Double-spike Fe isotope analyses of silicate minerals in volcanic rocks

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The development of high-resolution multiple collector inductively coupled plasma source mass spectrometry (HR-MC-ICPMS) has made it possible to investigate stable Fe isotope systematics in the geological record with precisions of ca. 0.03‰ (2 se) [1]. Recent experimental studies and Fe isotope studies of natural systems have begun to document significant high temperature fractionation of stable Fe isotopes [2, 3, 4, 5]. However, few mineral-melt fractionation factors have been precisely determined and our understanding of the kinetic and equilibrium isotopic effects that control stable Fe isotope fractionation in magmas and their crystallized components remains poorly understood.

We have developed techniques for high precision Fe isotope analysis using a ^{58}Fe-^{54}Fe double-spike to correct for instrumental mass bias and pseudo-high-resolution MC-ICPMS. Fe is separated from samples using conventional anion exchange techniques. Repeated measurements of IRMM-014 and samples yields reproducibilities of $\leq \pm 0.03$‰ (2 se) on δ^{56}Fe.

Preliminary results confirm that some magmatic minerals show significant stable Fe isotope variations. Olivine from a near primary continental flood basalt is significantly lighter than the groundmass and co-existing clinopyroxene ($\Delta_{\text{oliv-gmass}} = -0.40\pm0.04$‰; $\Delta_{\text{oliv-cpx}} = -0.41\pm0.04$‰). Conversely, plagioclase from rhyolitic rocks exhibits some of the heaviest measured Fe in igneous minerals with δ^{56}Fe = +0.42‰ ±0.04‰ and $\Delta^{56}\text{Fe}_{\text{plag-melt}} = +0.34\pm0.04$‰ and $\Delta_{\text{plag-amph}} = +0.35\pm0.07$‰. The mineral stable Fe isotope variations appear to be related to the amount of Fe^{3+} integrated in their structure with olivine dominated by Fe^{2+} in its structure having light iron and plagioclase dominated by Fe^{3+} having having heavy Fe. However, a range of basaltic rocks and rhyolitic glasses from a variety of tectonic setting display limited stable Fe isotope variations i.e., δ^{56}Fe = +0.02 to +0.22‰.

[1] Dauphas *et al*. (in press), *Chem. Geol.*[2] Williams *et al*., (2004), *Science*, **304**, 1656-1659. [3] Weyer *et al.*, (2007), *EPSL*, **259**, 119-133. [4] Shahar *et al*., (2008), *EPSL*, **268**, 330-338. [5] Teng *et al*., (2008), *Science*, **320**, 1620-1622

Tracing soil carbon cycle and the origin of needle fibre calcite

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Needle Fibre Calcite (NFC) is the most widespread habitus of terrestrial calcite. Several SEM (Scanning Electron Microscope) observations support the biological origin of the NFC: needles of calcite seem to be precipitated inside organic sleeves, which are interpreted as fungal hyphae acting as a mould (Cailleau et al., 2009 [1]). Different micromorphologies are observed corresponding to different stages of NFC evolution. In order to test the biogenic hypothesis, a new approach based on a systematic soil carbon tracing has been conducted. The aim was to define the source(s) of carbon incorporated in the NFC. Both organic and inorganic carbon pools were measured at the most accurate scale ever in a NFC study.

The negative value of NFC δ^{13}C (*ca* -9.56‰) is often interpreted as a biological signature. Tracing soil carbon over a year highlighted a gradient of ^{13}C fractionation from soil organic matter, to DIC, to secondary CaCO_3 (various morphologies of NFC). The host rocks (cryoclasts from Jurassic limestones) have a conventional marine limestone signature. This result emphasizes a complex behaviour of carbon that precludes the use of NFC δ^{13}C signature as an evidence for fungal influence. The NFC signature is close to the theoretical physicochemical CaCO_3 δ^{13}C values obtained using the physicochemical conditions of the studied soil (mostly in equilibrium with organic matter decay). Due to the fact that fungi are heterotrophic organisms, C from DIC does not transit through metabolic pathways. Consenquently, the NFC isotopic signature should not be influenced by an organic pathway. C uptake for biomass is separated from carbon absorption of DIC origin, which could be passive. In conclusion, ^{13}C investigations do not unequivocally demonstrate the biogenic origin of NFC. Other approaches, such as isotopic (^{87}Sr, ^{44}Ca) or multi-elemental methods have to be considered to prove the biological origin of NFC.

[1] Cailleau, G., Verrecchia, E.P., Braissant, O., Emmanuel, L. (2009) The biogenic origin of needle fibre calcite. *Sedimentology*, in press