

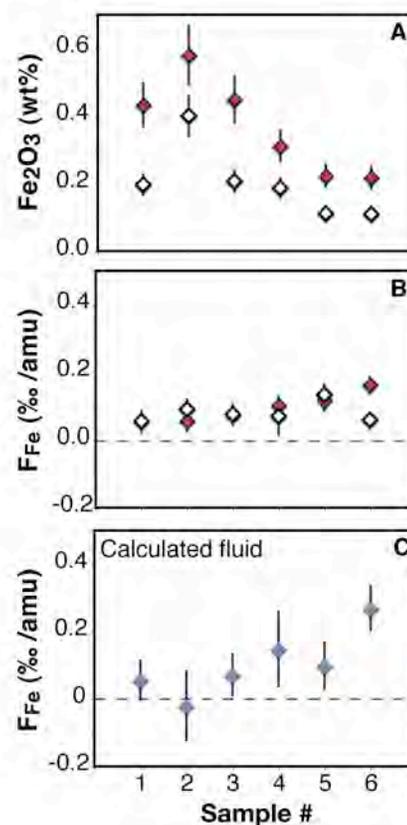
## IRON ISOTOPES IN SPHERICAL HEMATITE AND GOETHITE CONCRETIONS FROM THE NAVAJO SANDSTONE (UTAH, USA): A PROSPECTIVE STUDY FOR “MARTIAN BLUEBERRIES”.

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**Introduction:** Within the last ten years, several experimental studies have characterized the Fe isotopic fractionation associated with biotic and abiotic Fe dissolution, reduction, oxidation and precipitation. Some of these processes may have played a critical role in the formation of hematite spherules on Mars (the so-called “blueberries”) and could potentially be traced using Fe isotopes. Martian samples are not available and current studies aimed at demonstrating the usefulness of geochemical techniques to reconstruct Mars past surface history have to rely on terrestrial analogues. Spherical hematite and goethite concretions from the Jurassic Navajo Sandstone (southeastern Utah, USA) may represent a good analogue for “Martian blueberries” [1, 2]. In the present contribution, we report measurements of Fe concentrations and isotopic compositions in iron concretions and associated red (Fe-oxide coated) and white (bleached) host-rocks from Utah. The main goal of this study is to evaluate the potential of Fe isotopes for tracing Fe transport and the physico-chemical processes governing the formation of Fe concretions (redox/ligand changes, Fe adsorption and precipitation). Measurements were performed by MC-ICPMS (Micromass Isoprobe) at the Isotope Geochemistry Laboratory of the Field Museum. Iron isotopic composition ( $F_{Fe}$ ) is expressed as per mil per atomic mass unit (‰/amu) deviation relative to the IRMM-014 standard.

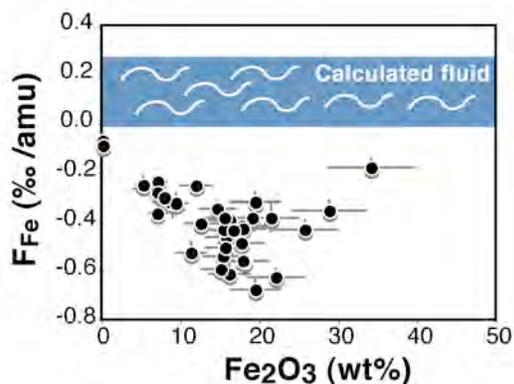
**Isotopic fractionation during Fe mobilization:** Previous studies suggested that the source of Fe found in hematite/goethite concretions from Utah derives from the bleaching of the Navajo Sandstone by reducing fluids [1, 2]. Comparison of adjacent red and bleached rocks provides a way of estimating (i) the isotopic fractionation during Fe-oxide dissolution and (ii) the isotopic composition of Fe removed by reducing fluids. Iron concentrations reveal that the bleached rocks are systematically depleted in Fe, by 31 to 55%, relative to the red rocks (Figure 1a). However, the Fe isotopic compositions of the bleached rocks are indistinguishable from the red counterparts (total range from 0.097 to 0.313‰/amu; Figure 1b). The large depletion in Fe content but near-constancy of Fe isotopic composition indicates that the dissolution of primary Fe-oxide coatings on quartz grains was not associated with any isotopic

fractionation. This result does not support the involvement of life because reductive dissolution of Fe(III) oxides/hydroxides by microbial activity is usually associated with negative Fe isotope fractionation [3-5]. In contrast, the lack of isotopic fractionation is consistent with abiotic dissolution, and compares well with previous experimental studies [6, 7]. Using a mass balance approach, the isotopic composition of Fe removed by reducing fluids was calculated for each pair of adjacent red and bleached sandstones and gave  $F_{Fe}$  values ranging from -0.020 to 0.269 ‰/amu (average  $0.104 \pm 0.196$  ‰/amu; Figure 1c).



**Fig. 1.** (a)  $Fe_2O_{3tot}$  concentrations and (b) Fe isotopic compositions of six pairs of adjacent red (red diamonds) and bleached (white diamonds) sandstones. (c) Isotopic composition of the primary dissolved Fe, calculated for each pair of adjacent red and bleached rocks.

**Iron isotopes as tracers of Fe transport, oxidation and precipitation:** After the mobilization and removal of Fe by reducing fluids, changes in e-pH conditions of the fluid induced the precipitation of hematite and goethite within the Navajo Sandstone. Chan et al. [2, 3] suggested that these changes resulted from the mixing of reducing fluids with oxidizing groundwater. The precipitation of hematite from  $\text{Fe(II)}_{\text{aq}}$  can be described as a two-stage process: the oxidation of aqueous  $\text{Fe(II)}_{\text{aq}}$  into  $\text{Fe(III)}_{\text{aq}}$  followed by the precipitation of  $\text{Fe(III)}_{\text{aq}}$  to solid ferric oxi-hydroxide  $\text{Fe(III)}_{\text{s}}$  [8-10]. The oxidation of aqueous  $\text{Fe(II)}_{\text{aq}}$  into  $\text{Fe(III)}_{\text{aq}}$  enriches the product in heavy Fe isotopes (up to +1.4 ‰/amu at 25°C) [11]. In contrast, hematite precipitation from aqueous  $\text{Fe(III)}_{\text{aq}}$  is associated with kinetic isotope fractionation, which enriches the precipitate in the light Fe isotopes [7]. This kinetic fractionation is proportional to the rate of hematite precipitation and close to 0 ‰ when the reaction is slow. In most cases, the net isotopic fractionation during hematite formation from  $\text{Fe(II)}_{\text{aq}}$  produces a precipitate enriched in the heavy isotopes of Fe. In Utah, the isotopic composition of the primary Fe dissolved by reducing fluids ranges from -0.020 to 0.269 ‰/amu (Figure 1c). Hematite concretions precipitated from this fluid should thus show Fe isotopic compositions  $\geq -0.020$  ‰/amu. On the contrary, spherical hematite/goethite concretions have negative  $F_{\text{Fe}}$  values, ranging from -0.071 to -0.677 ‰/amu (average =  $-0.398 \pm 0.141$  ‰/amu,  $1\sigma$ ; Figure 2). Various processes related to transport and precipitation of Fe can be advocated to explain the negative  $F_{\text{Fe}}$  values observed here. We estimated the feasibility and magnitude of the different scenarios.



**Fig. 2.** Iron isotopic composition versus  $\text{Fe}_2\text{O}_{3\text{tot}}$  concentration of spherical hematite/goethite concretions from Utah. The light-blue area represents the range of isotopic compositions of primary Fe dissolved by reducing fluids (see also Figure 1).

Although diffusion is an important process in controlling the growth of spherical concretions, the

associated Fe isotope fractionation (-0.02 ‰/amu) is negligible compared to the observed variations. Kinetic isotope fractionation during precipitation can be ruled out as well because no isotopic zoning is seen within indurated concretions and Fe isotope evidence supports the occurrence of dissolution-reprecipitation reactions consistent with equilibrium growth conditions. The Fe isotopic compositions of the concretions are best explained by evolution of the fluid composition through successive precipitation or adsorption of isotopically heavy Fe during fluid flow in the sandstone.

**Conclusions and perspectives:** Iron isotopes in Utah concretions and associated red and bleached sandstones shed light on the processes that governed the formation of the concretions. The influence of biological activity during Fe dissolution seems unlikely. The negative  $F_{\text{Fe}}$  values measured in the concretions can be explained by evolution of the fluid composition through successive precipitation and/or adsorption of iron. The isotope composition variations recorded in the concretions may be used to trace the direction and scale of paleofluid flows.

The present investigation opens several avenues of research for future work on “Martian blueberries”. If samples are returned from Mars, Fe isotopes have the potential to provide clues on fluid transport, reservoir sizes, redox variations, and biotic versus abiotic processes.

**References:** [1] Chan M. A. et al. (2004) *Nature* 429, 731-734. [2] Chan M. A. et al. (2005) *GSA Today* 15, 4-10 [3] Beard B. L. et al. (1999) *Science* 285, 1889-1892. [4] Icopini G. A. et al. (2004) *Geology* 32, 205-208. [5] Crosby H. A. et al. (2005) *Environm. Sci. Technol.* 39, 6698-6704. [6] Brantley S. L. et al. (2004) *Geochim. Cosmochim. Acta* 68, 3189-3204. [7] Skulan J. L. et al. (2002) *Geochim. Cosmochim. Acta* 66, 2995-3015. [8] Anbar A. D. (2004) *Earth Planet. Sci. Lett.* 217, 223-236. [9] Beard B. L. and Johnson C. M. (2004) *Rev. Mineral. Geochem.* 55, 319-357. [10] Dauphas N. and Rouxel O. (2006) *Mass spec. Rev.* in press. [11] Welch S. A. et al. (2003) *Geochim. Cosmochim. Acta* 67, 4231-4250. [12] Squyres S. W. and Knoll A. H. (2005) *Earth Planet. Sci. Lett.* 240, 1-10. [13] Morris et al. (2005) *Earth Planet. Sci. Lett.* 240, 168-178. [14] Tosca N. J. et al. (2005) *Earth Planet. Sci. Lett.* 240, 122-148. [15] McLennan S. M. et al. (2005) *Earth Planet. Sci. Lett.* 240, 95-121.