Benthic foraminiferal Mg/Ca ratios for paleotemperatures

K. FUKUDA[1], R.D. FREW[2] AND R.E. FOLDYCE[3]

[1]Department of Chemistry, University of Otago, New Zealand (kenichif@alkali.otago.ac.nz)
[2]Department of Chemistry,University of Otago, New Zealand (rfrew@alkali.otago.ac.nz)
[3]Department of Geology, University of Otago, New Zealand (ewan.fordyce@stonebow.otago.ac.nz)

Mg/Ca ratios in fossils have great potential in paleothermometry (Rosenthal et al., 1997). Paired studies of Mg/Ca and $\delta^{18}O_{calcite}$ should reveal the elusive $\delta^{18}O_{paleo\text{-}seawater}$ (Elderfield & Ganssen, 2000). We used field samples to determine correlation curves for modern Mg/Ca ratio versus water temperature in the foraminifera *Notorotalia* and *Cibicides*. Resulting modern correlation curves are: *Notorotalia*, Mg/Ca (mmol/mol) = $0.123e^{0.293T}$; and *Cibicides*, Mg/Ca (mmol/mol) = $1.23e^{0.126T}$. We collected and analysed two sets of fossil foraminifera; firstly, 12 samples at 33 cm intervals from the Early Miocene (~18 Ma; sedimentation rate probably >50 m/Ma), and secondly, 3 spot samples from the Late Eocene, Oligocene/Eocene transition and Early Oligocene (~30-35 Ma). Paleotemperature estimates from fossil Mg/Ca agree well for different forams. Early Miocene Mg/Ca paleotemperature estimates are 11.2 ± 0.3 ºC for *Notorotalia* and 11.4 ± 2.0 ºC for *Cibicides*. Late Eocene Mg/Ca paleotemperature estimates are 13.2 ± 0.4 ºC for *Cribrorotalia* [related to *Notorotalia*] and 14.0 ± 1.1 ºC for *Cibicides*. The 12 close-spaced Early Miocene samples produced uniform paleotemperatures for *Notorotalia* while *Cibicides* results are more scattered; however, the mean values for *Notorotalia* and *Cibicides* are concordant. Late Eocene results indicate similar trends. These results imply that the main factor influencing Mg/Ca ratios is environmental temperature. Oxygen isotope results for the Early Miocene samples provide a conventional paleothermometer to compare with Mg/Ca results.

References

Elderfield, H. and Ganssen, G., (2000), *Nature*, **405**, 442-445.
Rosenthal, Y., Boyle, E.A., and Slowey, N., (1997), *Geochim. Cosmochim. Acta* **61**, 3633-3643

Solid-solution reactions in As(V) sorption by schwertmannite

K. FUKUSHI[1], T. SATO[2], T. NAGANO[3], N. YANASE[4] AND H. YAMADA[5]

[1]Ecomaterials Center, NIMS, Tsukuba, Ibaraki 305-0049, Japan (kesukef@yahoo.co.jp)
[2]Institute of Nature & Environmental Technology, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan (tomsato@earth.s.kanazawa-u.ac.jp)
[3]Department of Environmental Sciences, JAERI, Tokai, Ibaraki 319-1195. Japan (nagano@sparclt.tokai.jaeri.go.jp)
[4]Department of Environmental Sciences, JAERI, Tokai, Ibaraki 319-1195. Japan, (yanase@sparclt.tokai.jaeri.go.jp)
[5]Ecomaterials Center, NIMS, Tsukuba, Ibaraki 305-0049, Japan (YAMADA.Hirohisa@nims.go.jp)

Introduction: Formation of schwertmannite, a poorly crystalline iron oxyhydroxysulfate, has been widely reported at acid mine drainage conditions. Schwertmannite has been recognized as one of the most important sinks for As(V) in acid mine drainage condition. However, its mineralogical properties and the sorption mechanisms have not been understood well. In the present study, As(V) sorption behavior of synthesized schwertmannite was examined under acidic condition. The results were interpreted in term of solid-solution reactions.

Experimental method: Sorption of As(V) by the schwertmannite suspension was examined as a function of initial As(V) concentrations (0 M ~ $10^{-2.5}$ M) at constant ion strength (I = 0.01 M, $NaNO_3$). The pHs of the solutions were adjusted to 3.95 ± 0.04 by addition of HNO_3. After 24 hours of reaction at 25ºC, the pHs of the suspensions were measured and the suspensions were filtered. The solutions were provided for the analyses of Fe, As and SO_4. The speciation analyses were performed using REACT.

Results and discussion: Results showed that schwertmannite released 0.62 mmol of SO_4^{2-} for every 1 mmol of $H_2AsO_4^-$ and 0.24 mmol of OH^- that has been sorbed. As(V) replaced SO_4 up to the half of total SO_4 in schwertmannite. The equivalent exchange relationship indicated that As(V) sorbed schwertmannite would behave as a solid solution between the As(V) free schwertmannite and schwertmannite containing maximum level of As(V). The equilibrium constant for the anion exchange in solid solution reaction was estimated from the reacted solution chemistries. The constant well described the As content in the natural precipitates formed in acid mine drainage, as well as the results of the laboratory experiment. Although schwertmannite is metastable with respect to goethite, the transformation is significantly inhibited by sorbing As(V) (Fukushi et al., 2003). The solid solution reactions also explain the stabilization of schwertmannite by sorbing As(V).

References

Fukushi, K et al. (2003) Appl. Geochem. *18*, 1267-1278.