

Measurement and reporting of natural mercury isotopic variability

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Hg isotope analysis by MC-ICP-MS (using SnCl reduction and Hg cold-vapor generation) is an important new tool for fingerprinting Hg sources and monitoring Hg redox reactions and bioaccumulation (Smith *et al.*, 2005; Foucher and Hintelmann, 2006; Jackson *et al.*, 2006; Bergquist *et al.*, 2006; Kritee *et al.*, 2007). Unfortunately research groups have adopted different standards, definitions of delta values, and approaches to isotopic measurement. We suggest that a single standard, NIST SRM 3133, be adopted for reporting the isotopic variability of Hg isotopes. Isotope ratios should be determined by sample-standard bracketing (SSB) during analysis and reported as permil (‰) deviation from NIST SRM 3133. For the highest precision and accuracy, a Tl internal standard should be used along with SSB to correct instrumental mass bias. Measurements should also include on-peak zero corrections and matching of concentration and matrix between the samples and bracketing standard.

We suggest reporting isotope ratios with ^{198}Hg in the denominator: $\delta^{xxx}\text{Hg}\text{‰} = \left\{ \left(\frac{^{xxx}\text{Hg}/^{198}\text{Hg}}{(^{xxx}\text{Hg}/^{198}\text{Hg})_{\text{SRM 3133}}} \right) - 1 \right\} * 1000$, where ^{xxx}Hg is the mass of each isotope between 199 and 204 amu. This results in higher $\delta^{xxx}\text{Hg}$ always being “isotopically heavier” as in other isotopic systems. For mass-dependent fractionation (MDF), only one delta value needs to be reported and we suggest $\delta^{202}\text{Hg}$. Mass-independent fractionation (MIF) of the odd-mass Hg isotopes has also been observed in aquatic systems (Jackson *et al.*, 2006; Bergquist *et al.*, 2006) and requires additional nomenclature. Following the convention used for MIF of O and S we report MIF as the deviation in isotope ratios from the theoretical mass dependent kinetic isotope fractionation ($\Delta^{xxx}\text{Hg}$).

External reproducibility should be monitored by analysis of secondary standards. For studies of MDF, we use an in-house secondary standard solution made from metallic Hg mined from Almadén Spain and we obtain a $\delta^{202}\text{Hg}$ of $-0.54 \pm 0.08\text{‰}$ (2SD), $\Delta^{201}\text{Hg}$ of $-0.04 \pm 0.04\text{‰}$ (2SD), and $\Delta^{199}\text{Hg}$ of $-0.01 \pm 0.02\text{‰}$ (2SD). For studies of MIF, we also use NRCC CRM DORM-2 (dogfish muscle) and obtain a mean $\delta^{202}\text{Hg}$ value of $+0.19 \pm 0.07\text{‰}$ (2SD), $\Delta^{201}\text{Hg}$ of $+0.88 \pm 0.06\text{‰}$ (2SD), and $\Delta^{199}\text{Hg}$ of $+1.06 \pm 0.04\text{‰}$ (2SD).

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Bergquist BA, Blum JD, Johnson MW, Biswas A (2006) *Eos Trans AGU* **87**:V13E-06

Foucher D, Hintelmann H (2006) *Anal. Bioanal. Chem.* **384**:1470-1478

Jackson TA, Whittle DM, Evans MS, Muir DCG (2006) *Geochim. Cosmochim. Acta* **70**(18S):A284

Kritee K, Blum JD, Johnson MW, Bergquist BA, Barkay T (2007) *Environ. Sci. Technol.* **41**:1889-1895

Smith CN, Kesler SE, Klaue B, Blum JD (2005) *Geology* **33**:825-828

Magma generation and ascent beneath arc volcanoes

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Explosive eruptions of andesite arc volcanoes are driven by the generation and subsequent ascent of magma from the deep crust. Magma generation involves a combination of crystallisation of H₂O-rich basalt derived from the mantle wedge and partial melting of pre-existing crustal rocks in deep crustal *hot zones*. Magma ascent can be divided into two regimes. The first regime involves the segregation and ascent of silicic magma through the crust. The H₂O-rich magma is buoyant and inviscid and likely to ascend rapidly along dykes. The magma is, however, H₂O-undersaturated and therefore will develop superheat during ascent, enabling it to partially digest residual source material and/or wall rocks. The corroded cores of many plagioclase phenocrysts may have originated in this way. Crystal retention and partial resorption by silicic melts leads to linear trends in whole-rock chemistry. We suggest that relatively few andesites represent true liquid compositions; most have an entrained cargo of ancestral crystal residues or accidental passengers acquired en route.

The second regime begins when the magma attains volatile saturation and degassing begins, preferentially removing CO₂ relative to H₂O. Crystallisation begins at slightly lower pressures when the volatile-saturated liquidus is encountered. The ensuing crystallisation and volatile loss due to decompression lead to a sharp increase in viscosity and density, which serve to slow magma ascent dramatically. We refer to this process as “viscous death” with the consequence that most andesite magmas are destined to form plutons. Decompression crystallisation releases latent heat and results in the paradoxical situation of magma both crystallising and getting hotter by $\leq 100^\circ\text{C}$. Because decompression crystallisation continues to low pressures melt SiO₂ contents can be up to 80 wt% (anhyd.). Such melts are too viscous to segregate from crystals on volcanic timescales. As a consequence rather little chemical differentiation occurs at shallow levels; most of a magma’s chemistry is defined by differentiation processes in the hot zone and the entrained crystal cargo. Nonetheless, low-pressure cumulates do occur in many andesites, testifying to some crystal deposition within the sub-volcanic edifice. Exposures of sub-volcanic complexes support the idea that successive magma batches may deposit a small fraction of their cargo en route to the surface and, in a complementary way, can entrain fragments of the cargoes of antecedent magmas. An individual phenocryst in an andesite may preserve snapshots of the entire complex magmatic evolution.