

Ocean redox during the Toarcian oceanic anoxic event: Constraints from chromium isotope ratios

R.H. JAMES^{1*}, A.M. KARJALAINEN¹, I. J. PARKINSON¹,
A.L. COE¹, C.R. PEARCE^{1,2} AND A.S. COHEN¹

¹Department of Earth and Environmental Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK
(*correspondence: R.H.James@open.ac.uk)

²Present Address: LMTG, Observatoire Midi-Pyrénées, 14 avenue Edouard Belin, 31400 Toulouse, France

A study of molybdenum isotope ratios has recently demonstrated, for the first time, that the widespread and relatively rapid (<1 Ma) deposition of organic carbon rich sediments in the early Toarcian (ca. 183 Ma) is linked to a change in ocean redox [1]. However, as with all proxies, interpretation of the Mo isotope record in terms of a single variable (i.e. marine anoxia) is not straightforward. Complications include (i) fractionation of Mo isotopes in sub-oxic settings and (ii) variations in the Mo isotope composition of the river input to the oceans.

For this reason, we are exploring the utility of other potential palaeoredox indicators. Here, we will present Cr isotope data for the same Toarcian mudrocks analysed by Pearce *et al.* [1]. In oxic conditions, Cr is present as Cr(VI), but reduction of Cr(VI) to Cr(III) occurs in oxygen-deficient conditions, resulting in isotopic fractionation of up to 7.6‰ [2]. We show that prior to the onset of marine anoxia, the mudrocks have $\delta^{53}\text{Cr}$ values of ~0‰, the same as the average $\delta^{53}\text{Cr}$ composition of the Earth's crust. At the onset of marine anoxia, the $\delta^{53}\text{Cr}$ value of the mudrocks decreases as Cr(VI) is reduced to Cr(III) and is removed from solution. Over time, as this process continues, the $\delta^{53}\text{Cr}$ value of the mudrocks increases as the fraction of Cr(VI) remaining in solution decreases.

[1] Pearce C.R., Cohen A.S., Coe A.L. & Burton K.W. (2008) *Geology* **36** 213-234. [2] Schauble E.A. (2004) *Rev. Mineral Geochem.* **55** 65-111.

Characterization of multiple secondary minerals in arsenic-rich gold mine tailings

H.E. JAMIESON^{1*}, S.R. WALKER¹, M.B. PARSONS² AND
G.E.M. HALL³

¹Queen's University, Kingston, ON K7L 3N6

(*correspondence: jamieson@geol.queensu.ca)

²Geological Survey of Canada, Dartmouth, NS B2Y 4A2

³Geological Survey of Canada, Ottawa, ON K1A 0E8

Intense oxidation of arsenopyrite-rich gold mine tailings from Nova Scotia has produced multiple secondary As phases. A suite of 29 samples from six abandoned mines has been studied in detail using optical microscopy, electron probe microanalysis, powder X-ray diffraction (XRD), synchrotron-based microXRD and microX-ray Absorption Near Edge Spectroscopy (XANES). Seventeen of these samples also underwent sequential extraction analysis designed specifically for As-bearing minerals. Total As concentrations in the <150 μm fraction vary from 195 to 313,000 ppm (mean = 36,000 ppm).

Petrographically, the tailings range from arsenopyrite-rich, relatively unweathered concentrates to strongly weathered tailings where essentially all As is present as oxidized secondary phases. The secondary phases occur as both replacement textures (discrete grains and rims on relic sulfides) and as precipitates that coat other grains (usually silicates). Secondary As phases include three forms of ferric arsenate: scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), amorphous Fe arsenate, kankite ($\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$), two forms of calcium iron arsenate (yukonite ($\text{Ca}_3\text{Fe}_7(\text{AsO}_4)_6(\text{OH})_9 \cdot 18\text{H}_2\text{O}$) and an amorphous form), one arsenite phase (tooeleite $\text{Fe}_6(\text{AsO}_3)_4(\text{SO}_4)(\text{OH})_4 \cdot 4\text{H}_2\text{O}$) and As bound to iron oxyhydroxides. Sequential extraction results demonstrate that scorodite-rich samples release most As in a 4M HCl step, whereas yukonite (a mineral studied by J. Jambor [1]) appears to release As more easily in the step associated with amorphous Fe oxides.

More than 64 historic gold mining districts in Nova Scotia contain small tailings fields with As concentrations, on average, 340 times background in local soils. Most of these sites are publicly accessible and used for recreational purposes such off-road vehicle racing or walking trails. Our sampling was guided by concern regarding human exposure and focussed on near-surface materials. Results will be used by the Province's Historic Gold Mines Advisory Committee to assess health risk and inform remediation decisions.

[1] Dunn, P.J. (1982) *Mineral. Mag.* **46**, 261-264.