

Reconsidering the proposed derivation of voluminous I and A-type high-silica primary magmas directly by crustal fusion

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There is widespread evidence for crustal contributions to arc and intraplate magmas. And the MASH hypothesis combined with the model for upper-crustal 'mushy zones' [1-4] provides a rationalizing framework for assimilation and melting of crustal protoliths for *both* arc (in normal or flare-up mode) and hot-dry intraplate magmatism.

However it has also been suggested that voluminous (metaluminous, I-type, A-type) high-silica magmas are produced directly by crustal fusion. It is presumed that direct crustal melting of *subsolidus* supracrustal, or hybrid (granodioritic) or mantle-derived mafic plutonic rocks is a plausible process for producing volumetrically significant rhyo-dacite and rhyolites that ascend and erupt directly.

The arguments for the direct production of "beheaded" voluminous primary silicic melts from crustal sources, are usually based on 1) the apparent failure of a (modelled) fractionation relationship with contemporaneous intermediate or mafic magmas, 2) mass balance requirements for production of very evolved composition from basalt by fractionation, 3) the absence of contemporaneous erupted intermediates, 4) the assumption that wide-spread migmatites in some crustal sections are putative analogs for direct production of voluminous crustal melts in arcs, 5) experimentally produced melts of crustal materials are like proposed silicic primary magmas, 6) isotopic data, particularly Nd and O. In addition, it is usually assumed that voluminous crustally-derived silicic melts result from basaltic inter-or-underplating.

In this presentation we demonstrate that these objections to the MASH-mush paradigm are often non-unique, are not in accord with geological examples, are unable to produce observed volatile contents, do not agree with physical models for rates of generation and transport, and/or are plausibly explained by assimilation and subsequent fractionation of shallow silicic igneous precursors or supracrustal materials in the deepest crust-lithospheric mantle [5].

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Mass dependent and mass independent fractionation of Mercury isotopes

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Mercury isotope fractionation, theory, and applications will be reviewed in this presentation. Mercury is a globally distributed and highly toxic pollutant. Although Hg is a proven health risk, much of the natural cycle of Hg is not well understood and new approaches are needed to track Hg and the chemical transformations it undergoes in the environment. Recently, we demonstrated that Hg isotopes exhibit two types of isotope fractionation: (1) mass dependent fractionation (MDF) and (2) mass independent fractionation (MIF) of only the odd isotopes [1]. The observation of large MIF of Hg isotopes (~5‰) is exciting because only a few other isotopic systems have been documented to display large MIF, the most notable of which are oxygen and sulfur. In both cases, the application of MIF has proven very useful in a variety of fields including cosmochemistry, paleoclimatology, physical chemistry, atmospheric chemistry, and biogeochemistry.

Both MDF and MIF isotopic signatures are observed in natural samples, and together they open the door to a new method for tracing Hg pollution and for investigating Hg behaviour in the environment. For example, fish record MDF that appears to be related to size and age. Additionally, fish display MIF signatures that are consistent with the photo-reduction of methylmercury. In order to utilize Hg isotopes, the mechanisms for Hg isotopic fractionation must be investigated and understood. Thus far, photochemical transformation of Hg species is the only mechanism experimentally proven to produce MIF of Hg isotopes [1]. Further, the relationship between the MIF of the two odd isotopes is distinct for different photochemical pathways. In contrast, biological and abiotic organic reduction follow only MDF [1, 2]. MIF of Hg isotopes is predicted by both the nuclear volume and magnetic isotope effects, and both of these mechanisms predict an even-odd signature. Proving with certainty which mechanism is responsible for the MIF observed in laboratory experiments and natural samples will be difficult, but we suggest the magnetic isotopic effect is the mostly likely cause of the photochemical MIF.

[1] Bergquist, B.A. & Blum, J.D. (2007) *Science* **318**, 417-420. [2] Kritee, K. *et al.* (2007) *ES&T* **41**, 1889-1895.