Crystal orientation effects on bias of $\delta^{18}O$ in magnetite by SIMS

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High precision *in situ* analyses by SIMS reveals fractionation of oxygen isotopes in magnetite due to crystallographic orientation effects. Multiple magnetite samples were analyzed conventionally (2 mg, BrF_5) and found to be homogeneous in $\delta^{18}O$, but showed variability of 4 to 5‰ during analysis by a Cameca IMS-1280 ion microprobe (10μm spot ~ 2ng). Magnetite standard #5830 has a $\delta^{18}O$ of 3.96 ± 0.2‰ (2SD) VSMOW by laser fluorination. $\delta^{18}O$ values by SIMS are within bracketed 2SD errors (0.4‰) within individual grains but vary by 4 to 5‰ between grains. Tests were made to rule out possible effects due to magnetism and thickness of the sample. Crystal orientation effects in magnetite by SIMS were suggested previously and attibuted to ion channeling along <110> (Lyon *et al*., 1998, Int. J. Mass Spec. Ion Proc.).

We used EBSD to determine the crystallographic orientation of randomly oriented magnetite grains cast in epoxy and polished. We plotted the orientation of the Cs^+ beam for each grain on a stereonet centered on [111]. Raw $\delta^{18}O$ values measured by SIMS were assigned to each beam orientation and the resulting equal area projection was contoured for measured $\delta^{18}O$. The results show that the highest (least fractionated) $\delta^{18}O$ values are obtained with the Cs^+ beam parallel to <*hk*0>. <*hk*0> corresponds to parallel planes of atoms along which the Cs^+ ions are channeled. Intermediate $\delta^{18}O$ values are obtained along <*hhl*>. Lower $\delta^{18}O$ values are obtained along <*hkl*> where the incident beam is not parallel to a channeling direction. SEM images of the ionprobe pits show enhanced development of sub-micron secondary pits when the Cs^+ beam is parallel to <100>, <110> or <111>.

SIMS precision for $\delta^{18}O$ in silicate minerals has improved from ±2‰ twenty years ago to ±0.3‰ 2SD today while at the same time analyses of magnetite have remained at ±2‰. The correlation between $\delta^{18}O$ in magnetite by SIMS and crystal orientation may provide the basis for accurate correction in conjunction with EBSD, and may significantly improve SIMS magnetite data allowing *in situ* quartz-magnetite thermometry among other potential applications.

Arsenic uptake by a natural vivianite material

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The mineral vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$] forms and is stable in a variety of anoxic environments such as lakes and urban water bodies [1, 2]. It has been suggested that vivianite may be an efficient sink of arsenic (As) in natural environments [3, 4]. We tested the efficiency of As(III) and As(V) uptake by a low-temperature natural vivianite material at acid, near-neutral and alkaline pH at T = 4°C, which is representative of Lake Baikal-type environments where natural vivianite is reported to occur, and 25°C, which is representative of As-polluted aquifer systems in southeast Asia. Uptake of As(III) and As(V) is pH-dependent, with higher percentage uptake occurring at pHs above 7.5, as previously reported [3, 4]. The uptake of As(III) and As(V) is also temperature-dependent. Detectable amounts of Fe, Mg, Mn and P were released during some of the acid sorption experiments, suggesting that some dissolution of the vivianite material took place. These data, together with characterization of the pre- and post-sorption solids, will yield information on the efficiencies of As uptake by natural vivianite.

[1] Fagel (2005) Glob. Planet. Change 46, 315-336. [2] Taylor *et al.* (2003) *Hydrol. Process.* **17**, 2049-2061. [3] Islam *et al.* (2007) *Geochim. Cosmochim. Acta* **71**, A432. [4] Thinnappan *et al.* (2008) *Appl. Geochem.* 23, 3187-3204.