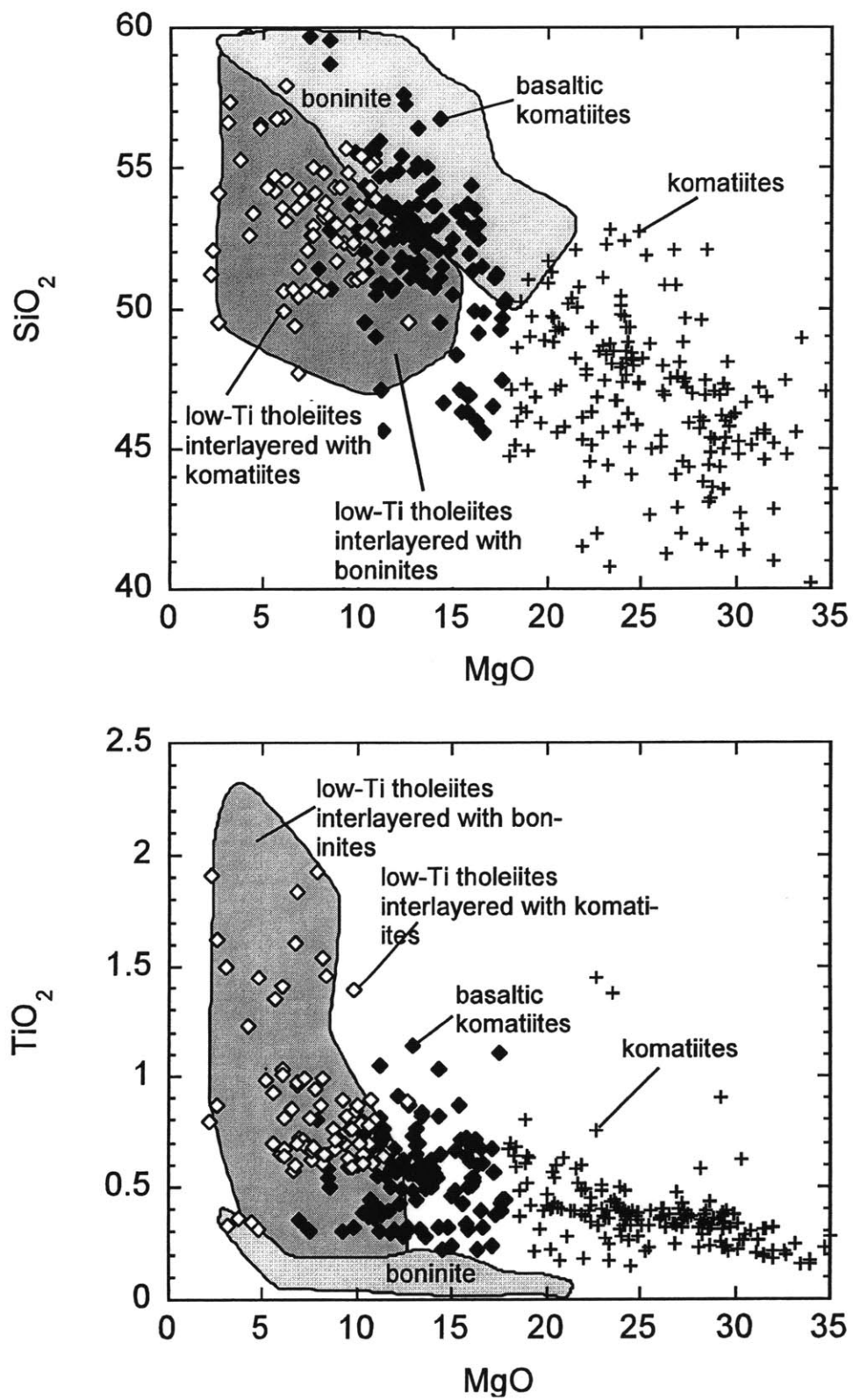


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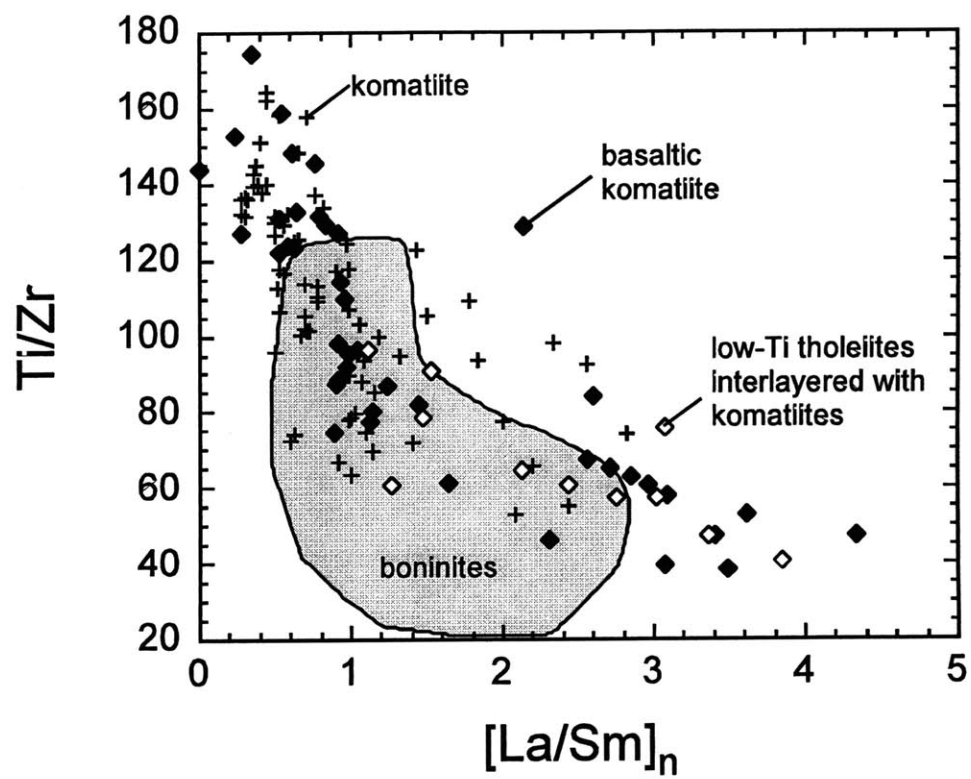


Figure 6

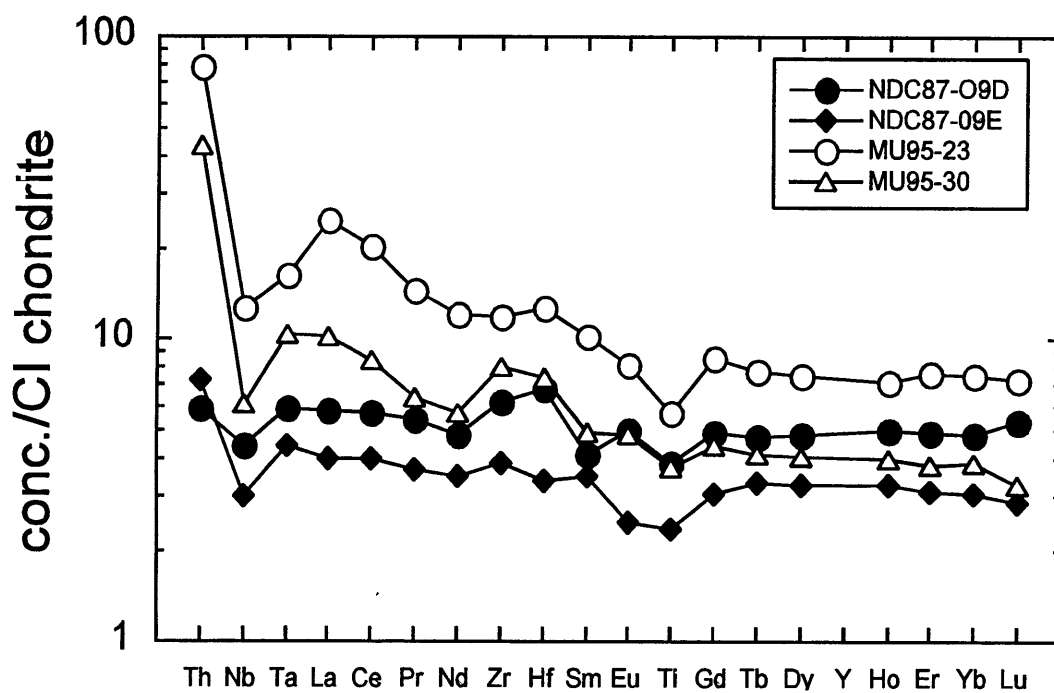


Figure 7

