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Systematics of metals, metalloids, and volatiles in MORB melts: Effects of partial melting, crystal fractionation and degassing (a case study of Macquarie Island glasses)

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ABSTRACT

Magnesian basaltic glasses from the Miocene Macquarie Island ophiolite (SW Pacific) are used for understanding the effects of progressive partial melting of the mantle peridotite, and subsequent magma crystallisation and degassing on the composition of mid-ocean ridge basalts. These glasses are represented by two suites, near-primitive (Group I) and fractionated (Group II), which show clear parent–daughter relationships. Their exceptional compositional diversity in major, trace lithophile and volatile elements is shared by a set of metallic elements and metalloids, analysed in this study by laser ablation ICPMS. The Group-I glasses provide concentrations of compatible metals before they are severely modified by crystal fractionation (e.g., V, Sc, Co, Ni, Cr, Zn) or melt degassing (Cu). The constant or nearly constant ratios of the elements in the Macquarie Island primitive and fractionated melts are used for identification of similar bulk distribution coefficients during melting and crystal fractionation, respectively. The estimated relative degree of incompatibility during mantle melting provides constraints on the siderophile, chalcophile and volatile element abundances in the model "primitive" and "depleted" mantle sources. The chemical systematics observed in the studied glasses can be further used to explore mantle source compositions, including mineral phases involved in magma generation, and processes controlling fractionation of chemical elements in both mantle source and mantle-derived melts.

1. Introduction

Mid-ocean ridge basalts (MORB) represent the global phenomenon of melting of the convecting upper mantle and generation of the most voluminous magma type on Earth. Significant compositional variability of MORB on both local and regional scales (e.g., Langmuir et al., 1992) has been increasingly documented in the melt inclusion studies (e.g., Sobolev, 1996; Kamenetsky et al., 1998; Saal et al., 2002; Danyushevsky et al., 2003; Kamenetsky and Gurenko, 2007). This led to recognition of multiple *primary* melts, whose compositions are controlled by different mantle sources and different conditions of partial melting (e.g., Sobolev, 1996). The original compositional variability of primary melts is further amplified by a number of processes that link primitive liquids to erupted magmas (i.e., rocks). While the interaction of primary melts with mantle and crustal rocks, crystallisation, and degassing increase the original compositional diversity, the pre-eruption mixing of melt batches tends to average compositions of MOR basalts.

Although the effects of partial melting and fractional crystallisation on the systematics of major elements and most lithophile trace elements are well known, the behaviour of many metalloids and compatible metals requires further studies. Many elements that are present in sub-ppm quantities are not routinely analysed (e.g., semi-metals Be, Ge, As, Se, Mo, Cd, In, Sn, Sb, W, Bi), whereas abundances of siderophile and chalcophile metals (e.g., Sc, V, Cr, Mn, Co, Ni, Cu, Zn) in primary melts are masked by crystallisation of common silicates and oxides, sulphide immiscibility and possibly degassing. Another common problem in the studies of MOR basalts, glasses and melt inclusions is that in a given magmatic suite the genetic relationships between different primary melts and between primary (parental) and fractionated melts remain largely unconstrained (Sobolev, 1996).

To the best of our knowledge, the only suite of basaltic glasses that directly reflects mantle melting in the origin of MORB has been found among volcanic rocks of the Macquarie Island ophiolite, SW Pacific (Kamenetsky et al., 2000; Varne et al., 2000; Kamenetsky and Maas, 2002; Daczko et al., 2009; Portner et al., 2010). This compositionally diverse, near-primary suite is ideal for understanding the chemical trends in the melts produced at low to moderate degrees of partial melting of a spinel lherzolite mantle source (Kamenetsky and Maas, 2002). The Macquarie Island ophiolite also contains a suite of basaltic glasses, whose compositions are linked to the near-primary melts by crystallisation and degassing. Both suites of the Macquarie Island glasses are employed in this study for constraining geochemical systematics in

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natural liquids during mantle melting and crystal fractionation, with emphasis on behaviour of metals, metalloids, and volatile elements.

2. Macquarie Island ophiolite

2.1. Geological information

A fragment of in-situ upper mantle and overlying oceanic crust, formed in Miocene times at the Australian–Pacific plate boundary, is represented by Macquarie Island in the Southern Ocean, between New Zealand and Antarctica (54°35′S and 158°55′E). The island is a ~37 km long and 3–5 km wide exposure above the sea level (250–300 m) of the seismically active, slow spreading Macquarie Ridge, which in this region has a double crest with a central valley. The island is elongated in a NNE direction along the eastern ridge crest of the Macquarie Ridge. The rocks of the island formed at the waning stage of magmatism within a spreading ridge system that consisted of short segments linked by large-offset transform faults. The details of tectonic position and complex evolution of this ridge–trench system, and geological features of the Macquarie Ridge–Island can be found in numerous publications over the last 40 years (e.g., Varne et al., 1969; Griffin and Varne, 1980; Kamenetsky et al., 2000; Varne et al., 2000; Goscombe and Everard, 2001; Daczko et al., 2003, 2009; Dijkstra and Cawood, 2004; Dijkstra et al., 2010).

All researchers agree that Macquarie Island is a unique and complete section of young ocean floor that is still embedded in its parental oceanic environment, although pervasive faulting displaced the blocks of different rocks from their original positions. The northern part of the island experienced greatest tectonic uplift, which exhumed a continuous middle to lower crustal section of sheeted dolerite dykes, massive gabbro, layered olivine gabbro, troctolite, wehrlite and dunite, and underlying residual mantle harzburgite (Griffin and Varne, 1980; Basylev and Kamenetsky, 1998; Dijkstra and Cawood, 2004; Dijkstra et al., 2010). Brittle faults separate this domain from the upper crustal volcanic rocks and marine sediments in the northeast and the south of the island. The volcanics are mainly basaltic pillow lavas with subordinate massive to tabular basalt flows, hyaloclastites, and rare picrites (with olivine phenocrysts up to 90 mol% Fo).

2.2. Macquarie Island glasses

Glasses occur as quenched rims of pillow lavas and, more commonly, as fragments in hyaloclastite breccias (Griffin and Varne, 1980; Kamenetsky et al., 2000; Varne et al., 2000; Daczko et al., 2009; Portner et al., 2010). The latter usually consist of subangular to angular or rounded glass lapilli, glassy and crystalline pillow fragments, up to 3 cm (~40% of breccias), and may carry olivine and/or plagioclase crystals, in a matrix of smaller glassy debris cemented by a greenish-grey aggregate possibly after shattered and dispersed glass. In thin section the glasses are transparent and dark to light brown in colour, and may contain scattered opaque zones rich in crystallites. Microphenocrysts of olivine (20–300 μm) with trapped spinel and glass inclusions are widespread, but make up less than 3–5 vol.%. In some glasses Cr-spinel and plagioclase crystals are also present, although no clinopyroxene was observed. Most glasses also contain abundant spherical bubbles of low-density CO_2 (<5 to 100 μm) and rare globules of Fe–Ni–Cu sulphides (Kamenetsky et al., 2002; Kamenetsky and Kamenetsky, 2010).

A unique feature of the Macquarie Island glasses is the occurrence of very primitive, weekly fractionated compositions (Mg# 63–69 mol%; hereafter, Group-I glasses, Fig. 1) that show extreme diversity in abundances and ratios of incompatible major, trace and volatile elements (e.g., 0.14–1.76 wt.% K_2O; 3.6–60 ppm Rb; 4.6–46.6 ppm La; La/Sm 2.1–7.9; *Supplementary data*) and are in equilibrium with $Fo_{87–90}$ (Kamenetsky et al., 2000; Varne et al., 2000). Calculation of primary melt compositions in equilibrium with the most forsteritic olivine (90.5 mol% Fo as found in the Macquarie Island picritic lavas) can be done by addition of only 5–8% of olivine to Group-I glasses (Kamenetsky et al., 2002).

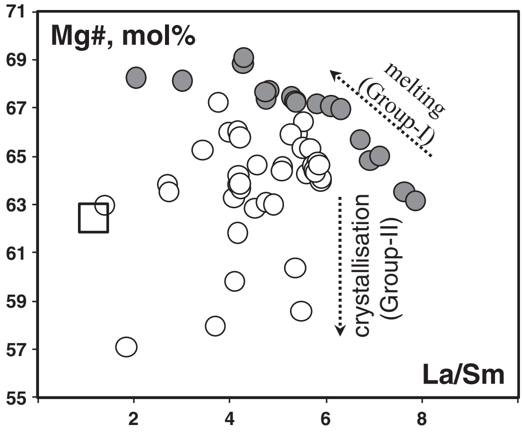

Fig. 1. La/Sm vs Mg# ([Mg/(Mg + Fe^{2+}) * 100%], where $Fe^{2+} = 0.9 * Fe^{total}$) for Group-I and Group-II glasses (closed and open circles, respectively). Global average MORB (Arevalo and McDonough, 2010) is shown by an open square.

Macquarie Island primary melts are characterised by well-correlated major and lithophile trace elements, and have homogeneous Sr and Nd isotope compositions ($^{87}Sr/^{86}Sr$ 0.702572–0.702764, $^{143}Nd/^{144}Nd$ 0.513013–0.513063). The compositional continuity in this suite strongly implies genetic relationships between the highly enriched and progressively more depleted melts that all derived from a single spinel lherzolite mantle source at increasing degrees of fractional melting (Kamenetsky et al., 2000; Kamenetsky and Maas, 2002). The lowest degree melts were inferred to represent a new ultra-enriched end-member in the MORB compositional spectrum, far more enriched than any known to date P-MORB or E-MORB (Kamenetsky et al., 2000).

Crystal fractionation processes that to different extent affected the Macquarie Island primary melts are reflected in the composition of fractionated glasses (hereafter, Group II, Kamenetsky et al., 2000). This suite is characterised by lower Mg# (57–67 mol%) at a given degree of enrichment (Fig. 1). The crystallisation of olivine, plagioclase and clinopyroxene from Group-I melts was considered to be responsible for lower abundances of Al, Ca, Sc, Sr, and Ba, and higher abundances of the lithophile trace elements in the Group-II melts (Kamenetsky et al., 2000). It was also noted that only the most enriched melts (La/Sm>7) lack the fractionated counterparts among the Group-II glasses.

3. Analytical techniques

Trace element concentrations in glasses were analysed by LA-ICPMS at the University of Tasmania. This instrumentation comprises a New Wave Research UP193SS Nd–YAG (193 nm) laser coupled to an Agilent 7500a quadrupole ICPMS. For this study, three analyses for each sample were performed in a He atmosphere by ablating 100 μm-diameter spots at a rate of 10 shots/sec using a laser power of ~2 J/cm^2. The instrument was optimized for sensitivity on mid- to high-mass isotopes (in the range 80–240 amu) and for minimal molecular oxide species (i.e., $^{232}Th^{16}O/^{232}Th<0.3\%$) and doubly-charged ion species (i.e., $^{44}Ca^{++}/^{44}Ca^{+}<0.3\%$) production. The analysis time for each sample was 90 s, comprising a 30 second measurement of background (laser off) and a 60 second analysis with laser on. Instrument calibration was performed by ablating the NIST612 glass standard. Data reduction was undertaken according to standard methods (Longerich et al., 1996) using the NIST612 glass as a primary reference material and SiO_2, analysed by the electron microprobe (EMPA), as the internal standard. USGS BCR-2 g glass was repeatedly analysed throughout analytical sessions (*Supplementary data*) and was used as a secondary reference material. The accepted values in BCR-2 g were reproduced within 5 rel% for most elements, but Cr, Cu and Sn values had stronger deviation (17, 21 and 21 rel%, respectively). The