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Fractional Crystallization of High-K Arc Magmas: Biotite- vs. Amphibole-dominated Fractionation Series in the Dariv Igneous Complex, Western Mongolia

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Abstract

Many studies have documented hydrous fractionation of calc-alkaline basalts producing tonalitic, granodioritic, and granitic melts, but the origin of more alkaline arc-sequences dominated by high-K monzonitic suites has not been thoroughly investigated. This study presents results from a combined field, petrologic, and whole rock geochemical study of a paleo-arc alkaline fractionation sequence from the Dariv Range of the Mongolian Altai. The Dariv Igneous Complex of Western Mongolia is composed of a complete, moderately hydrous, alkaline fractionation sequence ranging from phlogopite-bearing ultramafic and mafic cumulates to quartz-monzonites to late-stage felsic (63-75 wt.% SiO₂) dikes. A volumetrically subordinate more hydrous, amphibole-dominated fractionation sequence is also present and comprises amphibole(±phlogopite) clinopyroxenites, gabbros, and diorites. We present 167 whole rock analyses for the biotite- and amphibole-dominated series. First, we constrain the liquid line of descent (LLD) of a primitive, alkaline arc melt characterized by biotite as the dominant hydrous phase through a fractionation model that incorporates the stepwise subtraction of cumulates of a fixed composition. The modeled LLD reproduces the geochemical trends observed in the 'liquid'-like intrusives of the biotite series (quartz monzonites and felsic dikes) and follows the water-undersaturated albite-orthoclase cotectic (at 0.2-0.5 GPa). Second, as distinct biotite- and amphibole-dominated fractionation series are observed, we investigate the controls on high temperature biotite versus amphibole crystallization from hydrous arc melts. Analysis of a compilation of hydrous experimental starting materials and high-Mg basalts saturated in biotite and/or amphibole suggests that the degree of K-enrichment controls whether biotite will crystallize as an early high-T phase, whereas the degree of water

saturation is the dominant control of amphibole crystallization. Therefore, if a melt has the appropriate major element composition for early biotite and amphibole crystallization, as is true of the high-Mg basalts from the Dariv Igneous Complex, the relative proximity of these two phases to the liquidus depends on the H₂O-concentration in the melt. Third, we compare the modeled LLD and whole rock geochemistry of the Dariv Igneous Complex to the more common calc-alkaline trend. Biotite and K-feldspar fractionation in the alkaline arc series results in the moderation of K₂O/Na₂O values and LILE concentrations with increasing SiO₂ as compared to the more common calc-alkaline series characterized by amphibole and plagioclase crystallization and strong increases in K₂O/Na₂O values. Lastly, we suggest that common calc-alkaline parental melts involve addition of a moderate pressure, sodic, fluid-dominated slab component while more alkaline primitive melts characterized by early biotite saturation involve the addition of a high pressure potassic sediment melt.

Key Words: alkaline, biotite, cumulate, subduction zone, Mongolia

Introduction

Based on trace element similarities, it is well established that subduction-related magmatism is essential for the production of continental crust (CC). Understanding how primitive arc basalts evolve and form continental crust of an andesitic bulk composition, with granitic rocks dominating the upper CC, has been the focus of much research (Jagoutz and Schmidt 2012; 2013; Jagoutz 2010; Lee et al. 2007; Müntener and Ulmer 2006; Sisson et al. 2005). In general, two end member models have been proposed to produce silica-rich derivative liquids: (1) partial melting in the lower continental crust and (2) hydrous fractionation of Si-poor cumulates. Differentiating between these two end-member processes by only studying granites (or the residual/derivative liquids) is difficult as large degrees of fractional crystallization or small amounts of partial melting of basalt produce liquids of similar compositions. Indeed, Tuttle and Bowen (1958) lamented, “Field studies of granites deal with the end products of processes long since completed, and the most detailed mapping and study of these products may fail to give convincing evidence concerning the exact nature of the processes responsible for the relations.” Since Tuttle and Bowen’s early experimental work on granite genesis, however, several key field localities have been identified where relationships between cumulates/restites and derivative liquids have been observed. For primitive calc-alkaline magmas the importance of hydrous fractionation has been documented through careful study and analysis of preserved lower crustal paleo-arc sections of Kohistan (Pakistan) and Talkeetna (Alaska) (DeBari and Greene 2011; Greene et al. 2006; Jagoutz et al. 2011; Jagoutz 2010). In addition, experimental work on primitive basaltic melts have supported the evidence from the field (Grove et al. 2003; Müntener et al. 2001; Sisson and Grove 1993), indicating that in order to produce tonalites, granodiorites, and granites from primitive calc-alkaline basalts, cumulates dominated by SiO₂-poor minerals such as amphibole, garnet, oxides, or An-rich plagioclase must fractionate from the melt.

Although volumetrically less significant than calc-alkaline batholiths, the monzonitic series (monzodiorites, monzonites, and quartz monzonites) characterized by elevated total alkali contents at a given SiO₂ content, are widely present in arcs (e.g., Miller 1977; Miller 1978; Rapela and Pankhurst 1996; Sylvester et al. 1978). Due to their high Na₂O+K₂O and LILE contents, they may constitute significant contributors to the incompatible element budget of the continental crust. Nevertheless, the origin of this monzonitic series has only been investigated in the field to a limited extent. Several field studies on high-K granitoids have suggested that biotite- and clinopyroxene-dominated fractionation from high-K primitive melts is capable of producing these derivative granitic liquids (Fowler and Henney 1996; Fowler et al. 2001; Lobach-Zhuchenko et al. 2008). However, these studies lack exposure of high-K ultramafic and mafic cumulates in significant enough quantities to substantiate the volumes required by their fractionation models. The only other field evidence for biotite+clinopyroxene fractionation from high-K primitive melts comes from the fragmentary evidence provided by phlogopite-bearing ultramafic cumulate xenoliths in high-K volcanics (Buhlmann et al. 2000; Downes et al. 2004; Giannetti and Luhr 1990).

Here, we present whole rock geochemical data for the recently discovered Dariv Igneous Complex (~50 km²) in Western Mongolia, which is comprised of two distinct alkaline fractionation sequences. The first is a complete, moderately hydrous alkaline fractionation sequence ranging from phlogopite-rich ultramafic (wehrlites and clinopyroxenites) and biotite-rich mafic (monzogabbros and monzodiorites) cumulates through quartz-monzonites. The second, more incomplete sequence is comprised of isolated patches of amphibole(±phlogopite)-clinopyroxenites and stocks to km-sized intrusions of amphibole-bearing monzogabbros and (quartz-)monzonites. Through LLD modeling we show that evolved quartz-monzonites and felsic dikes associated with the biotite-dominated sequence can be produced through fractionation of the observed biotite-dominated cumulates from a primitive alkali-rich basalt. In light of the two fractionation sequences observed in Dariv (i.e., with early biotite versus amphibole saturation, respectively), we discuss the potential controls on high temperature amphibole and biotite crystallization in alkaline magmas with a particular emphasis on bulk magma chemistry and water content and highlight the effects of amphibole versus biotite crystallization on the fractionated melt chemistry. We then discuss the different subduction components influencing the mantle wedge and contributing to arc-related calc-alkaline versus high-K parental melts. The whole rock geochemistry and the modeled LLD are discussed in terms of the phase relationships in the quartz-K-feldspar-albite ternary and geochemical trends are compared to the more commonly studied calc-alkaline series.

Geological Setting

The Dariv Range is located in the Gobi-Altai Aimag (Province) of southwestern Mongolia and is part of the Mongolian Altai. The Mongolian Altai are part of the Central Asian Orogenic Belt (CAOB), a vast subduction complex that occupies a significant part of Asia, from the Urals to the Pacific Ocean and from the Siberian and Baltica cratons to the North China and Tarim cratons (Sengör et al.

1993). The Central Asian Orogenic Belt is comprised of amalgamated island arcs, ophiolites, accretionary wedges, and continental fragments that were accreted to the margin of Siberia beginning at *c.* 1.0 Ga and continuing until *c.* 250 Ma, when the Paleo-Asian ocean closed with the collision of the N. China craton along the southern Siberian margin (Buslov et al. 2001; Khain et al. 2003; Sengör et al. 1993; Sengör et al. 1994). The Dariv Range is located at the boundary between what we call here the Altai Allochthon, mostly composed of amphibolite- to granulite-facies Proterozoic metaigneous and metasedimentary lithologies, and the Lake Terrane, an Ediacaran-Early Paleozoic island arc system (Fig. 1a) (Badarch et al. 2002). The Lake Terrane is composed of ophiolites and arc-related plutonic and volcanic rocks, representing fragments of the Paleo-Asian ocean floor and an associated island arc systems (Khain et al. 2003). In the northern Dariv Range, six primary units are attributed to the Lake Terrane: (1) A mantle section (serpentinized harzburgite and dunite), which is intruded and overlain to the northwest by (2) an ophiolite sequence composed of gabbros, a dike complex, and lavas. The southern section of the ophiolite is intruded by an alkaline series ranging from (3) phlogopite-rich ultramafic and biotite-rich mafic cumulates to alkaline granitoids to (4) an amphibole-rich series of amphibole(±phlogopite) clinopyroxenites, hornblendites, amphibole-monzogabbros, -monzodiorites, and -monzonites that together are the primary focus of this study (Fig. 1b). The northern and western parts of the range are comprised of (5) Lake Zone volcanics/volcaniclastics and poorly-studied weakly metamorphosed igneous and sedimentary rocks, such as agglomerates and conglomerates. Lastly, a series of (6) large alkali-feldspar granites that intrude units 1-4 are also present (Fig. 1b). Rocks similar to units 1-4 and 6 are also found in the southern part of the Dariv Range, but the intrusive relationships have not been investigated as thoroughly (see Fig. 1c in Bucholz et al. (2014)). The few previous studies of the area have not recognized the hydrous magmatic sequences (3 and 4), but assigned them to the larger Dariv Ophiolite (also referred to as ‘Bayannur’ or ‘Bayannor’) ophiolite (Dijkstra et al. 2006; Khain et al. 2003; Kozakov et al. 2002; Kovalenko et al., 2014). Based on geochemical characteristics of the dike complex and gabbros, such as Nb-Ta depletions and enrichment in LILEs, the Dariv Ophiolite has been interpreted to have formed in a supra-subduction zone environment (Dijkstra et al. 2006).

Field Relationships and Petrography

Field relationships observed over four summers of fieldwork are described in detail in Bucholz et al. (2014), to which the reader is referred to for the field geology, including field photographs. We briefly present the salient features of the alkaline igneous complex of the northwestern part of the Dariv Range (Fig. 1b, Electronic Supplement Fig. 1-3).

A ~3.5 km wide ultramafic cumulate sequence is located within the central southern part of a 15 x 10 km serpentinized harzburgite/dunite body. The ultramafic cumulates are dominated by biotite-bearing lithologies, however there are minor volumes of amphibole(±biotite)-bearing ultramafic cumulates, which are described in more detail below. The contact between the serpentinite and the cumulate sequence is

marked by numerous small intrusions that cut into the serpentinite and are composed of cumulate minerals. A broadly systematic lithological variation is observed from northwest to southeast (Fig. 1c). Primitive wehrlites characterized by bright green Cr-diopside with minor phlogopite grade into biotite-dominated wehrlites and phlogopite-rich clinopyroxenites and biotite monzogabbros. Monzodiorite to quartz monzonite bodies are also present, sometime occurring as individual stocks cross-cutting other cumulate lithologies and other times gradually transitioning into the monzogabbros. Late stage 10-100 cm wide K-feldspar-rich felsic dikes and biotite-bearing basaltic dikes cross cut the cumulate sequence. Diffuse margins between the felsic dikes and monzonites indicate a comagmatic origin, whereas the margins of mafic dikes are sharply defined. Xenoliths of biotite cumulates and basaltic dikes are common in the monzonites. The serpentinite and both alkaline sequences are intruded by small (10-100 m in diameter) vertically oriented stocks and several large (up to 8 x 5 km wide) intrusions of alkali-feldspar-porphyric granite (Fig. 1b,c). Unpublished U-Pb zircon ages indicate that these (alkali-)granites are significantly younger than the alkaline complex and are neither cogenetic nor contemporaneous with the biotite-dominated lithologies. For this reason, we do not discuss them further.

The plutonic rocks with biotite as the dominant mafic, hydrous mineral comprise a common cumulate sequence resulting from a single LLD (Bucholz et al. 2014) and can be ascribed to a fractionation sequence defined by olivine + clinopyroxene ± Fe-Ti oxides → biotite + apatite → K-feldspar + plagioclase → amphibole + quartz. These rocks are generally very fresh and only clinopyroxene exhibits occasional alteration to actinolitic amphibole, particularly in the evolved rocks. None of the samples exhibit field or microstructural evidence of deformation.

The second sequence of alkaline cumulates, with amphibole as the primary hydrous mineral, is comprised of amphibole±biotite clinopyroxenites, hornblendites, amphibole-monzogabbros, -monzodiorites, and -monzonites which intrude both the biotite-dominated sequence and the serpentinite. The ultramafic cumulates occur as isolated outcrops or as centimeter- to meter-scale intrusions in the serpentinite each with variable modal abundances of constituent minerals. The feldspar-bearing lithologies are generally found as isolated stocks to km-scale intrusions intruding both the serpentinite and the biotite-dominated cumulate sequence (Fig. 1b,c). A detailed map showing the intrusive relationships of the evolved amphibole-bearing lithologies can be found in the Electronic Supplementary Material (Fig. 1-3). Monzodiorites and monzonites with amphiboles aligned due to magmatic flow are the predominant lithologies. These bodies are cross-cut by K-feldspar- and plagioclase-porphyric diorites to monzonites and numerous dikes, including felsic pegmatites, aplites, K-feldspar-plagioclase-quartz-porphyric felsic dikes, and basalts, which are mostly oriented E-W or NW-SE. Although cross-cutting relationships between the different dikes are complex in the field, it seems that the felsic and pegmatitic dikes are the oldest dikes as they are cross cut by the basaltic and K-feldspar porphyric dikes. Although the amphibole-dominated sequence is not continuous in the field, a general mineralogical progression can be observed from the ultramafic lithologies to the more-evolved, feldspar-dominated ones. For this

sequence, we infer a mineral crystallization order of clinopyroxene + apatite → amphibole + biotite → plagioclase + K-feldspar → quartz.

Petrography of the Biotite-Dominated Fractionation Sequence

Wehrlites and Phlogopite Wehrlites

The wehrlites are fine- to medium-grained (0.5-2 mm). The most primitive ($Mg\#^{bulk}=85-91$) phlogopite wehrlites consist of bright green clinopyroxene (~65%, all percentages in the text are modal) and olivine (25-30%) with intercumulus phlogopite¹ (2-10%) and occasional accessory titanomagnetite (Fig. 2a). Olivine occurs as subhedral to anhedral crystals that are commonly poikilitically enclosed within phlogopite. In some samples, olivine shows highly irregular margins surrounded by phlogopite. The modal percentage of phlogopite is variable in the wehrlites and gradually increases to a maximum of 45%, while that of olivine and pyroxene decrease (to <10% and to 45% respectively), resulting in a pronounced orthocumulate texture of olivine and clinopyroxene poikilitically enclosed within phlogopite (Fig. 2b).

Phlogopite clinopyroxenites and phlogopite

The phlogopite clinopyroxenites are comprised of phlogopite, clinopyroxene, and apatite with accessory hemo-ilmenite, titanite, and zircon (Fig. 2c). In the clinopyroxenites, brown-reddish phlogopite grows interstitially between the clinopyroxene and occasionally encloses clinopyroxene. In one sample (MO-11-10), phlogopite is the dominant phase (~75%) and apatite becomes an important constituent (4-5%). Phlogopite occurs both as an intercumulus phase and as elongate light brown euhedral laths up to 1-2 mm in length with subhedral clinopyroxene and stout prismatic apatites. Apatites are poikilitically enclosed by both euhedral and intercumulus biotite.

Biotite Monzogabbros

Monzogabbros consist of alkali feldspar and plagioclase (together 28-50%), biotite (13-25%), and clinopyroxene (31-55%) with accessory subhedral sphene, apatite, zircon, and hemo-ilmenite (Fig. 2d). Biotite grows both interstitially and in large laths (1-2 cm in length), and may poikilitically enclose sphene and apatite. Oligoclase to andesine (An ~20-40) and K-feldspar occur together in subsolvus intergrowth. Apatite occurs as stubby, subhedral 1-2 mm long crystals.

Clinopyroxene Monzodiorites to Quartz-Monzonites

The monzodiorites, monzonites, and quartz-monzonites are composed of large K-feldspar megacrysts (1-2 cm in length) surrounded by smaller grains of K-feldspar and andesine (together 50-60%), quartz (10-20%), biotite (10-15%), amphibole (5-15%), and clinopyroxene ($\leq 5\%$) with accessory apatite, sphene, zircon, and hemo-ilmenite. Biotite occurs as stubby laths, 1-4 mm in length. Clinopyroxene

¹ Throughout the text, we use 'phlogopite' when describing biotite in ultramafic lithologies and 'biotite' when describing biotite in feldspar-bearing lithologies.

contains both biotite and numerous apatite inclusions (5-100 μm diameter). Apatite is also enclosed in biotite.

Amphibole-Dominated Fractionation Sequence Petrography

Amphibole Clinopyroxenites and Hornblendites

Amphibole-bearing clinopyroxenites are comprised of subhedral, 1-2 mm interlocking pargasitic amphibole (~40-50%), 100-300 μm subhedral clinopyroxene (~40-50%), 20-100 μm elongated to stubby apatites (up to 5%), and minor magnetite (Fig. 2e-g). In some samples, minor andesine (An_{45} - An_{35}) and K-feldspar occur as interstitial anhedral grains. When present, phlogopite is a minor phase (<5 modal %), occurring as laths either enclosed in amphibole or interstitially. Apatite is generally poikilitically enclosed by amphibole. In some coarse-grained facies amphibole comprises up to 80% of modal mineralogy and reaches 3 cm in length, with more common dimensions of 1-2 cm.

Amphibole Monzogabbros

Monzogabbros generally display hypidomorphic equigranular textures with subhedral mm to cm-scale amphibole (~35-60%) surrounded by patchy intergrowths of K-feldspar and andesine (40-60%) and clinopyroxene (in part retrograded to actinolite) (<20%) (Fig. 2h). Biotite is often present, but limited to <10%. Accessory minerals include sphene, Fe-Ti oxides, and apatite. Apatite can be up to 1 mm in length and often occurs as inclusions within amphibole. Twinning within plagioclase is common.

Amphibole-rich Granitoids

Felsic intrusives of this series range from amphibole-bearing monzodiorites to quartz-monzonites. These intermediate to evolved lithologies are generally equigranular (though some more porphyric facies are present), and fine- to medium- grained. The rocks are generally undeformed, but locally display magmatic flow textures with distinct foliated appearance. Both plagioclase and K-feldspar occur as mm to cm scale phenocrysts and as smaller grains interlocking with quartz, amphibole, and biotite in the groundmass. Plagioclase often displays both Carlsbad and polysynthetic twinning. Accessory minerals include zircon, apatite, Fe-Ti oxides, and sphene.

Late-Stage Amphibole and Biotite-Bearing Basaltic to Andesitic Dike Petrography

Late stage basaltic to andesitic dikes that cross-cut the plutonic rocks of the alkaline fractionation series can be broadly grouped into three categories: 1) biotite-bearing, 2) amphibole-bearing, and 3) biotite- and amphibole-bearing. Group 1 dikes are comprised of phlogopite, plagioclase, and clinopyroxene with accessory apatite, zircon, and hematite. Phlogopite (50%) occurs in 100-200 μm long blocky laths often enclosing zircon and hematite. Subhedral, rounded 20-100 μm clinopyroxene crystals (5%) are surrounded by oligoclase-andesine (An_{28} - An_{44}) (45%). Plagioclase crystals display irregular margins and appear to have crystallized in between phlogopite. Zircon is an abundant accessory phase

occurring as 20-150 μm long prismatic crystals within both plagioclase and phlogopite. Group 2 amphibole-bearing dikes contain primarily amphibole (50-60%) and plagioclase (40-50%) in the groundmass with accessory Fe-Ti oxides and apatite. Groundmass amphibole is pale green, subhedral, and up to 300 μm in its longest dimension. Groundmass plagioclase has irregular margins, generally growing around amphibole. Up to 20 μm long euhedral, elongate apatite is poikilitically enclosed in plagioclase. In some dikes, amphibole and plagioclase occur as ~0.5-1 cm phenocrysts. Group 3 dikes are similar to Group 2 dikes in mineralogy and texture, however, biotite also occurs as a groundmass phase (10-15%) generally along the rims of amphibole.

Analytical Methods

168 whole rock major and trace element compositions are included in the presented data set. Most samples are from the northwestern part of the Dariv Range, though 14 are from the southeastern part of the range where a few similar alkali-rich lithologies are observed. Fresh pieces with no optical indication of weathering or veining were cut from samples to ensure uncontaminated and representative chemical analyses. Samples were powdered in an agate mill, which was cleaned with silica sand in between samples. The powders were then dried overnight at 105°C. Loss on ignition was determined from mass loss after heating to 1050°C for most samples and to 950°C for samples with high silica contents. Glass discs were prepared using a lithium tetraborate flux. Major elements were measured using a wave-length dispersive X-ray fluorescence (XRF) spectrometer at ETH in Zürich. Trace elements of the fusion discs were determined by laser ablation inductively coupled plasma mass spectrometer (LA-ICPMS) at ETH. The XRF glass discs were broken and analyses were performed on freshly broken surfaces. Samples were loaded along with the NIST610 glass standard and a lithium tetraborate blank in an ablation cell and the ablated material was transported to the ICP-MS by a He carrier gas. The ablation system consists of a 193 nm ArF Excimer laser (Lambda Physik) with a homogenized beam profile connected to an Elan6100 DRC quadrupole ICP-MS. The background was measured for ~40 s prior to each analysis and the laser signal was integrated over 40-50 s. Using a 90 μm laser spot size, a minimum of 3 shots per disc were done to ensure homogeneity of the analyzed pellet. The analytical set-up was tuned for optimum performance across the entire mass range and daily optimization of the analytical conditions were performed to ensure a ThO production rate of below 0.2% (i.e. Th/ThO intensity ratio <0.002), and a Th/U sensitivity ratio of 1 measured on the NIST610 glass standard. Two analyses on the NIST610 standard at the beginning and end of each set bracketed up to 20 analyses of unknowns. The blank was measured at the beginning of each session and its spectrum subtracted from the unknown spectra. The NIST610 standard was used as an external standard to calibrate analyte sensitivities and to correct for linear drift during analyses. Data reduction of LA-ICP-MS analyses followed the procedures described in Longerich et al. (1996). CaO was used as the internal standard element to correct for matrix effects and calculate trace element concentrations.

Whole Rock Geochemistry

Major Element Chemistry

GPS locations and whole rock major and trace element chemistry of the analyzed samples are provided as Electronic Supplementary Material. Based on total major element chemistry and modal mineralogy, both the biotite- and amphibole-dominated series follow a calc-alkaline trend. The feldspar-bearing rocks belong to the sub-alkalic trend of monzogabbros, monzodiorites, and (quartz-) monzonites (Fig. 3c) (Lameyre and Bowden 1982). Following the classification of Frost et al. (2001), the monzodiorites, monzonites, and quartz-monzonites are meta-aluminous, magnesian, and belong predominately to the alkali-calcic trend using the modified alkali-lime index (MALI: $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO}$). The late-stage felsic dikes are metaluminous to slightly peraluminous ($0.95 < \text{Al}/(\text{Ca}-1.67\text{P}+\text{Na}+\text{K}) < 1.1$) and predominantly magnesian.

Biotite-Dominated Sequence

With progressing fractionation, the Mg# (molar $\text{Mg}/(\text{Mg}+\text{Fe}^{\text{T}}) \times 100$) decreases from the most primitive ultramafic cumulates to the evolved (quartz-)monzonites (Fig. 3a). The major element chemistry of the ultramafic cumulates mainly depends on the mode of olivine, clinopyroxene and biotite. The phlogopite-free wehrlites contain 47-52 wt.% SiO_2 , 1.0-1.5 wt.% Al_2O_3 and almost no K_2O , while the phlogopite clinopyroxenites have 43-52 wt.% SiO_2 , 3.1-10.7 wt.% Al_2O_3 and up to 4.4 wt.% K_2O (Fig. 3b,d). SiO_2 increases with the increasing abundance of feldspar in the monzogabbros and more evolved rocks to ~63 wt.% in the monzonites and to 70-75 wt.% in the late-stage granitic dikes. CaO decreases constantly with decreasing Mg#, due to the decrease in modal abundance of clinopyroxene and the decrease in anorthite content in plagioclase with progressive fractionation. Al_2O_3 contents peak at ~19 wt.% in the monzodiorites and quartz-monzonites due to the abundance of feldspar (Fig. 3b). The felsic dikes are consistently lower in Al_2O_3 than the most evolved monzonites (14-16 wt.%). Na_2O contents remain low in the ultramafic cumulates (<0.3 wt.%) and do not increase much until alkali-feldspar becomes a fractionating phase. Total alkalis reach 8 wt.% in the quartz monzonites (Fig. 3c). Due to its compatibility in biotite, TiO_2 is strongly controlled by biotite mode in the ultramafic cumulates, increasing from the phlogopite-poor to the phlogopite-rich cumulates and reaching 2.7 wt.% in the phlogopite. TiO_2 then decreases with increasing SiO_2 in the monzogabbros and the monzonites (Fig. 3e). P_2O_5 contents in the ultramafic cumulates are controlled by apatite abundance with a maximum of 1.4 wt.% P_2O_5 in the apatite-rich phlogopite sample, but decrease steadily with increasing degree of fractionation.

Amphibole-Dominated Sequence

The major element chemistry of the ultramafic amphibole cumulates mainly depends on the mode of clinopyroxene, amphibole, and, to a lesser extent, biotite. Only two primitive amphibole (+ minor

phlogopite) clinopyroxenites (MO-10-398 and MO-10-373) were identified with Mg#’s of 85-86, SiO₂ contents of 53.5 wt.%, and Al₂O₃ of 1.7-3.4 wt.%. The next most primitive amphibole clinopyroxenites have Mg#s of 67-73 and SiO₂ contents of 48.5-52.8 wt.%. As the mode of hornblende increases, the Mg# of the cumulates decreases to ~50 and SiO₂ contents decrease to 38.1 wt.% in the hornblendites. In the amphibole-rich clinopyroxenites, Al₂O₃ contents are 7.9-12.5 wt.% (Fig. 3b) and FeO concentrations are high (10.4-18.3 wt.%). K₂O contents are lower in the amphibole-dominated clinopyroxenites than in the phlogopite-rich ultramafic lithologies, varying between 0.5 and 2.0 wt.% (Fig. 3d). Conversely, Na₂O contents are higher in the amphibole clinopyroxenites (2.4-4.7 wt.%) than in the phlogopite clinopyroxenites. With the onset of feldspar crystallization in the amphibole gabbros and diorites, SiO₂ increases to 53.9 and 59.8 wt.%. In the more evolved rocks, Al₂O₃ contents are primarily a function of feldspar mode and reach a maximum of 19.5 wt.% in an amphibole gabbro (Fig. 3b). CaO decreases constantly with decreasing Mg#, due to the decrease in modal abundance of clinopyroxene, with the amphibole clinopyroxenites and monzogabbros containing 11.9-16.0 wt.% and 5.1-9.6 wt.% CaO, respectively. TiO₂ concentrations are the highest in the amphibole clinopyroxenites (reaching 2.9 wt.% in sample MO-10-328) and generally decrease with increasing SiO₂ (Fig. 3e). P₂O₅ contents are generally high (up to 2.1 wt.%) in the amphibole clinopyroxenites due to high modal abundances of apatite, but then decrease with progressive fractionation.

Trace Element Chemistry

Biotite-Dominated Sequence

Ni and Cr are positively correlated with Mg# and strongly decrease with differentiation. This trend is concordant with early fractionation of olivine, clinopyroxene, and minor Cr-spinel. Ba enrichment in the ultramafic cumulates is controlled by phlogopite abundance, reaching 2290 ppm in the phlogopite with 60 modal % phlogopite. In the evolved rocks, Ba concentrations remain uniformly high (750-1500 ppm) due to its compatibility with alkali feldspar. Rb follows trends similar to Ba. The ultramafic rocks mostly exhibit depleted Pb and Sr signatures and depletion in the HREE relative to LREE ((La/Yb)_N = 2-12), (Fig. 4a-d). The more evolved feldspar-bearing rocks exhibit positive Pb anomalies and enrichment in LILEs, (Fig. 4e-h). No Eu enrichment is present in monzodiorites to quartz-monzonites, but there is strong Sr enrichment due to the presence of oligoclase to andesine (An₁₆₋₄₀) in these rocks (Fig. 4f,g). The evolved rocks are more enriched in LREE than the wehrlitic cumulates ((La/Yb)_N = 8-25) (Fig. 4). Trace element patterns normalized to primitive mantle for the biotite-dominated sequence exhibit depletions in Nb, Ta, Zr, and Hf except for the quartz monzonites which have normalized Zr and Hf concentrations comparable to other incompatible elements (Fig. 4). Th and U are depleted in most, but not all, phlogopite-rich ultramafic cumulates and monzonites, while there is no distinct depletion in the felsic dikes.

Amphibole-Dominated Sequence

Ni and Cr contents are highest in the ultramafic cumulates (up to 208 and 1790 ppm, respectively) and are positively correlated with Mg#. Ba and Rb contents in the ultramafic lithologies of the amphibole-dominated sequence are controlled by the modal abundance of biotite and are therefore generally lower than that of the biotite-only fractionation sequence (Fig. 5a). The ultramafic amphibole-bearing cumulates are variably enriched or depleted in Pb with respect to other incompatible elements, have negative Sr signatures, and are depleted in HREE relative to LREE ($(La/Yb)_N = 7-22$) (Fig. 5a). No Eu enrichment is present in the amphibole monzogabbros or diorites, but they generally exhibit a strong enrichment in Sr (Fig. 3f, 5b,c). The feldspar-bearing lithologies show a similar to slightly greater enrichment in LREE to HREE as the ultramafic cumulates ($(La/Yb)_N = 5-49$) (Fig. 5). The feldspar-bearing amphibole monzogabbros and granitoids exhibit enrichments in Pb and LILE relative to other incompatible elements (Fig. 5b,c). Nb, Ta, Th, and U are all depleted relative to other incompatible elements, while Zr and Hf are depleted in the ultramafic cumulates and monzogabbros but not in the more Si-rich intrusives

Discussion

Liquid Line of Descent (LLD) Modeling – Biotite-Dominated Series

Field relationships clearly indicate that quartz-monzonites that have biotite as the predominant hydrous mineral are intimately related to the biotite-dominated cumulate sequence (Bucholz et al. 2014). Therefore, in order to test whether these evolved quartz-monzonites and late stage felsic dikes could be produced by fractionation of the biotite-bearing ultramafic and mafic cumulates from a primitive melt, we model the LLD and compare the results to bulk rock analyses. We do not model the LLD of the amphibole-dominated sequence due to the lack of primitive amphibole cumulates (Fig. 3a) and the incomplete characterization of more primitive fractionating lithologies.

Model Description

The LLD of the magma parental to the biotite-series cumulates was modeled by stepwise subtraction of cumulates of fixed composition following the method described in Jagoutz (2010) (see his equation 1). Fractionation steps were 1%. This model was chosen over more traditional methods utilizing mineral-melt partition coefficients and corresponding equations for fractional or equilibrium crystallization because the fractionating lithologies and the parental melt composition could be constrained from field observations and chemical analyses. In addition, this method is also independent of the choice of partition coefficients and fractionation mechanism (i.e. fractional versus equilibrium crystallization). The parental melt composition was constrained by averaging the composition of three primitive (Mg# = 67-74, Ni = 144-171 ppm, and Cr = 520-643 ppm) late-stage basaltic dikes with biotite as phenocrysts or in the groundmass that cross-cut the cumulate sequence (samples MO-11-19, MO-9-228, MO-9-230). These synmagmatic dikes have phenocrysts and groundmass mineralogy similar to the

cumulate sequence (e.g., biotite and clinopyroxene) and trace element concentrations that are in equilibrium with clinopyroxenes from the most primitive phlogopite wehrlites (Bucholz et al., 2014). The range of compositions of these dikes corresponds to a K-rich basalt ($\text{Na}_2\text{O} = 1.84\text{-}2.66$ wt.%, $\text{K}_2\text{O} = 1.63\text{-}2.76$ wt.%, $48.7\text{-}52.9$ wt.% SiO_2).

Fractionating compositions were constrained by averaging 1 to 7 samples of representative cumulative lithologies (Table 1). Unaltered dunite (\pm clinopyroxene \pm phlogopite) with clear relationships to the biotite fractionation sequence was not observed in the field, but such dunites have been documented as xenoliths in alkali magmas and early olivine-only crystallization intervals are observed in crystallization experiments on high-K melts (e.g., Richter & Carmichael, 1996). As the most primitive wehrlite sampled is in equilibrium with a melt of Mg# ~66 (all Fe as ferric Fe), we included 5% fractionation of the average of phlogopite-bearing dunite cumulate xenoliths from the Bear Paw Mountains (Downes et al. 2004) to account for the gap between the primitive melt (Mg# 71.6) and a melt in equilibrium with the Dariv wehrlites. We chose these dunites as a range of phlogopite-bearing ultramafic cumulate xenoliths similar to the sequence in Dariv is observed in the Bear Paw Mountains (e.g., phlogopite wehrlites and clinopyroxenites) suggesting a similar crystallization sequence.

Evolved plutonic rocks may range from segregated cumulates to solidified bulk melts, which may be inferred from trace element systematics, such as positive or negative Eu anomalies. Although the evolved rocks do not display a positive Eu anomaly, this is not evidence against feldspar accumulation as all Eu was Eu^{3+} at the moderately elevated oxygen fugacity of +2 to +3 ΔFMQ (log-units above the fayalite-quartz-magnetite buffer) in this fractionation sequence (Bucholz et al. 2014). Instead, elevated Al/Si (>0.17) and Sr/Nd (>27) ratios were taken to indicate accumulation of feldspar and were used to identify the monzogabbros, monzodiorites, and monzonites of cumulate character.

As the areal extent of the various cumulate lithologies in the field is not necessarily representative of total volumes, the mass of each cumulate type crystallized was estimated by utilizing cumulate olivine and clinopyroxene Mg# to calculate the equilibrium melt Mg# and comparing that to the modeled melt Mg# (e.g., Greene et al. 2006) (Fig. 6). With approximately 35% of the total melt Fe present as Fe^{3+} (at the oxygen fugacity of the ultramafic cumulates of +2 to +3 Δ QFM (Bucholz et al., 2014)), the modeled melt Mg# is similar to slightly lower than the melt Mg# calculated to be in equilibrium with olivine- and clinopyroxene from the cumulates (using $K_D^{\text{Fe-Mg}}(\text{olivine-melt}) = 0.3$ (Roedder & Emslie, 1970) and $K_D^{\text{Fe-Mg}}(\text{clinopyroxene-melt}) = 0.23$) (following findings of Sisson & Grove, 1993). In general, calculated equilibrium melt Mg# (including the Fe oxidation state adjustment) for the ultramafic cumulates range from ~70 to 55. We therefore allow for an interval of ultramafic cumulate fractionation until the modeled LLD Mg# reaches ~60. The equilibrium melt Mg# calculated from clinopyroxenes in the more evolved cumulates (monzogabbros, monzodiorites, and monzonites) is lower than that of the modeled LLD. This could be due to uncertainties in the oxidation state of these lithologies or the limited number of samples with clinopyroxene analyses. Within the constraints of Fe-Mg partitioning between melt and crystallizing

phases, the amount of each cumulate type was varied iteratively until an optimal fit between the modeled LLD and more evolved lithologies was achieved. The final model fit yields the following cumulate mass percentages: 5% dunite, 3% wehrlite, 5% phlogopite-poor wehrlites (<0.3 wt.% K₂O in the bulk cumulate), 10% phlogopite-rich wehrlites (>0.7 wt.% K₂O in the bulk cumulate), 8% phlogopitite, 21% high Mg# monzogabbro (bulk Mg# > 65), 14% low Mg# monzogabbro (bulk Mg# < 59), 26% monzodiorite, 5% monzonite. Calculations were performed until 5% liquid mass remained. Furthermore, the composition of the average primitive melt from the three biotite-bearing primitive dikes was modified within error in order to optimally reproduce the geochemical trend defined by the bulk rocks. Oxides or trace elements were not modified more than $\pm 25\%$ of the average, with most to <10% and well within the $2\sigma_{SD}$ of the primitive dikes' average. Assimilation was not considered in the model, but we cannot exclude a minor contribution of this mechanism to the evolving plutonic series.

Uncertainties associated with this modeling approach are discussed in detail by Jagoutz (2010) and include variability in the composition of the primitive parental melt, estimates of the mass fraction of each cumulate type crystallized, and the degree to which the samples used in the average bulk cumulate compositions are representative of the actual fractionating compositions and chemical variability in a given lithology. Our methods of reducing the first two uncertainties are discussed above and we use the best estimates possible from the available constraints. The last source of uncertainty is inherent to a finite whole rock geochemical dataset, but is mitigated by our division of cumulate lithologies into nine coherent geochemical groups.

Model Results

The major and trace element compositions of the derivative melt at 10% fractionation intervals are given in Table 2 and the calculated LLD and fractionated cumulate compositions are shown in Figs. 3, 6, & 7. Beginning with a primitive alkali-rich basalt composition, the model successfully reproduces the major and minor trace element characteristics observed in the most evolved monzonites and late-stage felsic dikes.

SiO₂ Enrichment

A general difficulty in producing silica-rich granitoids by magmatic differentiation alone is that fractionation of gabbros, which have similar SiO₂ contents as basaltic to basaltic andesite melts (48-54 wt%), is inefficient for producing volumetrically significant silica-rich derivative liquids (Annen et al. 2006; Jagoutz 2010). Thus, early appearance of plagioclase and clinopyroxene as fractionating phases does not result in the silica-enrichment observed in upper crustal granitoids. Rather, silica-enrichment requires the fractionation of cumulates dominated by SiO₂-poor minerals. For calc-alkaline basalts, the importance of hydrous, high-P fractionation of silica-poor minerals such as amphibole, garnet, oxides, and An-rich plagioclase is well documented experimentally (Müntener et al. 2001; Grove et al. 2003; Sisson et al. 2005; Alonso-Perez et al. 2009) and from field studies (Greene et al. 2006; Jagoutz et al. 2010; Dessimoz et al. 2012). For the high-K parental basalt in Dariv, the primary fractionating low SiO₂

mineral is biotite, (with ~35 wt.% SiO₂). The phlogopite-rich wehrlites and phlogopites have the required low SiO₂ contents and their fractionation produces sufficient silica enrichment such that subsequent fractionation of monzogabbros and monzodiorites results in further SiO₂ enrichment (Figs. 3 & 6). The model reproduces the silica-content of the least evolved monzonites (55-60 wt.% SiO₂) with 24-63% melt remaining. The most evolved quartz-monzonites and late stage felsic dikes (63-75 wt.% SiO₂) can be produced through fractionation of cumulates when ≤16% of the melt remains. This amount of melt is in reasonable agreement with the volumes of (quartz-)monzonites and felsic dikes observed in the field. Interestingly, whereas moderate to high pressure fractionation has been demonstrated as an effective mechanism to produce SiO₂ enrichment in calc-alkaline basalts (Alonso-Perez et al. 2009; Jagoutz et al. 2011; Müntener et al. 2001), the fractionation sequence observed in Dariv occurred at relatively low pressures (< 0.2-0.4 GPa, Bucholz et al. 2014²) and still resulted in significant SiO₂-enrichment. This is primarily due to the stability of biotite on the liquidus of these melts, but also to the protracted fractionation of olivine resulting from a stability field increasing with decreasing pressure (Esperança and Holloway 1987; Righter and Carmichael 1996).

Other Major Elements

It is illustrative to inspect the behavior of several key oxides to determine the proportion and composition of cumulate lithologies as well as the parental magma composition. Al₂O₃ enrichment of fractionating melts to levels not observed in arc granitoids is a common problem in models of primitive arc magma fractionation (Annen et al. 2006; Blatter et al. 2013). One way to limit Al₂O₃ enrichment is for fractional crystallization to occur at greater pressures. Higher *p*H₂O stabilizes garnet (e.g., Alonso-Perez et al. 2009; Wolf and Wyllie 1994), aluminous amphibole (Grove et al. 2003) and anorthite-rich plagioclase (34-36 wt.% Al₂O₃) which all minimize Al₂O₃ enrichment in fractionating magmas (Annen et al. 2006; Jagoutz 2010). Nevertheless, it has been noted that deeper fractionation results in a larger interval of clinopyroxene crystallization and therefore an increase in the aluminum saturation index (ASI = Al/(2Ca+Na+K)) (Blatter et al., 2013). In Dariv, however, the observed alkaline sequence crystallized at relatively low pressures (0.2-0.4 GPa, Bucholz et al. 2014) and amphibole, garnet, and anorthitic plagioclase are not important fractionating phases in the biotite+clinopyroxene-dominated series. Due to its relatively high Al contents (13.5-16.8 wt.%), biotite crystallization limits Al-enrichment to some extent. The whole rock Al₂O₃ contents of the phlogopite ultramafic cumulates (1.0-10.8 wt.%, Fig. 3b), however, are still low compared to high pressure hornblende and garnetite cumulates from other paleo-arc sequences (e.g., 15.0-22.5 wt.% Al₂O₃ (Jagoutz 2010)) and a further mechanism is required to limit Al-enrichment. An alternative would be a primitive melt that itself has relatively low Al₂O₃ (Annen et al. 2006). Primitive arc basalts have highly variable Al₂O₃ contents of 10-18 wt.% with most between 14-16 wt.%. Primitive high-K basalts from Dariv have Al₂O₃ contents between 12.3-15.3 wt.%. Using a slightly

² Note that the errors of the Al-in-hornblende pressures of Table 2 in Bucholz et al. (2014) were reproduced incorrectly, the correct values are 0.15±0.08, 0.21±0.05, 0.20±0.10, 0.24±0.05, 0.15±0.02, and 0.34±0.02 GPa.

lower Al₂O₃ content (12.9 wt.%) than the average primitive basalt composition, Al-enrichment is sufficiently limited and the observed geochemical trends are reproduced well (Fig. 3b).

A decrease in TiO₂ with SiO₂-enrichment is observed in Dariv and other arc suites (Dessimoz et al. 2012; Greene et al. 2006; Jagoutz 2010). Initially, however, TiO₂ is incompatible during the fractionation of olivine- and pyroxene-rich cumulates. The observed decrease in TiO₂ must therefore be explained by crystallization of a TiO₂-rich phase. In the Kohistan and Talkeetna paleo-arcs amphibole and Fe-Ti oxides had sufficiently high TiO₂-contents to produce a decrease in TiO₂ concentrations with increasing fractionation (Greene et al., 2006; Jagoutz, 2010). In Dariv, the early crystallizing phlogopite has 2.1-4.9 wt.% TiO₂ and phlogopite-rich wehrlites and phlogopitites have the required high TiO₂ contents (1.3 and 2.8 wt.% on average, respectively), to drive fractionating liquids to lower TiO₂ contents (Fig. 3e). In addition, accessory titanomagnetite (3.5-23.0 wt.% TiO₂, Bucholz et al. 2014) contributes to the high TiO₂ concentrations of the phlogopite-rich wehrlites and phlogopitites.

The high K₂O contents of several of the fractionating lithologies (e.g., phlogopite, monzonite) necessitate a primitive starting composition with high K₂O in order to yield the elevated K₂O contents of the quartz-monzonites and late-stage felsic dikes. As we only have one phlogopite sample (MO-11-10), it is somewhat uncertain how representative its K₂O content (4.5 wt.%) is of the actual fractionating composition. For example, 4.5 wt.% K₂O is high compared to the average 3.4 wt.% K₂O of phlogopite clinopyroxenite xenoliths from other localities. If the latter K₂O value is used, a primitive melt with 2.96 wt.% K₂O yields the K₂O concentrations of the late stage felsic dikes (Fig. 3d). This value is similar to two of the K-rich primitive dikes (2.8 wt.% K₂O). Therefore, we treat 2.96 wt.% K₂O in our primitive melt as the value necessary to reproduce the trends observed in the most silica-rich dikes.

Trace Elements

Fractionation of a few percent of dunite is required to reproduce the Ni contents of the most magnesian olivines (1135±82 ppm, Bucholz et al. 2014), which are lower than typical mantle olivine values (3500-4500 ppm) (Arai 1994; Sato 1977). Cr and Ni then decrease dramatically in the evolving melt with fractionation of olivine-rich wehrlites. LILE concentrations in the Dariv primitive melts are high (Ba: 561-1007 ppm; Rb: 30-79 ppm). Rb increases with progressive fractionation due to the high initial concentration of the primitive melt and comparatively low concentrations in the fractionating cumulates. Ba is 1.5-13 times more compatible than Rb in biotite crystallizing from alkali basalts, (Green et al. 2000; LaTourrette et al. 1995; Villemant et al. 1981) and therefore displays more gentle enrichment trends. All REE follow a similar trend. Initially they are incompatible in the olivine and biotite-dominated ultramafic cumulates and therefore increase in the fractionating melt. In the apatite-bearing cumulate assemblages, however, REE become compatible and their concentrations in the melt begin to decrease. REE concentrations of the “liquid-like” granitoids and felsic dikes are best reproduced between 20-40% and 10% melt remaining, respectively (Fig. 7). Sr displays a similar pattern, but decreases in evolved

liquids due to plagioclase fractionation in the monzogabbros and monzodiorites (Fig. 3f). Nb and Ta concentrations are high in the primitive melt (~9 ppm, 0.53 ppm) and increase moderately with continued fractionation. Although the wehrlites and dunites contain little Nb or Ta, they are compatible in biotite, which moderates Nb and Ta enrichment in the evolving melt. For example, the phlogopite and other phlogopite-rich cumulate xenoliths contain 2-7 ppm Nb.

Biotite- and Amphibole-Series in Arcs

Controls on Biotite and Amphibole Crystallization in Hydrous Arc Melts

In the Dariv Igneous Complex, two distinct alkaline fractionation sequences are observed: one with early saturation of biotite and much later crystallization of amphibole and the second with early saturation of amphibole accompanied by minor biotite. As such, an important question to address is which parameters control high temperature, early crystallization of biotite and/or amphibole in hydrous arc-related basalts. To investigate the influence of melt composition and H₂O-content we compiled major element data from experiments on hydrous basaltic to andesitic starting materials and from natural high Mg# (>60) alkali-basalts and lamprophyres from the Mexican Volcanic Belt saturated with (i.e., had phenocrysts of) amphibole and/or biotite (Figs. 8 & 9). We take the high Mg# of the alkali-basalts as indicative of elevated liquidus temperatures and their phenocrysts assemblages as representative of near liquidus phases. The data set of lamprophyres from the Mexican Volcanic Belt is most useful because it constrains a variability of bulk compositions with amphibole and/or biotite phenocrysts including both very potassic and sodic types. We then compared this compiled dataset to the compositions of 13 high Mg# (>60) basaltic to andesitic dikes from the Dariv Igneous Complex. The primitive compositions used in the LLD modeling are included in this set, but not all of these dikes are primitive, but rather, were only selected by the elevated Mg# criterion. Three of these dikes contain biotite as phenocrysts or groundmass phase, seven contain amphibole as a groundmass phase or phenocrysts, and three contain biotite and amphibole in the groundmass.

For biotite, the dominant control on early crystallization is the major element composition, in particular K₂O, TiO₂, and Al₂O₃, of the melt. As to be expected, a high K₂O content and K₂O/Na₂O are critical in determining whether biotite will crystallize near the liquidus (Edgar and Arima, 1983). Biotites have K>>Na while igneous amphiboles have Na>K at crustal pressures. Consequently, higher K/(K+Na) values in a melt will favor biotite crystallization at higher temperatures. Expanding upon an early experimental compilation on high-K starting materials of Edgar and Arima (1983), Figure 8 shows K₂O and K₂O/Na₂O plotted against the difference between the liquidus and biotite crystallization temperatures (ΔT_{liq-bt}) for various experiments on high-K hydrous basalts at pressures of 0.05-1.0 GPa. With increasing K₂O and K₂O/Na₂O, ΔT_{liq-bt} decreases at all pressures (Fig. 8a,b). This finding is supported by the fact that high Mg# lamprophyres with relatively high K₂O/Na₂O (> 0.8) have phenocrystic biotite (Fig. 8a). High TiO₂ contents also increase the thermal stability of biotite (Edgar and Arima 1983; Righter and

Carmichael 1996), a fact which is reflected in a decrease in $\Delta T_{\text{liq-bt}}$ with increasing TiO_2 content (Fig. 8c). High Mg# lamprophyres with elevated TiO_2 contents (>1.2 wt.%) generally contain biotite, but not amphibole phenocrysts (Fig. 9c). In contrast, low Al_2O_3 concentrations in a melt appear to stabilize biotite (Fig. 8d). In support of this observation, high Mg# lamprophyres and experimental starting materials with biotite as a near liquidus phase tend to have lower Al_2O_3 contents (mostly <14 wt.%) than those with amphibole (generally >14 wt.%) (Fig. 9b). It is important to note that in the dataset several of the investigated compositional variables are correlated with each other. For example, K_2O and TiO_2 are positively correlated with $\text{K}_2\text{O}/\text{Na}_2\text{O}$, whereas Na_2O and Al_2O_3 are negatively correlated (see the Electronic Supplementary Material). F has been shown to stabilize biotite to significantly higher temperatures (Foley et al. 1986), however, as the biotites from Dariv do not have particularly high F contents (generally 0.2-0.6 wt.%, Bucholz et al. 2014) we do not explore the effect of this compositional parameter further.

In contrast, the water content of the melt is perhaps the strongest control on the appearance of amphibole. Numerous experimental studies have demonstrated that with increasing $P_{\text{H}_2\text{O}}$ the temperature difference between the liquidus and the onset of amphibole crystallization decreases (Grove et al. 2003; Holloway and Burnham 1972; Krawczynski et al. 2012). Conversely, biotite may crystallize under strongly water-undersaturated conditions. For example, Naney (1983) on a granodioritic melt, found that amphibole crystallized only at relatively high water contents (4 wt.% H_2O at 0.2 GPa and 2.5 wt.% H_2O at 0.8 GPa) whereas biotite crystallized at significantly lower water concentrations (<0.5 wt.% H_2O). Further, in water under-saturated andesites at 0.8-1.2 GPa, 4 wt.% H_2O is required to stabilize amphibole at high temperatures (Alonso-Perez et al. 2009). Experimental studies on K-rich basaltic starting compositions have also found biotite as a stable phase under H_2O -undersaturated conditions (Barton and Hamilton 1979; Esperança and Holloway 1987). However, as biotite is a hydrous phase, some water is required for its crystallization and at very low pressures and thus low $P_{\text{H}_2\text{O}}$, biotite is depressed from the liquidus (e.g. at 0.05 GPa, Fig. 8).

Thus, while biotite crystallization strongly depends on the degree of K-enrichment in a melt, amphibole crystallization requires a certain H_2O -content. It is important to note that amphibole and biotite are not necessarily in direct ‘competition’ as crystallizing phases, their relative proximity to the basalt liquidus being controlled in part by different parameters. There is a critical threshold in $\text{K}_2\text{O}/\text{Na}_2\text{O}$ and in TiO_2 and Al_2O_3 contents where near-liquidus biotite crystallization is strongly enhanced, rendering it the primary hydrous high temperature phase. At lower $\text{K}_2\text{O}/\text{Na}_2\text{O}$ or TiO_2 and higher Al_2O_3 contents, amphibole, not biotite, is the stable hydrous phase at high temperatures. K_2O -concentration by itself does not lead to such a clear distinction: at >4 wt%, biotite is the near-liquidus hydrous phase, but at lower K_2O contents, low Al_2O_3 (< 14 wt.%) and/or high TiO_2 (>1.3 wt.%) result in biotite as the high temperature hydrous phase. Surprisingly, CaO concentrations or $\text{Na}_2\text{O}/\text{CaO}$ ratios are of secondary importance within the range of natural magmas (Fig. 9d). SiO_2 concentrations are generally (though not

exclusively) lower in the biotite- than amphibole-saturated melts. There is a range within these chemical parameters, i.e. near the thresholds of approximately 14 wt.% Al_2O_3 , a $\text{K}_2\text{O}/\text{Na}_2\text{O}$ of 0.7-0.9, increasing with Si-content, or 1.3 wt.% TiO_2 , where the melt is compositionally appropriate for both early biotite and amphibole crystallization (Fig. 9). The few phenocrystic amphibole+biotite MVB lamprophyres and one experimental starting material characterized by high temperature crystallization of both amphibole and biotite fall in this range. Also, the high Mg#, biotite±amphibole-bearing dikes from Dariv are situated near these thresholds. As the Dariv high Mg# melt compositions are compositionally suitable for early biotite and amphibole crystallization, it is likely that the H_2O -concentrations of the Dariv primitive melts were critical in controlling whether biotite or amphibole crystallized close to the liquidus. Higher concentrations enhance while lower concentrations depress the amphibole crystallization temperature leading to biotite as the high temperature hydrous phase.

In Dariv, amphibole-crystallization occurs in the amphibole-dominated crystallization at much higher temperatures (i.e., in the ultramafic amphibole clinopyroxenites) than in the biotite-dominated sequence, where amphibole only appears in the monzodiorites and more evolved lithologies. Temperatures calculated from clinopyroxene or amphibole-plagioclase thermometry for the amphibole clinopyroxenites and biotite monzodiorites are 1102-1165°C and 693-726°C, respectively (Bucholz et al. 2014). We note that the temperature estimates for the amphibole clinopyroxenites are at or above the experimentally established thermal stability of amphibole in hydrous basalts (~1050°C) (Grove et al. 2003; Krawczynski et al. 2012). This is likely due to errors associated with the clinopyroxene-only thermometer ($\pm 50^\circ\text{C}$), which would bring the estimates into accord with amphibole crystallization at 1050-1100°C. Clearly, the ultramafic amphibole clinopyroxenites crystallized at high temperatures suggesting that the melts crystallizing these cumulates had higher water contents than the parental melts of the biotite-dominated sequence. The high Mg# of amphibole (81.0-82.8) and clinopyroxene (84.4-86.2) in the most primitive amphibole clinopyroxenite (MO-10-398) suggest that when the fractionating melt reached Mg#'s of 57-59, H_2O -contents were ≥ 4 wt.% in the amphibole-dominated fractionation series. Using mineral-melt Fe-Mg equilibrium partitioning constraints, we calculate that the parental melts of the amphibole-dominated sequence crystallized ~10-11% clinopyroxene and olivine by mass to reach an Mg# of ~58. This requires that the parental melts of the amphibole-dominated sequence must have had ≥ 3.5 -3.6 wt.% H_2O to reach 4 wt.% H_2O (the minimum amount of H_2O required for amphibole saturation) at a Mg# of 58. In contrast, using mass balance and constraints on the H_2O content required for amphibole crystallization, Bucholz et al. (2014) calculated that the parental melt of the biotite-dominated sequence would contain 2.2-2.6 wt.% H_2O in order to saturate in amphibole when the fractionating melt reached a monzodioritic composition.

Effects of Biotite versus Amphibole Crystallization on the Geochemistry of Fractionating Arc-Related Melts

The Dariv alkaline arc series allows for the reconstruction of a LLD dominated by biotite fractionation. Amphibole fractionation has been previously well documented in the field and in experiments and is thought to constitute the dominant mechanism for generating the geochemical trends of calc-alkaline magmatic sequences (Cawthorn and O'Hara 1976; Dessimoz et al. 2012; Grove et al. 2003; Jagoutz 2010; Sisson and Grove 1993). As such, we are able to discuss the effect of biotite versus amphibole crystallization on the geochemistry of a fractionating primitive arc melt by comparing the high-K LLD modeled here with that ascertained for the calc-alkaline series.

Crystallization of biotite vs. amphibole each result in some key trends observed in arc magmatic sequences. First, as TiO_2 is compatible and SiO_2 contents are low in both minerals, their fractionation is able to produce the characteristic decrease in TiO_2 with increasing SiO_2 in arc related plutonic and volcanic rocks. Conversely, amphibole and biotite crystallization will result in distinctly different trends in terms of Na and K. This is most clearly seen in the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio of the cumulates and evolving melts. The biotite ultramafic cumulates from Dariv reach 4.5 wt.% K_2O , depending on the mode of biotite. Conversely, Na_2O contents are <0.8 wt.% resulting in $\text{K}_2\text{O}/\text{Na}_2\text{O} > 1.4$ for the ultramafic phlogopite cumulates. $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios of the mafic biotite cumulates decrease to ~ 1 , due to the crystallization of oligoclase to andesine. Importantly, K-feldspar co-crystallizes with plagioclase ($\text{An}_{13}\text{-An}_{40}$) resulting in bulk $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios that do not decrease much further in the biotite-series. In contrast, hornblendites and hornblende gabbros from paleo-arc fractionation sequences have significantly higher Na_2O (typically 1.7-2.2 wt.%) whereas their K_2O content is almost at trace levels leading to $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios of <0.2 in bulk cumulates (Jagoutz, 2010). Consequently, biotite and K-feldspar crystallization will serve to moderate $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios in crystallizing melts that initially have $\text{K}_2\text{O}/\text{Na}_2\text{O}$ of 1-2, whereas amphibole crystallization will increase this ratio in calc-alkaline series. The resulting convergence of $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios with fractionation is exemplified by comparing the Dariv high-K LLD to that of a modeled calc-alkaline LLD for the Kohistan paleo-island arc (Fig. 10). The primitive melts identified for the Dariv Igneous Complex have $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios of 0.74-1.15. The modeled LLD does not deviate from this range of values, varying between 0.94-1.18 from 52-74 wt.% SiO_2 . In contrast, the primitive melt identified for the Kohistan paleo-arc has a relatively low $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio (~ 0.25), but the modeled LLD results in a strong increase of this value with increasing SiO_2 content (to 0.76 at 69 wt.% SiO_2). Comparison to a compilation of arc-related granitoids from the Sierra Nevada, S. California, and the Peninsular Range Batholith reinforces these distinct trends resulting from biotite versus amphibole fractionation (Fig. 10). High-K or monzonitic granitoids generally have high $\text{K}_2\text{O}/\text{Na}_2\text{O}$ (>0.6) values across a wide array of SiO_2 contents (50-75 wt.%) and are in good agreement with the Dariv high-K LLD. Conversely, calc-alkaline granitoids show a general trend of increasing $\text{K}_2\text{O}/\text{Na}_2\text{O}$ with increasing SiO_2 content, indicative of fractionation of low $\text{K}_2\text{O}/\text{Na}_2\text{O}$ cumulates, such as in magmatic hornblendites. Nevertheless, absolute K_2O , and consequently $\text{K}_2\text{O}+\text{Na}_2\text{O}$ contents, are higher in the biotite-dominated monzonitic series than the calc-alkaline series (Fig. 3c,d).

Though not as distinct, trends similar to K_2O are observed for trace elements compatible in biotite, such as Rb and Ba. In the Dariv high-K LLD, these have high concentrations in the primitive melt, but because of their compatibility in biotite and also K-feldspar, their enrichment during fractionation is moderated with increasing SiO_2 . As these elements are incompatible in amphibole (and other typical fractionating minerals in the calc-alkaline sequence), these elements show a distinct enrichment with increasing SiO_2 in the calc-alkaline LLD and granitoids. Another interesting feature is the general high levels of Sr in monzonitic series relative to the calc-alkaline series. Although both series generally display Sr depletion with increasing SiO_2 due to feldspar fractionation, the monzonitic trend is offset several hundred ppm higher from the calc-alkaline trend (Fig. 3f). This is mostly due to the elevated initial Sr concentrations in the primitive high-K basalts consistent with higher levels of addition of an also K-, Rb-, and Ba-rich subduction component.

Implications for the Mantle Wedge and Subduction Component

The amphibole- and biotite-series arise from two contrasting primary magma compositions. The normal calc-alkaline, amphibole series has a relatively sodic and H_2O -rich primitive melt as a parental magma, while the biotite-series has a comparatively more potassic and LILE-rich, but less hydrous parental melt. Apparently, LILE (including K) and H_2O in the subduction component are decoupled for these two series and we envision two different scenarios for the generation of their parental melts in the mantle wedge.

For the the calc-alkaline amphibole series, the addition of a sodic subduction component concomitant with mantle wedge melting leads to common hydrous sodic primitive arc basalts as, for example, compiled in Jagoutz and Schmidt (2013). In this scenario, the subduction component is likely to be dominated by fluids (Stolper & Newman, 1994; Grove et al. 2002), but may also include a minor sediment melt component which is sodic at moderate pressures (to 3 GPa) and relatively hydrous slab melting conditions (Hermann and Spandler 2008).

For the high-K, biotite series, the subduction signature is increased, but the concentration of H_2O is decreased, leading to two possible scenarios. In the first scenario, one may decouple K+LILE from H_2O by an intermittent stage of crystallization in the mantle wedge. Phlogopite (<1200 °C) and possibly also amphibole (at <1050-1100 °C) could form in a mantle wedge with a temperature colder than that characteristic for primitive arc melts (1250-1350 °C, from multiple saturation experiments, Kushiro 1986, Tatsumi et al. 1994), leading to a sequestration of LILE in these phases, but to further ascent of remnant H_2O through the wedge. Upon heating and/or further fluid-input, this enriched mantle wedge may then deliver a potassic LILE-rich, moderately hydrous primitive arc melt. The first stage may occur when changes in subduction geometry lead to a relatively cooler mantle wedge, most likely causing a hiatus in arc magmatism. In principal, the first stage could also happen in the colder forearc of an active subduction

zone, but more potassic magmatism is characteristic for the main or back arc regions (Kuno, 1965; Dickinson 1975), rendering biotite crystallization in the forearc mantle unlikely.

In the second scenario, a subduction component with a higher (K+LILE)/H₂O ratio than characteristic for normal calc-alkaline magmatism is required. A much less hydrous subduction signal results from slab melts instead of fluids. With increasing pressure sediment melts become highly potassic, particularly when little fluid is available for slab melting (Schmidt et al. 2004). In this scenario, the slab component addition and mantle wedge melting would occur concomitantly, but in contrast to normal calc-alkaline magmas, the slab-component would be dominated by deep (≥ 3.5 GPa) sediment melts.

For the Dariv Igneous Complex, neither the paleo-geometry of the slab nor the relative time difference between the biotite- and amphibole-series are well-constrained, hence we cannot distinguish which of the above scenarios lead to the spatially overlapping occurrence of the two series. In several modern arcs, potassic volcanism occurs towards the back-arc concomitantly with typical calc-alkaline volcanism in the main arc (e.g., Sunda, Sumatra, Wheller et al. 1987) favoring the second scenario. However, high-K, biotite-phenocrystic basalts in the Sierra Nevada and the Western Mexican Volcanic Belt have been suggested to have formed through a secondary melting event of a previously metasomatized mantle based on their occurrence after subduction had ceased and/or low trace element ratios (e.g., B/Be) indicating little direct input of slab-derived fluids into their source region (Hochstaedter et al. 1996; Ducea and Saleeby, 1998; Farmer et al., 2002). Thus, both scenarios presented above may occur in arcs, depending on the specific geodynamic setting of a particular subduction zone.

Comparison of Hydrous Basalt LLDs to Quartz-Albite-Orthoclase Ternary Phase Relationships

The fractionation paths leading to evolved granitic melts both for the high-K and calc-alkaline LLDs are well illustrated in the melting diagram of the system Quartz-Albite-Orthoclase-H₂O (Qz-Ab-Or-H₂O, Fig. 11). This ternary system is well constrained over a range of pressures (0.05-1.0 GPa) and from dry to water-saturated conditions (Ebadi and Johannes 1991; Holtz et al. 1989; Luth et al. 1964; Tuttle and Bowen 1958). Notably, the Or/(Ab+Or) ratio of the minimum or eutectic melt increases markedly with decreasing water activity, whereas the normative Qz content remains almost invariant. Conversely, with increasing pressure normative Qz decreases dramatically.

Figure 11 shows CIPW normative compositions of feldspar-bearing lithologies of the Dariv alkaline fractionation sequence plotted onto the Qz-Ab-Or ternary. The monzogabbros, monzodiorites, and several of the monzonites plot just slightly into the silica-undersaturated side of the Ab-Or join. The modeled LLD is also plotted and follows the water-undersaturated ($a_{H_2O} = 0.4-0.5$) Ab-Or cotectic toward SiO₂-enrichment. A few monzonites and late stage felsic dikes fall along this cotectic suggesting that they are representative of liquid compositions. The LLD ultimately ends at the minimum/eutectic at 0.2-0.5 GPa where the majority of the late-stage granitic dikes plot. A pressure range of 0.2-0.5 GPa is in good agreement with intrusion pressures of the Dariv Igneous Complex (Bucholz et al. 2014). Alkali-rich

granitoids from the upper crust of preserved arcs have compositions similar to the calculated LLD. For example, the feldspar-bearing lithologies and LLD of the Dariv alkaline sequence overlaps remarkably well with the compilation of California monzonites of Miller (1977) (Fig. 11b). Instead, amphibole-dominated fractionation sequences lie along the water-saturated cotectic, further supporting our conclusion that the amphibole-dominated fractionation sequence was characterized by higher H₂O contents. For comparison, we also show a compilation of calc-alkaline granitoids from the Sierra Nevada and the modeled calc-alkaline LLD for the Kohistan paleo-arc (Fig. 11b). In contrast to the Dariv LLD, the calc-alkaline granitoids and LLD follow a water-saturated trend towards the eutectic composition. In the Qz-Ab-Or ternary, the relationship of water content and amphibole versus biotite crystallization is directly visible: the calc-alkaline trends are near water-saturated and correspond to amphibole-dominated fractional crystallization, whereas those for the high-K LLD correspond to low water contents and are produced through biotite-dominated crystallization.

Conclusion

In contrast to the well-studied liquid lines of descent of calc-alkaline and tholeiitic primitive melts, high-K LLDs have received little attention, perhaps due to the lack of field exposure documenting the cumulative counterpart to the evolving liquids. We present such a LLD based on actual cumulate compositions for the newly discovered alkaline Dariv Igneous Complex in Western Mongolia. We demonstrate that relatively low pressure (0.2-0.4 GPa), hydrous, but not water-saturated fractionation of a primitive alkaline arc magma produces a K-rich monzonitic granitoids series. Critically, fractionation of silica-poor biotite is required to derive such liquids. Although the biotite-dominated ultramafic and mafic cumulates are dominant in the Dariv Igneous Complex, there is a volumetrically subordinate second sequence characterized by early appearance of amphibole. The high temperature appearance of amphibole in this second sequence necessitates higher H₂O contents in its parental melt as compared to the biotite-dominated sequence. Biotite crystallization will moderate enrichments of K₂O and other LILEs with increasing SiO₂. These differences result in distinct geochemical signatures for a high-K LLD dominated by biotite crystallization versus a sequence controlled by amphibole fractionation, such as the common calc-alkaline magmatic series.

Although calc-alkaline plutons dominate batholiths in volcanic arcs, high-K granitoids are observed in many continental arcs. These high-K granitoids may critically contribute to the incompatible element budget of continental arcs and hence the bulk continental crust. Hypotheses on the origin of these high-K alkaline granitoids are numerous and include melting of a subducted alkali-rich quartz eclogite (Miller 1977; Miller 1978), partial melting of a garnet-bearing lower crust (Rapela and Pankhurst 1996), and melting of an enriched mantle (Sylvester et al. 1978). Here we document the generation of high-K granitoids through biotite- and clinopyroxene-dominated fractional crystallization of a primitive, alkali-enriched melt. The global spatial and temporal distribution of these high-K suites in relationship to calc-

alkaline arc magmatism, however, has not been cohesively studied and remains essential to fully understand the magmatic and geochemical evolution of volcanic arcs.

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FIGURE CAPTIONS

Fig. 1: (a) Simplified terrane map of Mongolia. Notably, Mongolia consists of Pre-Cambrian autochthonous terranes surrounded by accreted allochthonous terranes, ophiolites, and island arc-related units to the south and west. The Dariv Range is located at the boundary of the Pre-Cambrian Altai Allochthon and the Lake Terrane and is isolated from neighboring ranges by >25 km wide, mainly tertiary basins. (b) Geological map of the detailed study area in the NW part of the Dariv Range showing relationships between the Lake Terrane (the tholeiitic ophiolite sequence, the mantle section, the alkaline fractionation sequence, and low grade metasediments) and the metamorphic Altai Allochthon. The geologic map is based on own field mapping, interpretation of Landsat images, and previously constructed maps of the area (Dijkstra et al. 2006, Khain et al. 2003). (c) Cross-section through Dariv Range showing the overall structure and relationship between various units. Profile location is indicated in Fig. 1b. Note that most contacts in this profile are intrusive in nature. The only two major faults are within the red (alkali-)granites.

Fig. 2: Representative photomicrographs illustrating the ultramafic and mafic lithologies of the two studied fractionation sequences. Photomicrographs in the left column (a-d) are from the biotite-dominated sequence, whereas those in the right column (e-h) are from the amphibole-dominated sequence. Whole rock Mg# (molar $Mg/(Mg+Fe^T)$) are plotted in the upper right corners of the images. All images, except g, were taken in plane-polarized light. g is a backscattered electron image. All thin sections are 100 μ m thick. Mineral abbreviations are as in Fig. 4. a) Phlogopite-poor wehrlite (MO-10-394). b) Phlogopite-rich wehrlite (MO-10-392) with increased modal percent of biotite. c) Clinopyroxene phlogopitite (MO-11-10) with abundant and large apatite crystals. d) Biotite monzogabbro (MO-11-12) with biotite, clinopyroxene, and feldspar. e) Clinopyroxenite with amphibole and minor biotite (MO-10-398). f) Amphibole-rich clinopyroxenite with apatite (MO-9-251). g) Amphibole clinopyroxenite with apatite (MO-10-329). h) Amphibole monzogabbro (MO-10-309a).

Fig. 3: Whole rock Mg#, major, and trace elements versus SiO_2 with results of the LLD model described in the text. All analyses are plotted on an anhydrous basis. The black dashed line marks the calculated LLD. Ticks on LLD indicate the melt composition at 10% intervals of melt remaining. Larger faded symbols indicate average cumulate compositions used in the LLD modeling. Red arrows represent the general trend for the calc-alkaline series based on whole rock data from the Sierra Nevada Batholith (Lackey et al., 2008) and the Kohistan Arc (Jagoutz (2010)). Xenolith data is from Buhlmann *et al.* (2000), Downes *et al.* (2004), and Giannetti and Luhr (1990). (a) Mg#, (b) Al_2O_3 , (c) $Na_2O + K_2O$ (TAS plot modified for plutonic rocks (Le Bas et al. 1986; Middlemost 1994)) (d) K_2O , (e) TiO_2 , (f) Sr.

Fig. 4: Trace element spider diagrams normalized to primitive mantle for the biotite-dominated fractionation sequence, (Sun and McDonough 1989) for (a) wehrlites, (b) phlogopite-poor wehrlites, (c) phlogopite-rich wehrlites, (d) phlogopite clinopyroxenites and phlogopitite, (e) monzogabbros, (f) monzodiorites, (g) (quartz-)monzonites, and (h) late-stage felsic dikes.

Fig. 5: Trace element spider diagrams normalized to primitive mantle for the amphibole-dominated fractionation sequence, (Sun and McDonough 1989) for (a) amphibole(\pm biotite) clinopyroxenites, (b) amphibole monzogabbros, and (c) granitoids divided based on SiO_2 content. Shaded gray areas indicate the range in composition for similar lithologies of the biotite-dominated sequence.

Fig. 6: Summary of Mg# constraints on LLD modeling. Central panel shows Mg# versus SiO_2 (wt.%) of modeled LLD (dashed line) which is colored according to which lithology is crystallizing. Ticks with increments of 10 adjacent to them represent the mass % crystallized at a given point in the LLD trajectory. Large colored circles are the average bulk compositions of the cumulate lithologies used in the model. "Phl" = phlogopite. The gray area indicates field of analyzed dike compositions from the Dariv Range, which are assumed to mostly represent liquid compositions. However, a few outlier dyke groups from the main trend likely result from crystal accumulation. Adjacent panels show Mg# of olivine (left) and

clinopyroxene (right), in addition to the Mg# of calculated equilibrium melts. Open colored circles are averages (with $2\sigma_{SD}$ error bars) of analyzed Mg# of olivine and clinopyroxene for available samples (data from Bucholz et al., 2014). Error bars are omitted for clinopyroxene calculated melts for clarity, but are equivalent to those shown for measured minerals. Filled symbols are the calculated equilibrium melt Mg#. The equilibrium melt Mg# was calculated assuming a $K_d(\text{Fe-Mg})$ of 0.3 for olivine-melt (Roeder & Emslie, 1970) and 0.23 for clinopyroxene-melt (Sisson and Grove (1993)). Two calculated melts are shown, one considering all Fe present as Fe^{2+} and the other assuming that $\text{Fe}^{3+}/\text{Fe}^T = 0.35$. This ratio value is equivalent to an oxygen fugacity of +2.3 ΔQFM at 1200°C and 3000 bars (Kress & Carmichael, 1991), an intermediate value for the estimated oxygen fugacity of crystallization for the phlogopite ultramafic cumulates (+1.8 to +3.2 ΔQFM ; Bucholz et al., 2014). Lower and higher $\text{Fe}^{3+}/\text{Fe}^T$ ratios would shift the calculated melt Mg# to lower and higher values, respectively. A black dashed line is included for clarity to separate the two different melt calculations.

Fig. 7: Trace element spider diagram showing results of LLD modeling compared to “liquid-like” whole rock compositions of the biotite dominated fractionation sequence. “Liquid-like” feldspar-bearing samples were identified by their lack of cumulate signature as described in the text under “Model Description”. Elements are normalized to primitive mantle composition (Sun and McDonough 1989). Modeled LLD are shown at 80, 40, 20, and 10% melt mass remaining.

Fig. 8: Difference in temperature between the liquidus and biotite saturation versus various compositional parameters of high-K basaltic experimental starting materials at various pressures. Experimental data is from Barclay and Carmichael (2004), Barton and Hamilton (1978), Esperança and Holloway (1987), Nicholls and Whitford (1983), and Righter and Carmichael (1996). (Barclay and Carmichael 2004; Esperança and Holloway 1987; Nicholls and Whitford 1983; Righter and Carmichael 1996). T_{liquidus} of the experiments vary between 1090-1230°C. (a) K_2O , (b) $\text{K}_2\text{O}/\text{Na}_2\text{O}$, (c) TiO_2 , (d) Al_2O_3 .

Fig. 9: Geochemistry of high-K basalts and hydrous experiments saturated with biotite and/or amphibole in comparison to the Dariv high-Mg# dike compositions. (a) $\text{K}_2\text{O}/\text{Na}_2\text{O}$ v. SiO_2 (note that y-axis is a logarithmic scale), (b) Al_2O_3 v. SiO_2 , (c) TiO_2 v. SiO_2 , (d) $\text{CaO-NaO-K}_2\text{O}$. Mexican Volcanic Belt high Mg# alkali-basalts and lamprophyre data (colored circles) are from Allan and Carmichael (1984), Carmichael et al. (1996), Luhr et al. (1989), Luhr and Carmichael (1985), Maria and Luhr (2008), Ownby et al. (2008), Righter and Rosas-Elguera (2001), Vigouroux et al. (2008), Wallace and Carmichael (1989), and Wallace and Carmichael (1992). Amphibole-saturated experimental data (red crosses) are from Alonso-Perez et al. 2009, Di Carlo et al. 2006, Grove et al. 2003, Müntener et al. 2001, Sisson and Grove 1993, and Sisson et al. 2005. Biotite-saturated experimental data (blue crosses) are from Barton and Hamilton (1978), (1979), Edgar and Arima (1983); Edgar and Condliffe (1978), Edgar et al. (1976), Elkins-Tanton and Grove (2003), Esperança and Holloway (1987), Nicholls and Whitford (1983), and Righter and Carmichael (1996). The biotite- and amphibole-saturated experimental data (purple crosses) are from Barclay and Carmichael (2004) and Sisson et al. (2005).

Fig. 10: Comparison of $\text{K}_2\text{O}/\text{Na}_2\text{O}$ with SiO_2 -enrichment for a high-K versus calc-alkaline LLD and arc-related plutonic rocks ($45 < \text{SiO}_2 < 80$ wt.%). Data is from the Sierra Nevada, the Peninsular Range Batholith, Southern California Permo-Triassic intrusion, and GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/>). High-K versus calc-alkaline designation is defined by the K_2O v. SiO_2 classification of Pecерillo and Taylor (1976). Sierra Nevada data is from Lackey et al. (2008) and Bateman (1961). Peninsular Range Batholith data is from Lee et al. (2007). Southern California Permo-Triassic granitoid data is from Barth and Wooden (2006). Arc-related monzodiorites, monzonites, and quartz-monzonites are from the GEOROC database. Note that y-axis is shown with a logarithmic scale. Probability density function contours are plotted using GCDKit 2.3 (Janousek et al., 2006).

Fig. 11: Ternary phase diagram in nepheline-kalsilite-quartz system. Figures are zoomed into the section containing the end members albite-K-feldspar-quartz (Ab-Or-Qz). Phase boundaries are from Ebadi and Johannes (1991), Holtz et al. (1989), (1991), Luth et al. (1964), and Tuttle and Bowen (1958). The position of the minimum/eutectic at different water activities are shown by white, gray, and black circles

for water activities of 0.3, 0.5, and 1.0, respectively. Minimum/eutectic positions are shown for pressures of 0.1, 0.2, 0.5, and 1.0 GPa. (a) Projected whole rock data from the Dariv Igneous Complex in the $\text{SiO}_2 \geq 60\%$ portion of the Qz-Ne-Ks ternary. Data is projected using calculated CIPW norm compositions (mass %) following the projection scheme of Blundy and Cashman (2001) to account for normative anorthite component. For both the amphibole-dominated and biotite-dominated sequence, monzogabbros mostly have >35 wt.% Qz-Ks-Ne (including Or + Ab recalculated into Qz, Ks, and Ne). Biotite monzodiorites and amphibole sequence granitoids with <60 wt.% SiO_2 have 40-52 wt.% and 47-74 wt.% Qz-Ks-Ne, respectively. (Qtz-)monzonites, amphibole sequence granitoids with >60 wt.% SiO_2 , and late stage felsic dikes have 60-95 wt.% Qz-Ks-Ne. All symbols as in Fig. 3. The primitive melt composition (yellow diamond) used in the LLD model (dashed line) is shown for reference. Bulk cumulate compositions used in LLD model are shown as larger faded symbols. Cotectics at water-saturated conditions at 0.1 and 1.0 GPa are shown as gray lines with arrows. (b) Modeled Dariv high-K LLD and Kohistan paleo-arc calc-alkaline LLD compared to arc-related granitoids in the Qz-Ab-Or ternary. Blue field of California monzonites is from Miller (1977). Red field for calc-alkaline granitoids from the Sierra Nevada is from compilation described in Fig. 10.

Table 1 Compositions used in LLD model.

	PARENTAL MELT		FRACTIONATED CUMULATE COMPOSITIONS																	
	Model Composition**	Average (N=3)*	***Phlogopite		Wehrlite		Phlogopite-Poor Wehrlite		Phlogopite-Rich Wehrlite		Phlogopite-Rich Clinopyroxenite		High Mg# Monzogabbro		Low Mg# Monzogabbro		Monzodiorite		Monzonite	
			2σ	N=3*	2σ	N=3*	2σ	N=7*	2σ	N=4*	2σ	N=1*	N=5*	2σ	N=5*	2σ	N=4*	2σ	N=3*	2σ
SiO ₂	52.00	51.35	3.57	42.81	1.32	52.07	0.66	48.62	2.33	46.38	1.54	44.25	50.23	3.75	51.57	2.24	54.27	2.81	61.69	5.55
TiO ₂	1.10	0.90	0.56	0.10	0.04	0.26	0.12	0.40	0.16	1.25	0.88	2.83	1.10	0.44	1.32	0.36	1.10	0.14	0.63	0.29
Al ₂ O ₃	12.90	14.28	1.59	1.55	0.64	1.34	0.62	2.12	1.33	5.46	1.95	8.55	15.55	4.02	17.53	2.61	16.68	1.17	17.34	2.09
FeO	7.85	7.66	1.59	8.06	1.99	5.60	1.98	10.26	2.21	9.94	2.82	10.60	8.08	0.91	8.14	1.48	7.69	1.37	4.52	1.93
MnO	0.16	0.18	0.05	0.12	0.04	0.14	0.05	0.24	0.05	0.20	0.06	0.19	0.17	0.02	0.17	0.06	0.16	0.04	0.08	0.03
MgO	11.26	10.83	2.88	45.45	1.74	19.74	1.21	21.94	5.34	20.65	4.46	16.14	9.47	1.86	5.98	1.72	4.80	1.77	2.58	1.82
CaO	8.70	9.96	1.12	1.01	0.23	20.34	1.01	15.96	4.10	13.51	3.04	11.97	8.85	1.58	8.54	1.42	7.31	2.02	3.67	2.09
Na ₂ O	2.50	2.21	0.72	-	-	0.15	0.10	0.17	0.20	0.29	0.16	0.41	2.68	0.44	3.39	0.95	3.83	0.44	4.36	0.92
K ₂ O	2.96	2.21	1.14	0.52	0.17	0.07	0.06	0.10	0.16	2.09	1.13	3.52	3.25	1.58	2.73	1.14	3.57	1.46	4.82	0.12
P ₂ O ₅	0.49	0.40	0.39	0.06	0.02	0.02	0.01	0.02	0.01	0.05	0.13	1.43	0.56	0.28	0.60	0.22	0.59	0.14	0.30	0.21
Cr ₂ O ₃	0.08	0.03	0.09	0.32	-	0.28	0.18	0.16	0.22	0.19	0.06	0.11	0.06	0.07	0.03	0.04	0.02	0.01	0.01	0.01
Total	100.00	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	100.00	-	100.00	-	100.00	-	100.00	-
Mg#	71.9	71.50	9.35	91.0	2.3	86.3	4.9	79.1	4.5	78.8	2.9	73.1	67.6	3.4	56.6	3.1	52.7	4.2	50.4	12.2
Sc	24.3	25.3	6.0	4.7	1.2	47.2	12.0	51.4	19.1	44.2	17.6	40.6	22.9	2.7	20.6	5.0	18.6	7.9	7.3	6.4
V	203	172	58	28	22	85	56	186	122	267	213	558	189	63	189	77	200	86	64	61
Cr	579	602	241	2967	800	1750	1139	1262	653	1206	384	739	390	451	185	194	151	32	50	59
Ni	239	160	127	2330	81	208	15	355	244	331	233	289	120	116	50	30	53	11	17	29
Zn	59.0	62.8	10.7	55.7	26.1	25.0	14.4	53.3	25.2	51.2	10.5	64.0	63.1	14.1	66.9	14.5	68.1	9.6	46.8	13.5
Rb	85	71	25	23	8	2	2	2	4	58	33	152	105	83	84	47	83	41	116	6
Sr	889	856	478	36	4	121	13	96	42	137	73	197	1397	1199	1154	786	1300	287	1139	419
Y	18.9	21.8	8.3	1.9	1.0	6.3	4.1	12.7	10.0	10.0	2.1	30.4	23.3	11.5	23.5	8.8	22.2	6.6	14.9	3.2
Zr	120	159	153	7	4	14	15	22	19	24	9	28	102	48	165	186	204	139	293	85
Nb	9.0	9.3	10.8	0.6	0.2	0.2	0.4	0.2	0.5	1.6	0.3	5.3	9.3	8.4	13.4	5.7	13.0	3.2	14.9	2.5
Cs	1.55	1.83	1.41	1.15	0.92	0.20	0.19	0.17	0.26	0.94	0.56	1.80	1.88	3.92	1.65	0.54	1.83	1.05	2.10	1.58
Ba	1125	766	516	197	71	11	14	27	50	1217	1227	2287	1382	1060	797	689	1173	557	1421	587
La	30.7	42.4	27.4	1.7	0.7	3.4	2.6	3.5	2.4	4.2	4.3	28.2	43.8	24.6	38.5	8.7	39.7	9.1	47.1	35.8
Ce	67.0	87.7	56.6	3.7	1.9	10.5	8.0	12.1	7.7	14.4	10.8	70.8	101.9	61.0	80.5	18.4	81.9	13.4	89.6	58.8
Pr	8.2	10.3	6.7	-	-	1.6	1.2	2.1	1.3	2.4	1.4	10.3	12.8	8.1	9.9	2.9	9.6	1.0	9.7	4.7
Nd	35.6	42.4	26.4	2.2	1.5	8.8	5.3	12.2	7.6	13.1	6.4	51.3	54.8	34.0	42.2	14.5	40.3	4.5	36.4	12.8
Sm	7.22	7.65	4.46	0.55	0.38	2.27	1.10	3.73	2.29	3.77	1.82	11.84	10.17	6.01	8.36	3.17	8.12	1.86	6.22	0.74
Eu	1.82	1.93	1.06	0.17	0.16	0.58	0.27	0.94	0.49	1.04	0.45	1.83	2.72	1.59	2.28	0.97	2.17	0.45	1.83	0.46
Gd	5.80	6.04	2.68	-	-	1.87	1.19	3.75	2.45	3.52	0.98	9.49	7.78	4.98	6.92	2.68	6.69	1.54	4.38	0.31
Tb	0.700	0.791	0.364	0.068	0.047	0.264	0.156	0.483	0.333	0.446	0.123	1.085	0.949	0.532	0.810	0.236	0.777	0.161	0.591	0.092
Dy	3.85	4.18	1.84	0.42	0.27	1.42	1.16	2.69	1.94	2.41	0.44	6.25	4.96	2.57	4.55	1.73	4.36	0.91	3.00	0.42
Ho	0.680	0.810	0.210	-	-	0.262	0.236	0.488	0.346	0.378	0.049	1.139	0.847	0.483	0.863	0.325	0.785	0.222	0.500	0.084
Er	1.81	2.15	0.81	-	-	0.53	0.62	1.27	0.87	1.00	0.38	2.92	2.23	0.98	2.37	0.86	2.08	0.71	1.44	0.33
Tm	0.230	0.282	0.177	-	-	0.084	0.072	0.169	0.131	0.114	0.032	0.337	0.272	0.077	0.287	0.099	0.291	0.164	0.203	0.074
Yb	1.58	1.80	0.75	0.19	0.04	0.40	0.68	1.10	0.85	0.82	0.41	2.02	1.82	0.72	1.98	0.99	2.06	0.78	1.38	0.49
Lu	0.235	0.281	0.135	0.032	0.006	0.084	0.063	0.145	0.132	0.112	0.044	0.313	0.266	0.086	0.311	0.117	0.291	0.086	0.154	0.057
Hf	3.25	3.81	3.34	0.25	0.01	0.56	0.44	0.92	0.75	0.95	0.31	0.97	2.68	0.97	5.48	3.24	4.71	2.61	6.82	1.90
Ta	0.53	0.57	0.67	0.03	0.01	0.01	0.04	0.02	0.05	0.08	0.03	0.31	0.43	0.43	0.69	0.21	0.80	0.18	0.80	0.28
Pb	7.3	5.0	4.9	2.0	1.1	0.3	0.3	0.4	0.7	0.6	1.2	1.0	5.6	6.2	7.5	2.8	11.0	6.7	20.9	4.5
Th	4.0	7.6	5.3	0.6	0.2	0.3	0.4	0.2	0.5	0.2	0.4	1.0	3.3	4.4	4.2	4.9	3.4	1.8	8.9	9.1
U	1.11	1.82	0.12	3.81	2.87	0.07	0.14	0.08	0.17	0.06	0.14	0.32	1.02	1.39	1.28	1.24	0.97	0.45	2.02	1.18

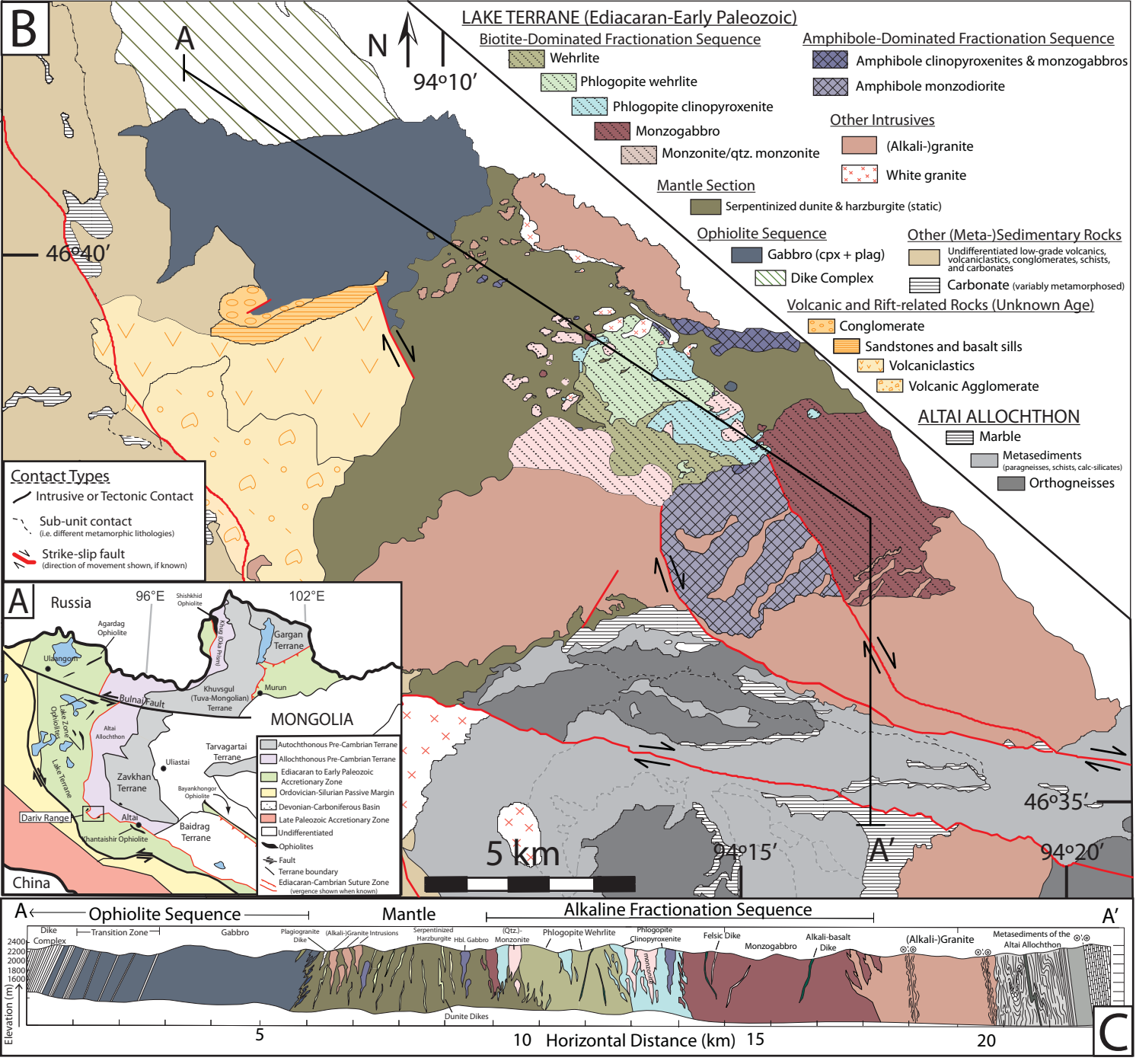
* N equals the number of samples of a lithology included in average. Analyses recalculated on an anhydrous basis with all Fe calculated as FeO'.

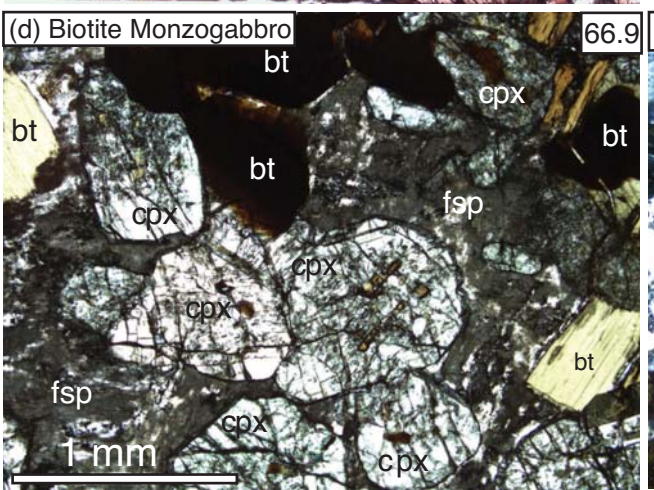
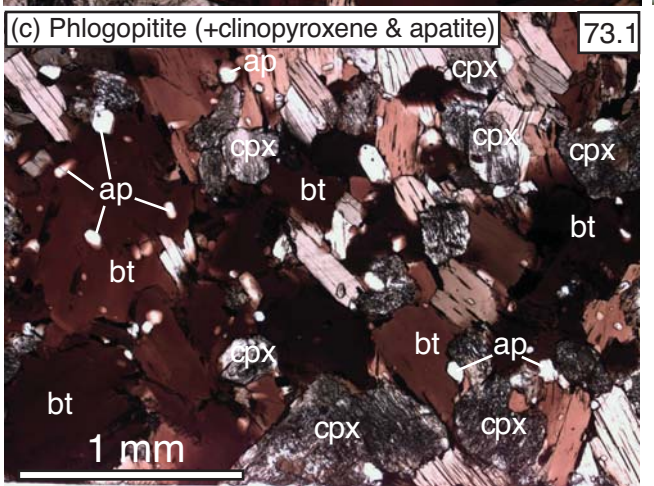
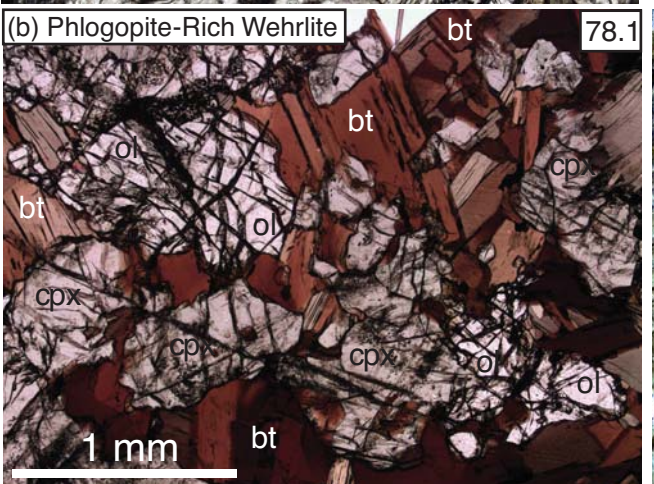
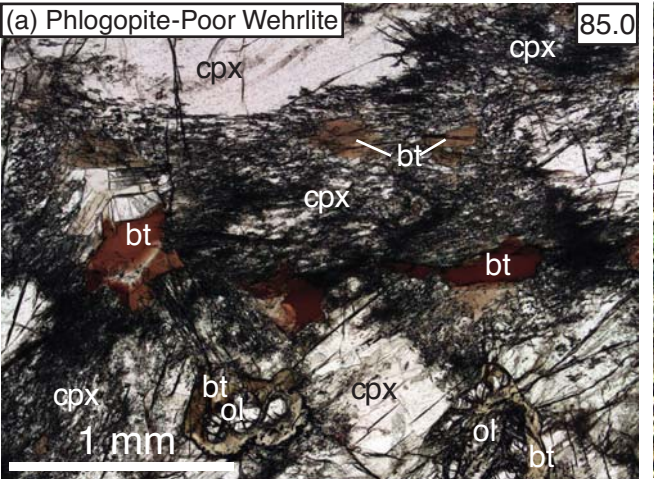
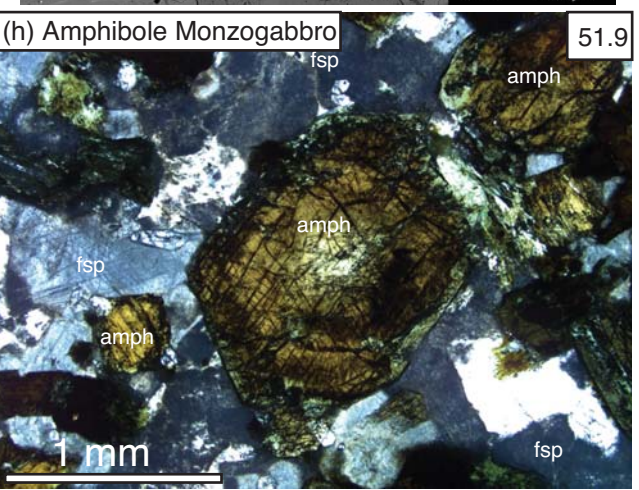
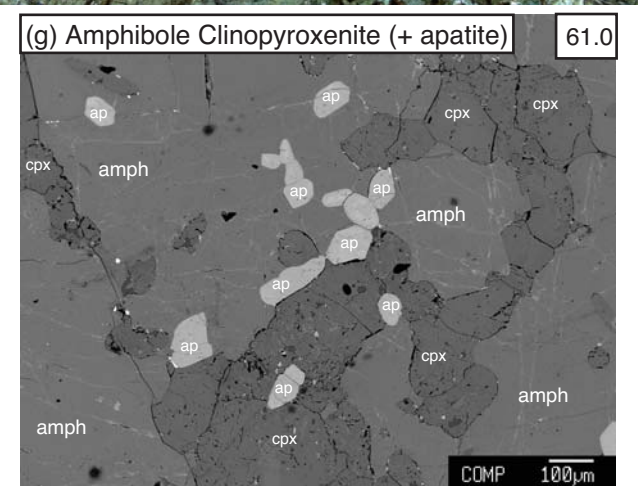
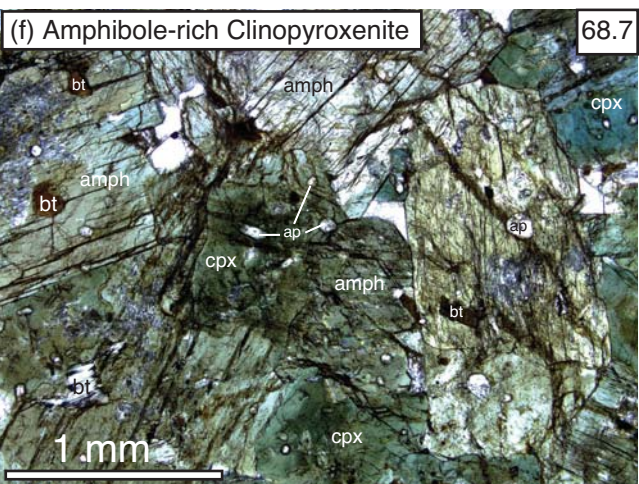
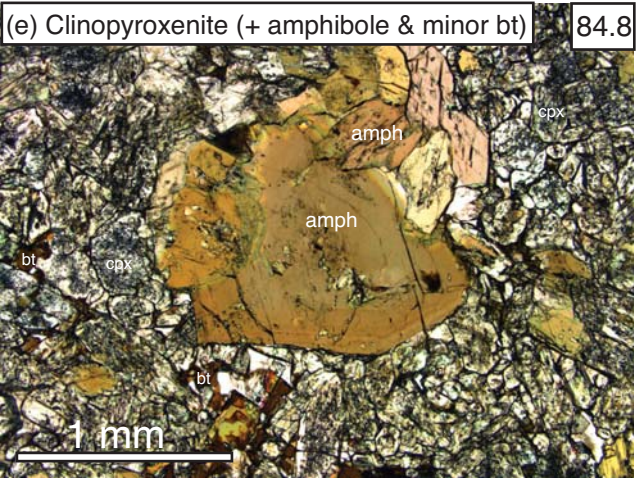
** Composition used in LLD model.

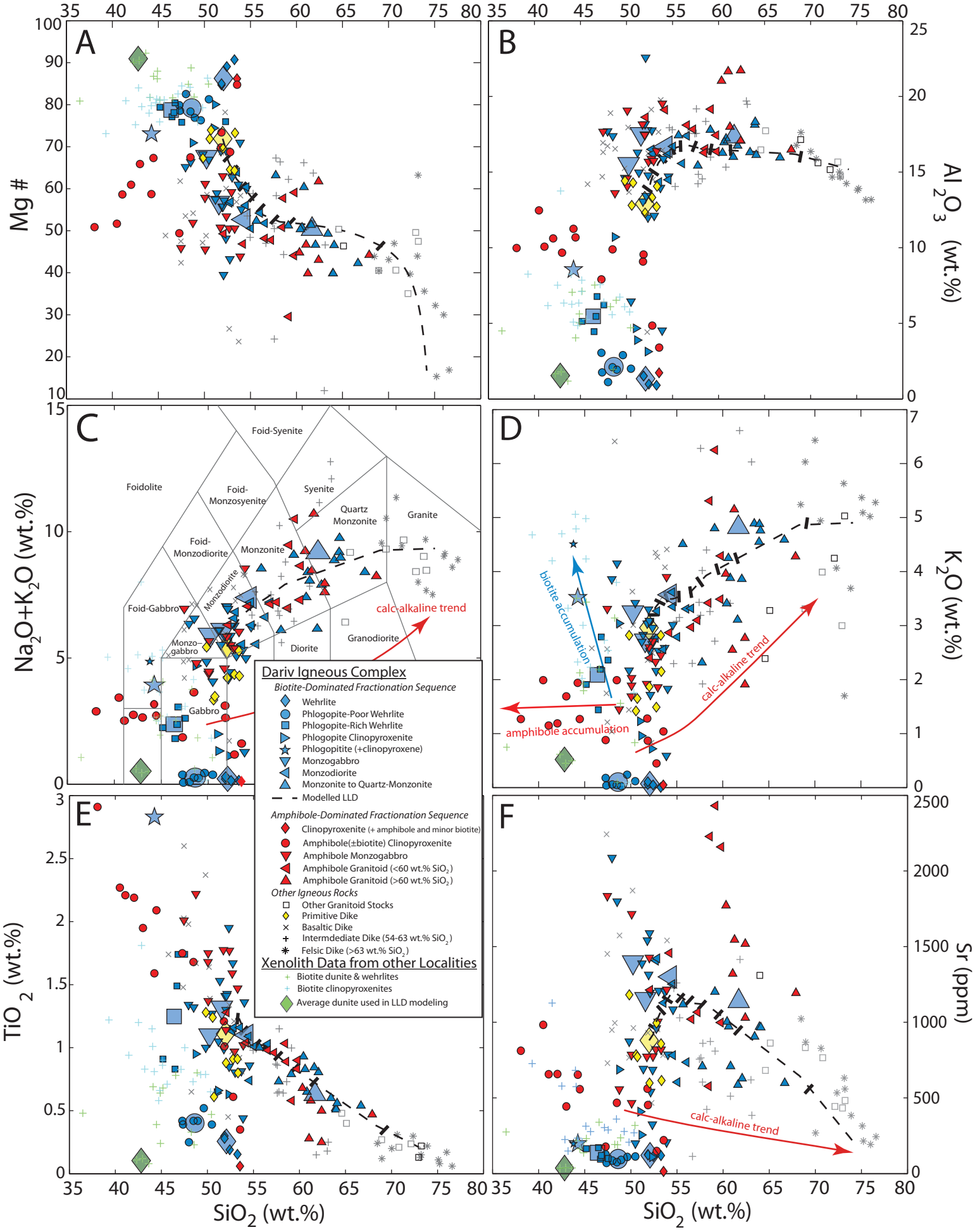
*** Average of WC-232, WC-253, & WC-251 from Downes *et al.* (2004)

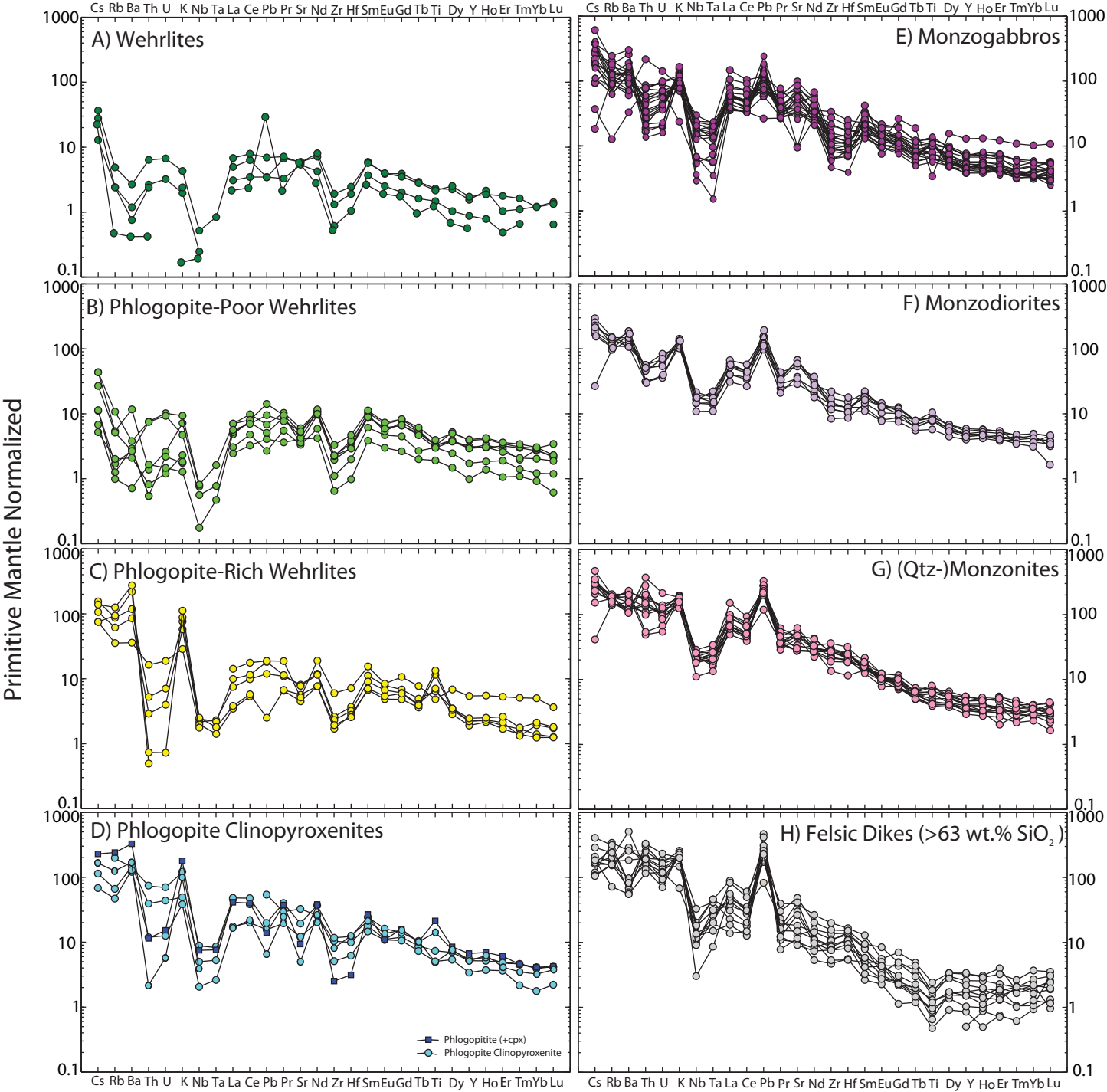
Table 2 Calculated LLD Compositions

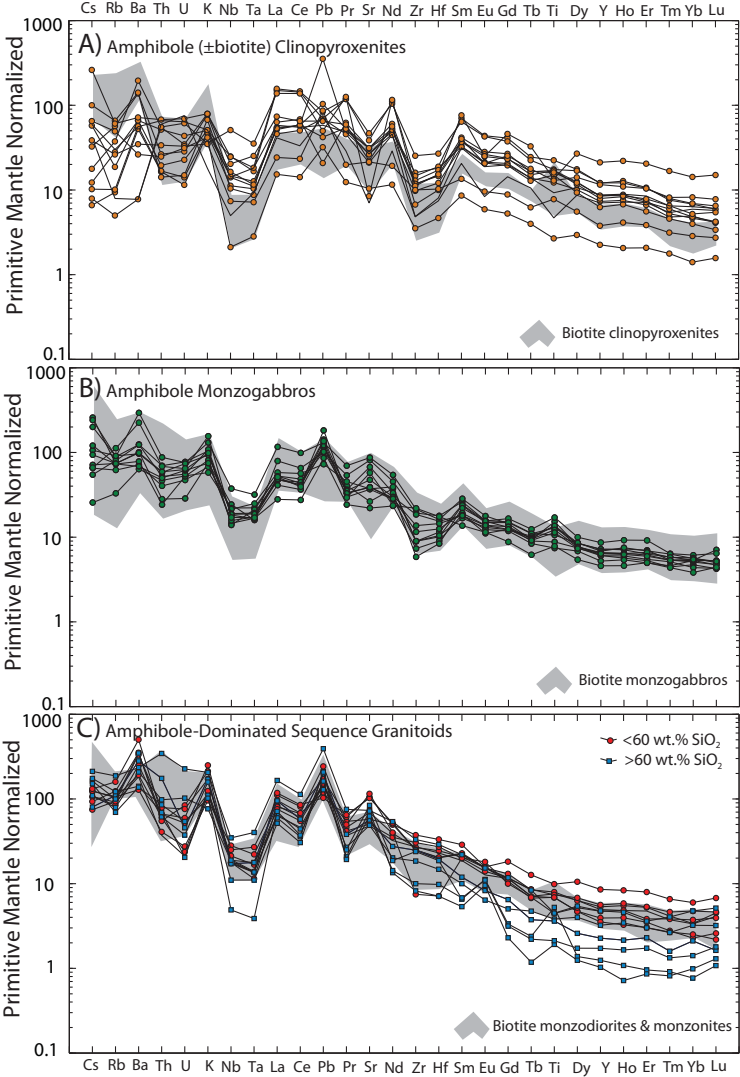
% Melt Remaining	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10
SiO ₂	52.56	53.28	54.47	55.28	56.28	57.48	58.98	61.31	68.36
TiO ₂	1.18	1.20	1.03	1.00	0.98	0.90	0.80	0.64	0.19
Al ₂ O ₃	14.10	15.31	16.36	16.59	16.79	16.66	16.52	16.44	16.19
FeO	7.86	7.58	7.18	7.00	6.78	6.45	5.96	5.11	2.54
MnO	0.16	0.15	0.15	0.14	0.14	0.13	0.12	0.10	0.04
MgO	8.93	7.38	6.01	5.33	4.51	4.05	3.62	3.04	1.28
CaO	8.61	7.89	7.27	6.96	6.59	6.10	5.50	4.60	1.90
Na ₂ O	2.76	3.08	3.45	3.62	3.80	3.92	4.02	4.11	4.39
K ₂ O	3.24	3.45	3.49	3.53	3.59	3.79	4.00	4.21	4.85
P ₂ O ₅	0.53	0.60	0.53	0.51	0.50	0.48	0.45	0.38	0.17
Cr ₂ O ₃	0.06	0.05	0.03	0.03	0.02	0.02	0.02	0.01	0.00
Total	100	100	100	100	100	100	100	100	100
Mg#	66.9	63.5	59.9	57.6	54.2	52.8	52.0	51.5	47.4
Sc	24.1	21.3	18.5	17.5	16.4	15.3	13.9	11.6	4.5
V	217	213	174	168	163	157	144	117	33
Cr	399	294	216	181	140	124	109	89	27
Ni	124	97	69	58	46	43	40	33	14
Zn	60.4	61.5	61.5	61.3	60.9	59.5	56.8	51.2	34.3
Rb	93	99	95	92	90	91	93	98	113
Sr	975	1084	1210	1191	1151	1144	1113	1021	741
Y	20.3	21.5	21.0	20.5	19.9	19.0	17.7	15.5	8.9
Zr	131	145	162	173	187	194	197	193	183
Nb	9.9	11.0	11.9	12.5	13.1	13.1	13.1	13.1	13.2
Cs	1.64	1.76	1.78	1.76	1.74	1.76	1.76	1.72	1.62
Ba	1232	1274	1169	1121	1070	1123	1163	1158	1142
La	33.7	37.5	39.6	39.0	38.1	37.8	37.4	36.3	32.9
Ce	73.3	80.9	84.3	81.5	77.5	76.2	74.5	70.8	59.8
Pr	9.0	9.9	10.1	9.6	9.0	8.7	8.4	7.7	5.9
Nd	38.7	42.0	42.0	39.9	36.9	35.3	33.3	29.8	19.3
Sm	7.81	8.33	8.11	7.73	7.25	6.93	6.49	5.68	3.24
Eu	1.97	2.09	2.15	2.06	1.93	1.84	1.71	1.47	0.77
Gd	6.28	6.62	6.43	6.17	5.85	5.56	5.15	4.39	2.09
Tb	0.752	0.790	0.771	0.738	0.696	0.665	0.622	0.545	0.312
Dy	4.14	4.35	4.21	4.06	3.89	3.71	3.46	3.02	1.67
Ho	0.734	0.776	0.751	0.730	0.707	0.669	0.618	0.535	0.284
Er	1.96	2.07	2.02	1.97	1.92	1.82	1.68	1.49	0.89
Tm	0.248	0.264	0.261	0.258	0.256	0.248	0.235	0.207	0.122
Yb	1.70	1.81	1.82	1.81	1.81	1.77	1.69	1.51	0.96
Lu	0.253	0.269	0.270	0.270	0.271	0.263	0.250	0.230	0.168
Hf	3.54	3.88	4.29	4.59	4.96	4.91	4.85	4.93	5.14
Ta	0.58	0.65	0.71	0.76	0.82	0.86	0.90	0.95	1.10
Pb	7.9	8.9	10.0	10.8	11.9	13.0	14.2	15.8	20.6
Th	4.4	4.9	5.5	5.9	6.4	7.0	8.0	10.3	17.3
U	1.02	1.14	1.26	1.31	1.37	1.40	1.50	1.76	2.55

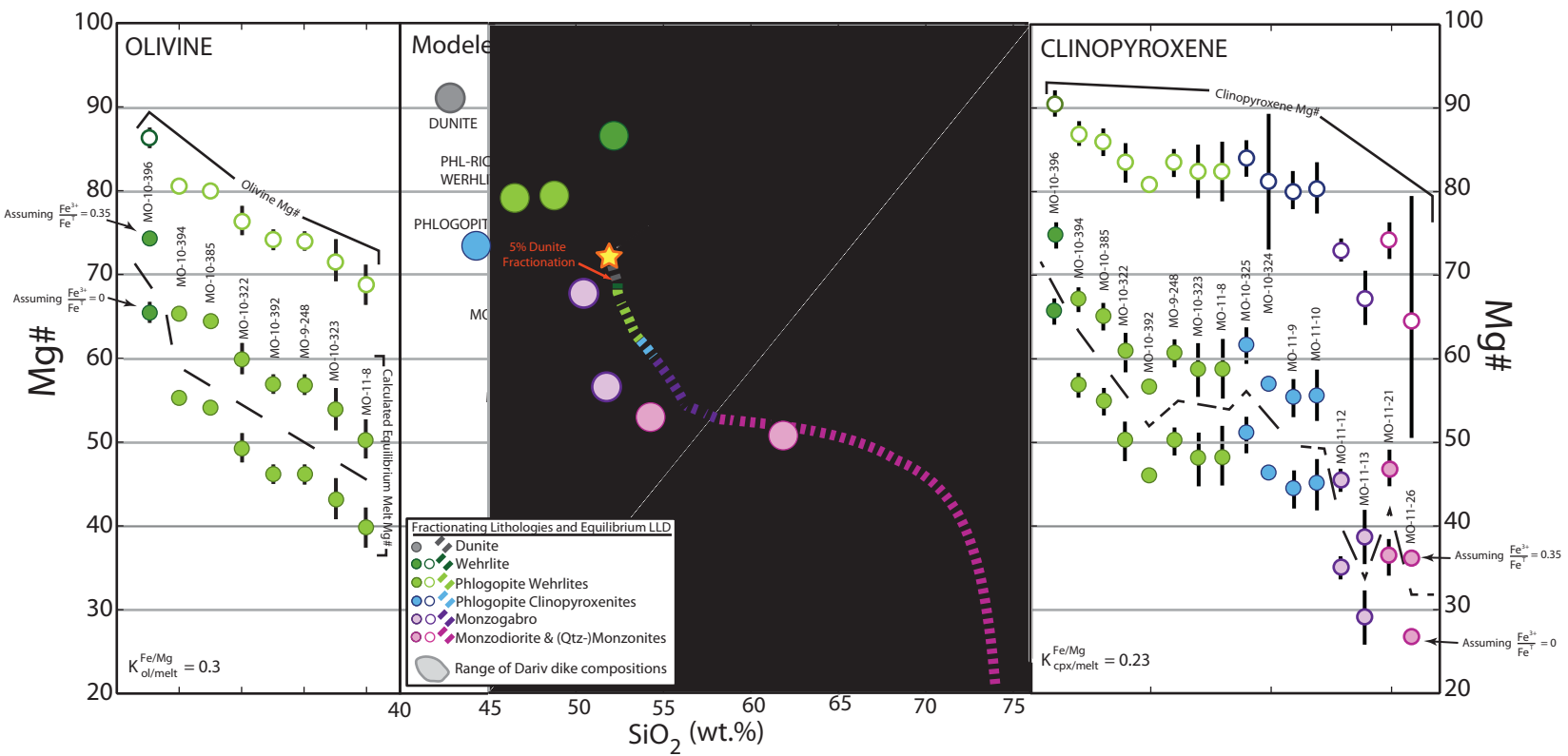


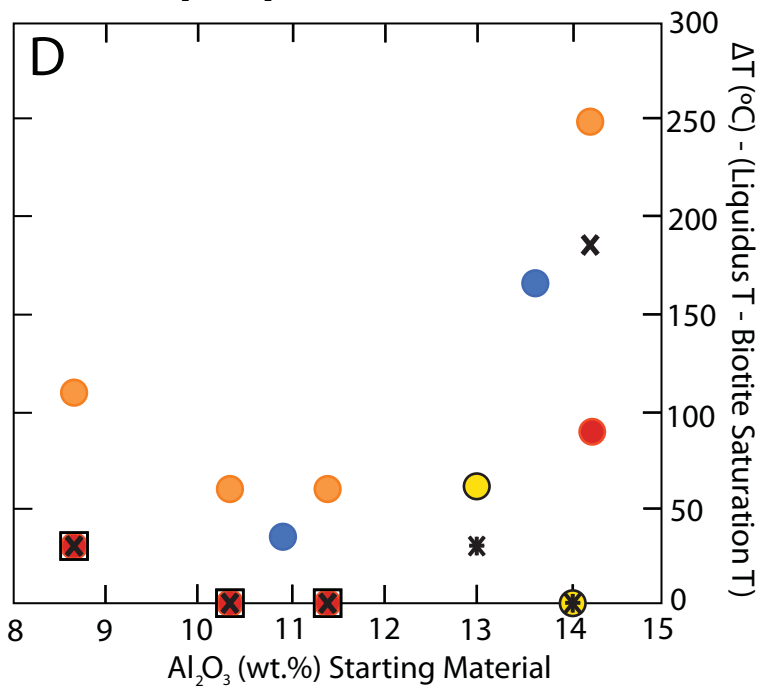
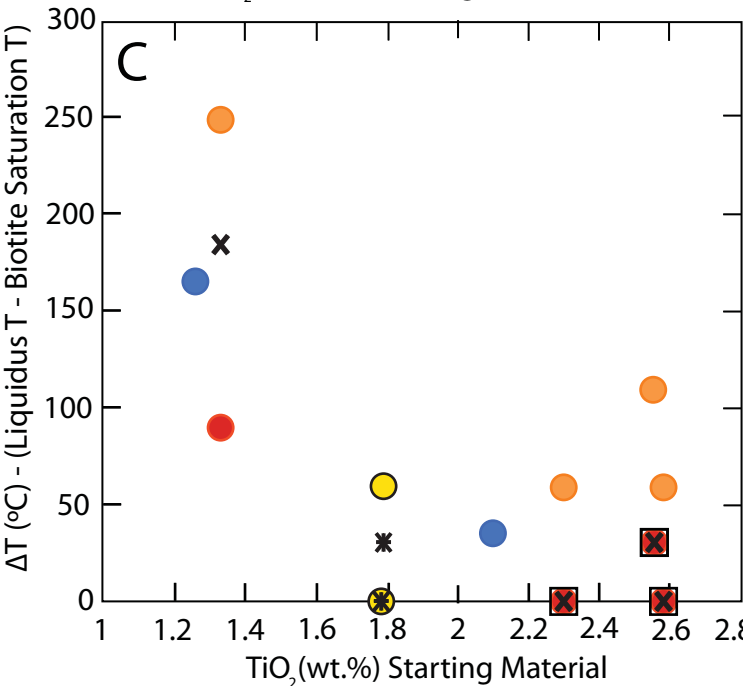
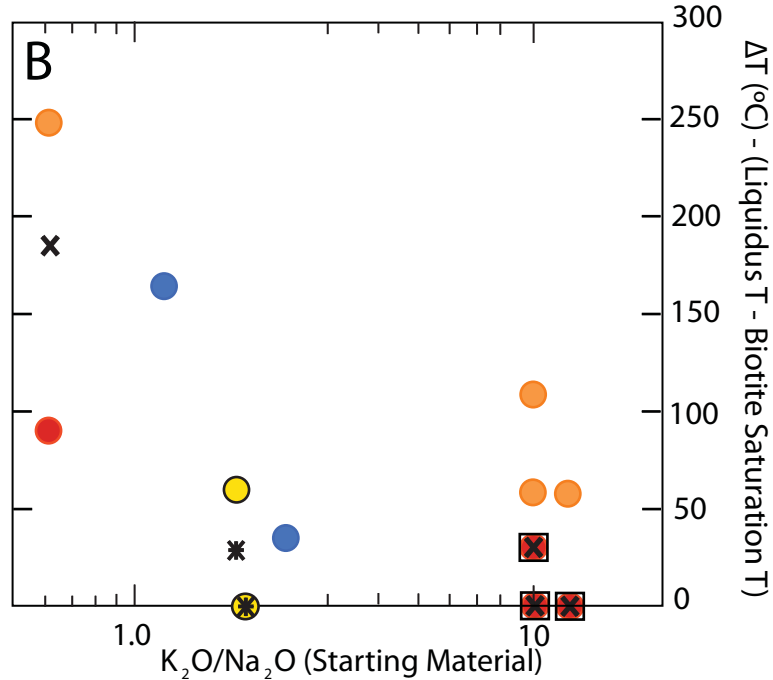
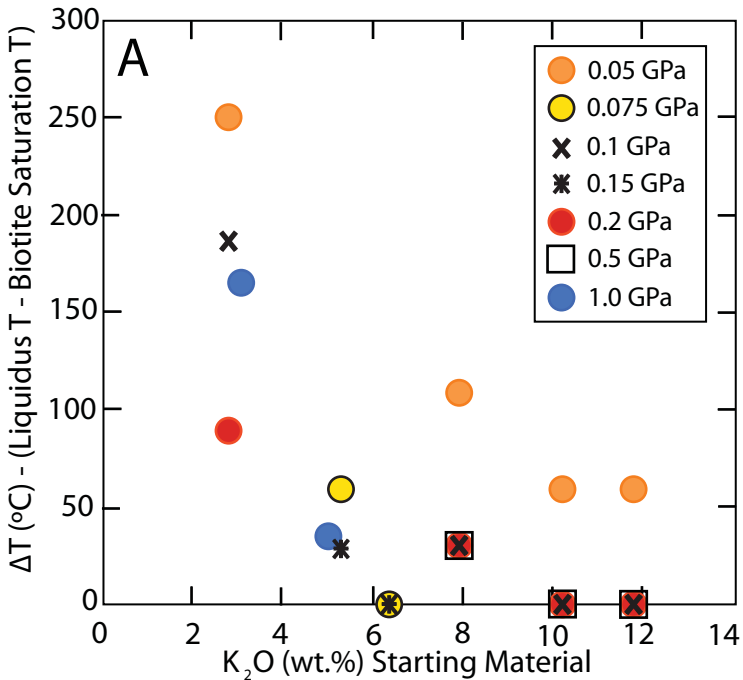
BIOTITE-DOMINATED SEQUENCE**AMPHIBOLE-DOMINATED SEQUENCE**

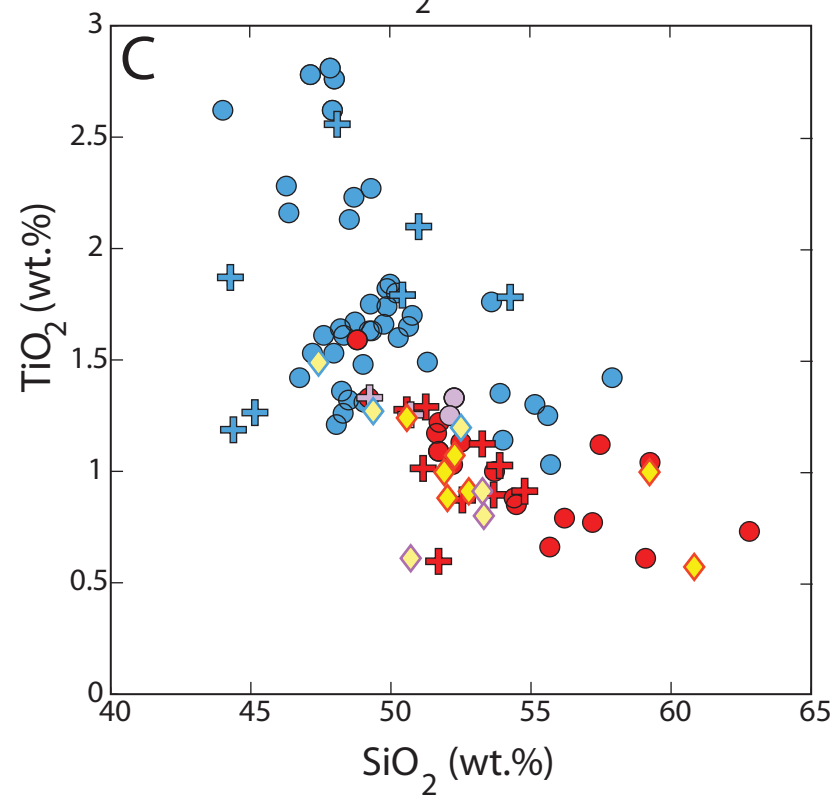
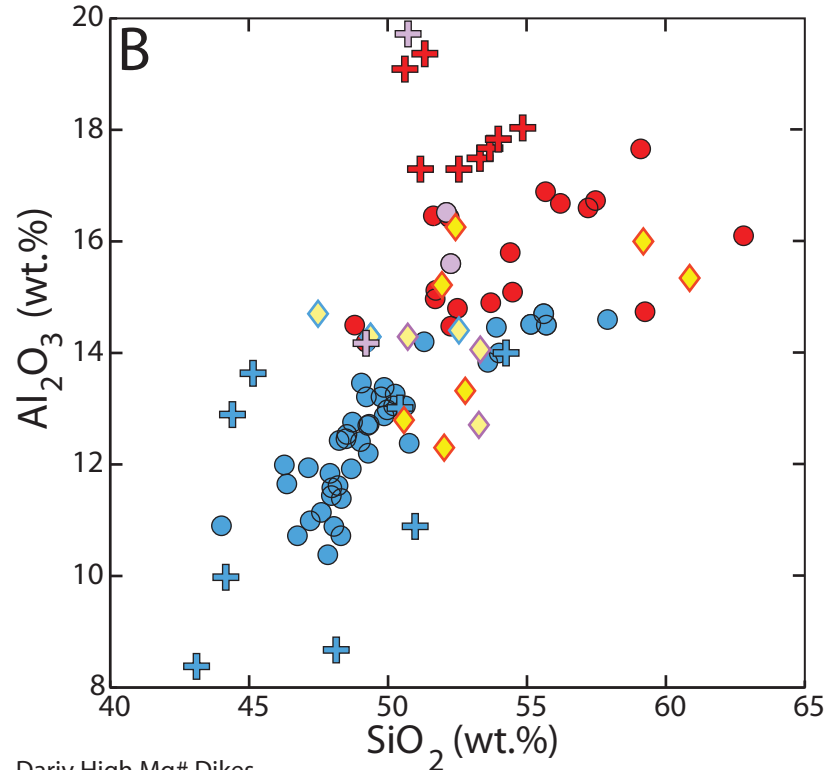
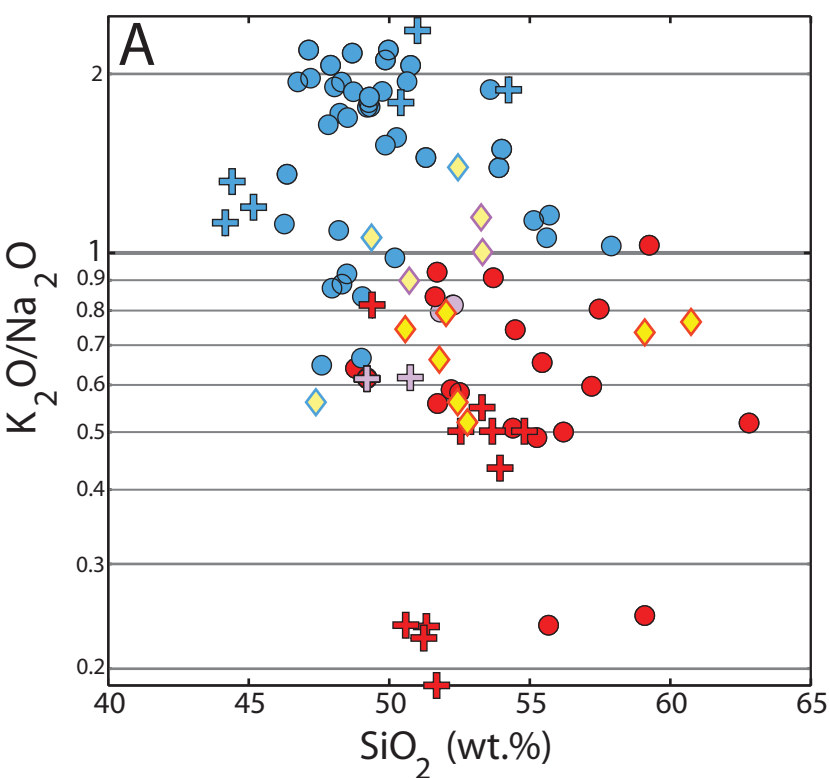












Dariv High Mg# Dikes

Phenocrystic or Groundmass Phases

- ◆ biotite
- ◆ biotite + amphibole
- ◆ amphibole

MVB High-Mg# Alkali-Basalts & Lamprophyres

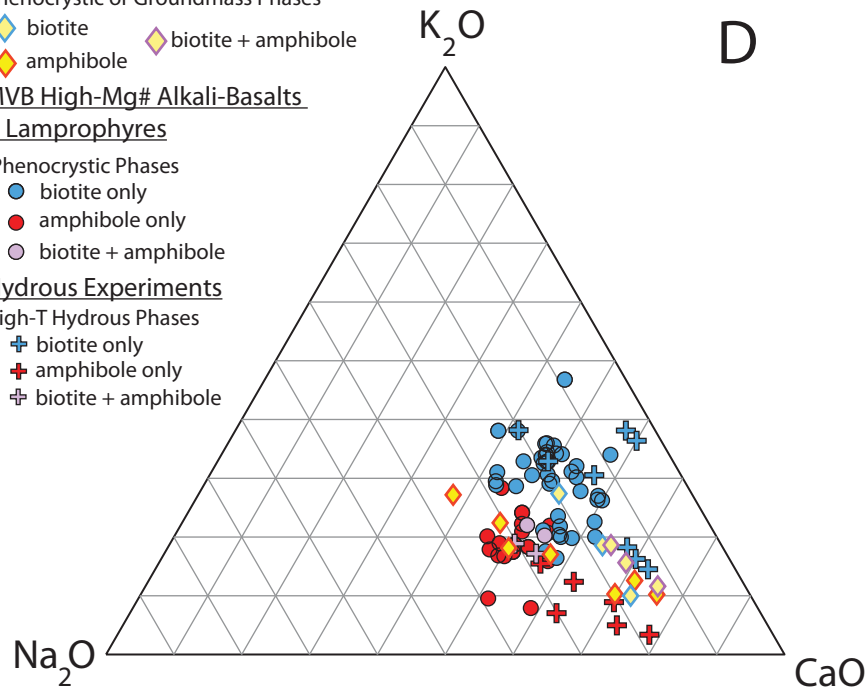
Phenocrystic Phases

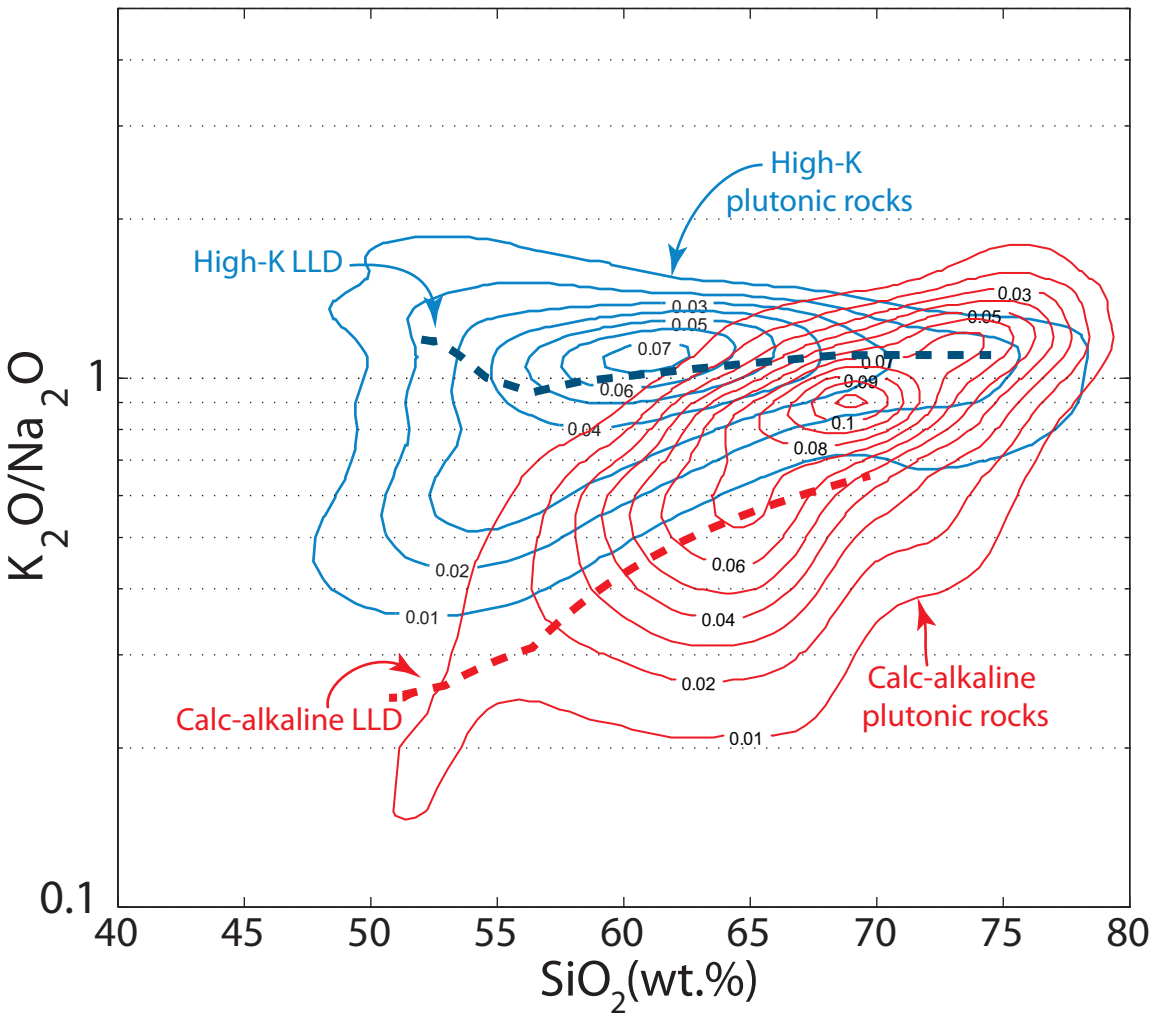
- biotite only
- amphibole only
- biotite + amphibole

Hydrous Experiments

High-T Hydrous Phases

- + biotite only
- + amphibole only
- + biotite + amphibole

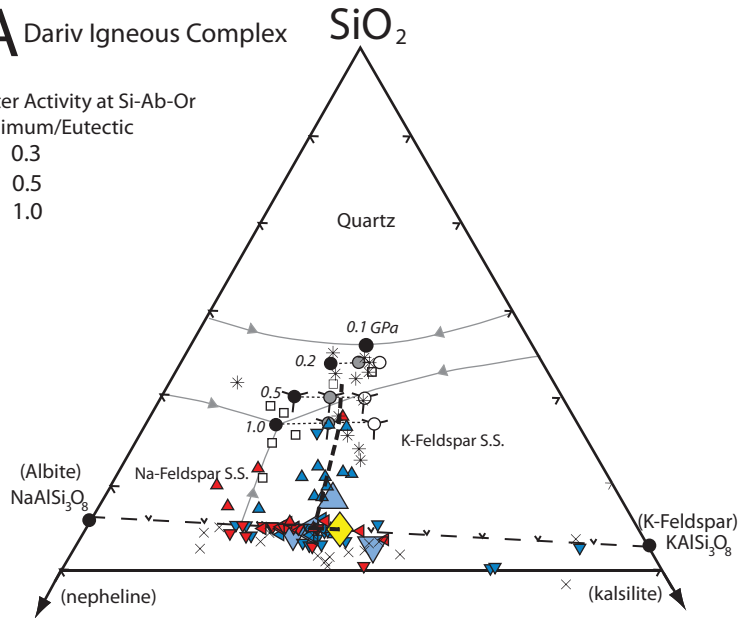




A Dariv Igneous Complex

Water Activity at Si-Ab-Or
Minimum/Eutectic

- 0.3
- 0.5
- 1.0



B Arc-Related Granitoids and modeled LLDs

