

Response of pre-edge details from Fe K-edge XANES spectra to the large cation in jarosites

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Frequent in acid mine drainage (AMD), "jarosites" are environmentally important because these iron sulphate minerals configure an ultimate sink of lead and other hazardous metals, reducing their spread in soils and rivers.

With general formula $AB_3(OH)_6(SO_4)_2$, where \underline{A} is mainly K^+ , Na^+ , plus minor Ag^+ , Tl^+ , Pb^{2+} , Bi^{3+} , and \underline{B} is Fe^{3+} (jarosite *s.s.*) or Al^{3+} (alunite), jarosites (*s.l.*), this mineral group has trigonal symmetry and display Kagomé-type layers of corner-sharing \underline{B} octahedra, $[Fe/AlO_2(OH)_4]$. The large cation \underline{A} stays in a pseudo-icosahedral site, coordinated by 6 O-atoms from $[SO_4]$ tetrahedra and 6 OH shared with \underline{A} octahedral cations.

By analogy with what happens with the white line in sulphur K-edge XANES spectra of sulphates [1], it is then expectable that the pre-edge details of Fe K-edge XANES spectra will respond to the different nature of the large cation in Pb-jarosite compared to K- and Na-jarosite. An X-ray absorption experiment was carried out on beam line ID-21 of the ESRF (Grenoble/France). XANES spectra were collected from well crystallized minerals (K-, Na- and Pb-jarosites plus other model iron sulphates) in fluorescence yield mode using an energy-dispersive Ge-detector and a Si(220) monochromator to assure a 0,3 eV energy resolution at the iron K-edge. The pre-edge region was deconvoluted into Pseudo-Voigt components using the Fityk program [2].

Two components were obtained positioned at 7113.4 and 7114.7 eV as expected for Fe^{3+} in octahedral coordination and high spin state [3]. However, the relative intensity of these components appears reversed for K- and Na-jarosite and quite identical for Pb-jarosite. An explanation is advanced and discussed, based on the nature of \underline{A} cations: K^+ and Na^+ are closed shell, non-polarisable alkaline ions with different radius (inducing a decrease in *c/a* ratio for natrojarosite); conversely, and similarly to what occurs for beudantite [4], Pb^{2+} ions are expected to stay off-centered within the large coordination polyhedron in order to accommodate the lone-pair of $6s^2$ electrons but in a disordered way without breaking the symmetry.

[1] Figueiredo, M.O., Silva, T.P. (2009), *Europ. J. Miner.* **21** 79-83. [2] <http://www.unipress.waw.pl/fityk>. [3] Westre, T.E. *et al.* (1997) *J. Am. Chem. Soc.* **119** 6297-6314. [4] Szymanski, J.T. (1988) *Canad. Min.* **26** 923-932.

Global shallow marine euxinia triggering the latest Permian mass extinction: Evidence from Mo-isotopes

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The Late Permian Mass extinction (LPME) was one of the most catastrophic biologic crisis's of Earth history. Although increasing lines of evidences point to global euxinic conditions in the ancient seas as the most likely kill mechanism [1,2], the true extent of oceanic oxygenation during the LPME is still contentious.

Mo-isotope geochemistry is a new and promising tool to investigate oceanic oxygenation. Variations in the Mo-isotope composition of the ocean result from variations in the extent of incorporation of light Mo isotopes (⁹⁵Mo) into oxic sediments [3]. Because the Mo-isotope composition of euxinic sediments deposited under $[H_2S_{aq}] > 10\mu M$ and non skeletal carbonates reflect the Mo-isotope composition of coeval seawater ([4] Voegelin *et al.*, submitted) the Mo-isotope composition of ancient euxinic shales and oolites can be used to investigate the extent of oceanic oxygenation. $\delta^{98/95}Mo_{(std)}$ values around 1‰ are displayed by both, late Permian-early Triassic shallow marine oolites (NE Italy) and euxinic black shales (British Columbia, Canada). This consistency supports the interpretation of this values as reflecting homogeneous coeval ocean water. This suggests a generally larger proportion of euxinic Mo deposition, during the late Permian, compared to today. A negative shift to $\delta^{98/95}Mo_{(std)}$ values near 0‰ -indistinguishable from continental input- is displayed by black shales and oolites spanning the LPME. Such low values for the ocean water can only be reconciled by a quasi complete removal of Mo from the oceans, which in turn needs quasi total global marine euxinia. Together with an observed major perturbation of the S cycle (Newton *et al.*, 2004), the Mo data thus strongly suggest delivery of lethal levels of H_2S to the shallow ocean as the killing mechanism. Some of the Western Australia black shales exactly from the extinction level display significant lighter Mo isotopic compositions than their Italian (oolites) and Canadian (euxinic black shales) correlatives. The data outside the extinction level are identical -and low- in all sections. Global euxinia persisted until the early Triassic, though a slight increase in oxic Mo scavenging and oxygenation is evidenced by a transient Mo-isotope signal across the P-Tr boundary for several sections.

[1] Newton *et al.* (2004), *Earth Plan. Sci. Lett.* **218** 331-345;

[2] Grice *et al.* (2005), *Science* **307** 709-709; [3] Siebert *et al.* (2003), *Earth Plan. Sci. Lett.* **211** 159-161; [4] Neubert *et al.* (2008), *Geology* **36** 775-778.