Hadean-Archean oxygen isotope fractionation

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The Terrestrial Fractionation Line (TFL) for oxygen isotopes is defined by $^{17}O/^{16}O$ and $^{18}O/^{16}O$ analyses of meteoric waters, seawater, sedimentary, metamorphic, and igneous rocks and constituent minerals. Steeper slopes of mass fractionation lines on $\delta^{17}O$ vs. $\delta^{18}O$ diagrams indicate an approach towards isotope exchange equilibrium. Lower slopes are expected when isotope equilibration is inhibited and fractionation is kinetically controlled [1]. Interlaboratory measurements of the slope of the TFL on a plot of $\delta^{18}O$ vs. $\delta^{17}O$ show eclogitic garnets with a slope of 0.526 and hydrothermal quartz whose slope was 0.524 [2] from rocks younger than 0.8 Ga. New measurements show Archean metamorphic rocks and minerals from Barberton, (3.2 Ga, S. Africa), Isua (3.8 Ga, Greenland), and Acasta (4.0 Ga, Canada) have a slope of 0.524 ± 0.002 (95% confidence, MSWD = 0.66 [3]). Continuing analyses of samples from Porpoise Cove (4.3 Ga, Canada) give a slope of 0.528 ± 0.004 (MSWD = 0.47).

Analysis of Ag_3PO_4 prepared from apatite mineral separates from Isua meta-sediments gives a slope of 0.509 ± 0.022 (MSWD = 0.59). Ongoing analyses seek to improve the precision of this slope. The lower slope of 0.509 for Isua apatite suggests the formation of orthophosphate was kinetically controlled.

Conclusions: (1) Mixing accompanying the violent birth of the Earth-Moon system had already succeeded in establishing Earth's current oxygen isotope composition by 4.3 Ga; and (2) No trace of an episode of meteorite bombardment remains in the oxygen isotope compositions of Earth's oldest rocks.

[1] Young *et al*. (2002) *GCA* **66**, 1095-1104. [2] Rumble *et al*. (2007) *GCA* **71**, 3592-3600. [3] Ludwig (2003) http://www.bgc.org/isoplot_etc/software.html/

Volatiles and melt inclusions in high-Mg Andesite from Mt. Shasta, CA

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High-Mg andesites (HMA), though relatively uncommon in volcanic arcs, are potentially important in the formation of continental crust. Their primitive chemical characteristics suggest equilibration with mantle wedge peridotite, and they may form through either shallow, wet partial melting of the mantle or re-equilibration of slab melts migrating through the wedge. A well studied example of HMA from near Mt. Shasta, CA has been a topic of recent debate as petrographic evidence for magma mixing calls into question whether HMA melts exist (as opposed to hybrid bulk rocks containing harzburgite debris) or have a mantle origin [1]. We have re-examined naturally-quenched, glassy, olivine-hosted (Fo_{87-94}) melt inclusions from this locality (*cf.* [2]). Inclusions were analyzed by FTIR and electron probe. Compositions (uncorrected for post-entrapment modification) are quite variable (54-63 wt% SiO_2; 2-8 wt% MgO) and can be divided into high-CaO (>10 wt%) melts in Fo>90 olivines and low-CaO (<10 wt%) melts in Fo<90 olivine hosts. There is evidence of extensive post-entrapment modification in many inclusions, and we evaluated the effects using three methods. High-CaO inclusions experienced 2-3 wt% FeO^T loss by diffusion and 20-40 wt% olivine crystallization. In contrast, low-CaO inclusions experienced lesser amounts of both FeO^T loss and olivine crystallization (≤12 wt%). After correction for these effects, we find that melt inclusions in Fo_{87-88} olivine have HMA compositions (55-58 wt% SiO_2; 8-8.5 wt% MgO) whereas those in Fo_{93-94} olivine are primitive basalt to basaltic andesite (50-54 wt% SiO_2; 14.2-16.2 wt% MgO). Importantly, both types of inclusions are volatile rich, with maximum values in HMA and basaltic melt inclusions, respectively, of 3.1 and 3.2 wt% H_2O, 800 and 1800 ppm S, 1500 and 2200 ppm Cl, and 460 and 590 ppm CO_2. Measured S Kα peak positions suggest oxidizing conditions (≥NNO+1), similar to other arc magmas. Our results demonstrate that H_2O-rich, HMA melts exist within the magmatic system in the Mt. Shasta region and have similar major element compositions as bulk rock samples (*e.g.* [3]) despite clear petrographic evidence for mixing and entrainment of crystal debris. In addition, the presence of basaltic to basaltic andesite melts trapped in the Fo_{93-94} olivine provides evidence that these are magmatic phenocrysts that crystallized from unusually primitive, subduction-related magmas.

[1] Streck (2007) *Geology* **35**, 351-354. [2] Anderson (1974) *J. Pet.* **15**, 243-267. [3] Grove (2003) *CMP* **145**, 515-533.