Recent progress of small spot oxygen isotope analysis at WiscSIMS

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In situ, high precision oxygen two and three isotope analysis with a sub-μm to a few μm beam by SIMS is valuable technique to investigate records preserved in finely zoned samples [1-3]. Here, we report results of recent developments for high precision and accurate small spot oxygen isotope analysis at WiscSIMS laboratory.

FC-EM (-EM) detectors: The quasi-simultaneous arrival (QSA) effect [4] would be a problem for isotope analyses when we use a small spot and low current (e.g. <1 μm, <10 pA) Cs^+ primary beam. We observed more than +80‰ fractionated $\delta^{18}O$ value with two electron multipliers (EM), which is probably a result of the QSA effect, while fractionations are generally less than ±10‰ with Faraday Cups (FC). To minimize bias, we use a FC to detect $^{16}O^-$, which is the major oxygen isotope. The instrumental mass bias of oxygen two (or three) isotope analysis with FC-EM (-EM) detectors and a small beam is consistent with that of multiple FC analysis with a 10 μm beam within a few permil.

Matrix effect correction: The matrix effect of the instrumental mass bias (dependence on elemental composition of samples) with a small beam is different from that with a 10 μm beam. The matrix effect should be determined in the same analytical session.

Blue LED luminous source for CCD camera image: For better spatial resolution of the CCD camera image to aim analysis points, we converted to a blue LED. We can recognize ~2 μm texture of sample with the CCD camera image vs. ~3 μm with white light.

Sample preparation: A well-polished flat sample surface is important for an accurate isotope analysis [5, 6]. In addition, this is important for not only an aiming of tiny samples but also reducing $^{16}OH^-$ signal which interferes to $^{17}O^-$ signal. Since epoxy of sample mounts elevates pressure of the sample chamber and causes higher $^{16}OH^-$ signal, minimum usage of epoxy for sample mount is helpful for small spot oxygen isotope analysis [e.g. 2, 7].

[1] Page *et al.* (2007) *Am. Mineral.* **92**, 1772–1775. [2] Nakamura *et al.* (2008) *Science* **321**, 1664–1667. [3] Kozdon *et al.* (2009) *Chem. Geol.* **258**, 327–337. [4] Slodzian *et al.* (2004) *Appl. Surf. Sci.* **231–232**, 874–877. [5] Kita *et al.* (2009) *Chem. Geol.* **264**, 43–57. [6] Valley & Kita (2009) *MAC short course* **41**, 19–63. [7] Nakashima *et al.* (2010) *LPSC* **41**, #2309 (abstract)

Magnetite formation *via* Fe^{II} induced mineralogical transformations of ferric oxyhydroxides

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The reactivity of various ferric oxyhydroxides (ferrihydrite 'F', goethite 'G' and lepidocrocite 'L') against Fe^{II} species was investigated to induce mineralogical transformations into magnetite (Fe_3O_4) at different aging times (1 hour, 1 day and 1 month). A parallel study was also conducted on three kinds of lab-synthesized goethite having different crystal structures, crystal morphologies and surface properties. The starting and final solid products were characterized by XRD analysis, Transmission Electron Microscopy and Mössbauer spectroscopy.

The order of reactivity to transform into magnetite found was: F > L > G. Difference in morphology and particle size of generated magnetite was also observed dependent on the nature of initial substrates.

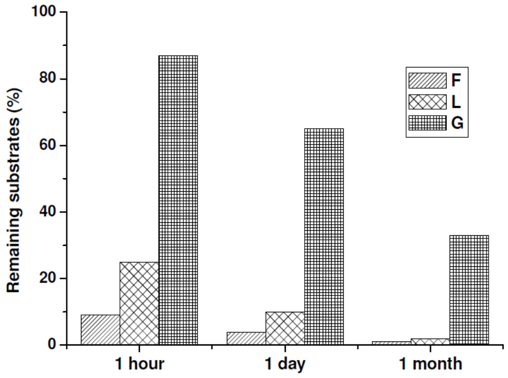

Figure 1: Untransformed amount (%) of ferric substrates at each time point. Rest was transformed into magnetite.

Goethite was the least reactive as 33% was still present after one month. Reaction with other kinds of goethite suggest that the reactivity was independent of the specific surface area emphasizing the importance of the crystal structure for their reactivity. Different coordination modes of Fe^{II} with the different crystal faces of Fe^{III}-hydroxide, which affect the Fe^{II}-Fe^{III} electron transfer could explain this discrepancy in reactivity.

Experiment with ferrihydrite mixed sand showed that silica sand (Quartz, 200-300μm) had no effect on this Fe^{II} induced transformation into magnetite.