The role of organic ligands in Fe isotope fractionation during dissolution of hornblende

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Dissolved Fe in some rivers is isotopically light by ~ 1 ‰ ($\delta^{56/54}$Fe) compared to average crustal Fe [1,2]. Fe isotopes are thus fractionated by one or more processes during weathering of crustal rocks, resulting in preferential transport of light isotopes of Fe toward the oceans and retention of heavy isotopes in weathering residues. Our ability to understand the Fe isotope budget of the crust-ocean-biosphere system, past and present, depends critically on understanding how isotope effects originate during weathering of major Fe-bearing crustal minerals.

An experimental study of hornblende dissolution by Brantley *et al*. [3] suggests that Fe-binding ligands play an important role not only in promoting dissolution of Fe-bearing silicate minerals, but in fractionating Fe isotopes. In those experiments, which were 4-6 days long, hornblende dissolved in the presence of acetic, oxalic, or citric acid or a siderophore molecule, desferrioxamine B. Fe-release rates correlated with Fe-binding affinity. In addition, the results suggested a relationship between Fe-binding affinity and the Fe isotope composition of the Fe released into the solvent medium. Brantley *et al*. hypothesized that fractionation occurs during incongruent dissolution of hornblende and that the isotope effect should decrease over time as Fe concentration in the leached layer approaches steady state.

To test this hypothesis, we have extended these experiments from 4-6 days to 70 days. We see a continuation of the relationship between Fe-release rates and Fe-binding affinity up to 22 days, beyond which precipitation of Fe (oxyhydr)oxides obscures the effect. Isotopic analyses of the solvent media up to 22 days will reveal whether the isotope effect indeed diminishes as dissolution progresses toward a steady-state leached layer. Whether this happens or not is important for constraining the mechanism of isotope fractionation. Understanding this mechanism is key to predicting how isotope effects in natural weathering environments influence the Fe isotope budget of natural waters. In addition, if siderophores leave a distinct isotopic fingerprint on weathering residues, as suggested by our preliminary work, it may be possible to detect where and when such molecules were produced in the past.

References

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Non-heterogenous oxygen isotopic distribution in coral microstructures

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Massive corals have been widely used as proxies for past changes in sea surface temperature (SST) of the tropical and subtropical oceans because the oxygen isotopic and strontium/calcium (Sr/Ca) ratios of their aragonitic skeletons are believed to vary as a function of the temperature of the ambient seawater. However, recent microanalytical studies using secondary ion mass spectrometry (SIMS) have revealed large chemical heterogeneities for Sr/Ca and oxygen isotopic ratios in coral skeleton, which cannot be explained by temperature variation (e.g. Meibom *et al*., 2004, Rollin-Bard, *et al*., 2003)

We report the micro-scale image of oxygen isotopic distribution within the two basic building blocks of the coral skeleton; centres of calcification (COC) and fibers. With Hokudai isotope microscope (Cameca ims 1270 + SCAPS), obtained image for relative $^{18}O/^{16}O$ ratio in the microstructure of coral *Porites* ,which is the most widely used species for paleoclimatic studies, shows small variation in COC and few isotopic difference between COC and fibers at least within ~1 ‰. This result is inconsistent with the large oxygen isotope heterogeneities previously reported (Rollin-Bard, *et al*., 2003, Meibom *et al*., 2006), although their spot analysis could not capture full image of oxygen isotopic composition in COC. These recent works suggested that coral biomineralization processes are governed strongly by biological control (Meibom *et al*., 2006) or rapid environmental changes (Rollin-Bard, *et al*., 2003) occurred in ultra structure level. Therefore, it implied that such heterogeneities must mask significantly geochemical signal for reconstructing past temperature changes. However, our result indicates that in the case of coral *Porites*, such dynamic process seem not to be happened, or even happened in some degree, oxygen isotopic ratio in coral skeletons could be still robust paleoclimatic proxy for tropical SST, which play important rule for understanding earth climate system. Further investigations using these microanalytical technique with ion probe can provide important informations for establishing new biomineralization model and help constrain the degree to which temperature and/or biological processes affect the composition of skeleton in corals, as well as in biogenetic carbonates formed by other marine organisms.

References

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