Secular trends in the global ocean revealed through trace elements in sedimentary pyrite

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Sedimentary pyrite incorporates trace elements (TE) during growth at levels far beyond the host bulk rock, making it a potentially powerful proxy for seawater chemistry in the marine rock record. We have developed a novel approach to simultaneously quantify a suite of TE via LA-ICPMS in sedimentary pyrite from marine black shales, as a proxy for chemical changes in palaeo-oceans. When our sedimentary pyrite data is compared with published whole-rock data, we see similar trends. We show that the temporal TE curves for 22 elements in sedimentary pyrite can be related to secular changes on Earth over 3.5 billion years.

The Mo trend increases through time attributed to the significantly lower levels of oxygen in the atmosphere and oceans in the early Earth system [1]. The effects of the Great Oxidation Events are shown by the jumps in Mo at ~2500 Ma and 650 Ma, similar to what is seen in the bulk shale data. The broad Ni and Co trends are the opposite to Mo, attributed to cooling upper mantle temperatures and decreased eruption of komatiitic lavas from ~2700 Ma [2]. Pulses of elevated Ni and Co correspond to episodes of Large Igneous Province eruptions, particularly obvious with the Siberian Traps at the Permian-Triassic boundary. Phanerozoic trends in all TE are far more cyclical. We identify Se as being particularly redox sensitive, which allows us to explore finer-scale fluctuations through the Phanerozoic [3]. As our database expands in both scope and temporal detail, this new approach in measuring TE in sedimentary pyrite has exciting potential for chemical palaeo-ocean research.

[1] Scott *et al* (2008) *Nature* **452**, 456-459. [2] Konhauser *et al* (2009) *Nature* **458**, 750-753. [3] Large *et al* (2013) *Min. Mag.*, this volume.

The oxidation state of uranium in basaltic magmas

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Recently erupted mid-ocean ridge basalt (MORB) often exhibits disequilibria between the series of isotopes associated with the radioactive decay of U to Pb. This suggests rates of melt trasport that are fast relative to the half-lives of the isotopes that are of anomalous abundance. Current U-series models are based on the assumption that U^{4+} is the only oxidation state of U important during the generation, transport, and differentiation of MORB magmas. However, if U^{5+} and/or U^{6+} were stable in the melt, then the chemical behaviour of U relative to Th^{4+} (and the other elements of the decay series) would vary significantly.

High resolution U M_4-edge X-ray absorption near edge structure (XANES) spectra were recorded for synthetic MORB and anorthite-diopside eutectic compositions glasses containing 0.5 wt % U_3O_8. Glasses were quenched from melts equilibrated at 1400 °C and a range of oxygen fugacities (fO_2) at one-atmosphere. The spectra were recorded in fluorescence mode at beamline ID26 of the European Synchrotron Radiation Facility, which allows U M_4-edge spectra to be acquired with an energy resolution that is not accessible at most synchrotron facilities. In addition, U L_3-edge XANES spectra were recorded for the same melt compositions *in situ* at magmatic temperatures at beamlines I18 and B18 of the Diamond Light Source.

The L_3- and M_4-edge spectra both vary systematically with fO_2. The M_4 spectra exhibit more complexity than the L_3 spectra and allow U^{5+} to be unambiguously identified as a major component in both glass compositions, and U redox ratios to be quantified. The proportions of U^{4+}, U^{5+}, and U^{6+} vary systematically in the glasses. U^{5+} is a significant oxidation state at the fO_2 conditions of MORB generation, with $U^{5+}/\sum U$ (where $\sum U = U^{4+} + U^{5+} + U^{6+}$) varying from ~0.25 at the QFM (quartz-fayalite-magnetite) fO_2 buffer to ~0.1 at IW (iron-wüstite) +2.

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