

Trace element partitioning and redox states in a ferromanganese nodule from the SW Pacific

M.A. MARCUS^{1*}, S.C. FAKRA¹, B.M. TONER²,
G. HORN³ AND K.J. EDWARDS³

¹Advanced Light Source, Lawrence Berkeley Laboratory,
Berkeley CA USA 94720

(*correspondence: mamarcus@lbl.gov)

²Department of Soil, Water, and Climate, University of
Minnesota – Twin Cities, St. Paul, MN USA 55108
(brandy.toner@gmail.com)

³Department of Biological Sciences University of Southern
California, Los Angeles, CA, USA (ghorn@usc.edu,
kje@usc.edu)

Marine ferromanganese nodules have attracted much interest for economic reasons due to their Ni and Co content. Nodules are composed of chemically-active materials (nanostructured oxides) which effectively sorb trace metals delivered to the seafloor by sorption onto biogenic particles which then settle to the bottom and undergo reactions which grow the nodules. This process results in growth rates measured in mm/Mya, making nodules some of the slowest-growing materials known. Yet, they are made of nanophase material which has resisted coarsening for tens of Mya. We present μ -XRF, μ -XRD, and μ -XAS measurements for a nodule from a deep ocean site underlying biologically unproductive waters. The Fe oxides in this nodule mostly consist of goethite and ferrihydrite in an Fe-rich matrix plus disordered phases in Mn-rich regions. These disordered phases display long Fe-Fe distances indicative of possible phosphate incorporation in the oxides. The near-surface ("Outer") and interior ("Inner") exhibit differing; the Inner region is richer in Mn, Co and oxidized forms of Co, Ti and V than the Outer. In the Outer region, Co, Ce, and V are reduced to their low-valent forms, while in the Inner, these elements are partially oxidized. Correlations of μ -XANES spectra and XRF maps suggest that Ce and V are sorbed to Fe oxides as Ce(III) and V(IV), and Mn oxides, as Ce(IV) and V(V). Principal component analysis of the μ -XRF map suggests that in each region there are three patterns of distribution such that the distribution of each element may be represented as a linear combination of these basis images. These results suggest that common processes control the deposition of major and trace elements.

Micro-scale study of $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ in Precambrian cherts: Implications for oceanic temperatures reconstructions

J. MARIN^{1*}, M. CHAUSSIDON¹ AND F. ROBERT²

¹CRPG-CNRS, Nancy Université, 15 rue Notre Dame des
Pauvres 54501 Vandoeuvre-lès-Nancy, France

(*correspondence : jmarin@crpg.cnrs-nancy.fr,
chocho@crpg.cnrs-nancy.fr)

²Laboratoire de Minéralogie et Cosmochimie du Muséum -
UMR-CNRS 7202 Case 52 - 57 Rue Cuvier 75231 Paris
Cedex 05(robert@mnhn.fr)

Variations of the oxygen and silicon isotopic compositions of archean cherts can be used to reconstruct oceanic paleotemperatures (Knauth and Lowe, 1978 [1], Robert and Chaussidon, 2006 [2]). For O however it is assumed that seawater $\delta^{18}\text{O}$ remained constant around 0‰ (Holmden and Muehlenbachs, 1993 [3]). However, these isotopic records can be reset during burial diagenesis or through isotopic exchange with hydrothermal fluids. At a given age, cherts show a range of isotopic compositions, which makes paleo-temperatures reconstructions more difficult. In order to better understand these variations, we performed a microscale study of $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ in five precambrian cherts of the Gunflint Iron formation (1.9 Ga, Canada) by ion microprobe (Cameca 1270, CRPG-CNRS, Nancy). Around 100 analytical spots were made in each sample to detail the variation of isotopic composition in the different forms of silica (microquartz, megaquartz, fibrous quartz, detrital quartz and quartz vein).

The Gunflint cherts show a typical 4.5 - 6.6 ‰ range for $\delta^{18}\text{O}$ in microquartz and different $\delta^{18}\text{O}$ values for the different forms of silica. Microquartz has preserved at a μm -scale a strong heterogeneity inherited from its diagenetic history. These cherts show $\delta^{30}\text{Si}$ between -2.07‰ to +3.06‰, a larger range than found previously (Robert and Chaussidon, 2006). The $\delta^{30}\text{Si}$ variations, contrary to $\delta^{18}\text{O}$, cannot be explained by a model based on dissolution-precipitation of an opal precursor. The formation of Gunflint cherts must involve fluids with different $\delta^{30}\text{Si}$, i.e. different sources of silicon (seawater, hydrothermal, ...). This approach may bring new evidences on the origin of the Gunflint cherts and may permit to better constrain oceanic paleo-temperatures.

[1] Knauth L.P., Lowe R.D., (1978). *Earth and Planetary Science Letters* **41**, 209-222. [2] Robert F., Chaussidon M., (2006). *Nature* **443** 969-971. [3] Holmden C. Muehlenbachs K., (1993) *Science* **259**, 1733-1736