Mo isotope signature of OAE 1a: New insights from the Western Tethys

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Oceanic anoxic events (OAEs) record profound and rapid changes in the chemistry of the world ocean. Quantifying the oxygenation state of the oceans through OAEs is of fundamental importance to understanding the global perturbation of the carbon cycle observed during these events. The aim here is to trace global redox change in the wolrd ocean through the early Aptian anoxic event (OAE 1a, Selli event), one of the most significant and widespread black shale events of the Cretaceous.

We selected the Gorgo a Cerbara section (Italy), where evidence of euxinic conditions has recently been provided by biomarkers [1-2], and investigated the redox-sentive trace element (RSTE) distribution and the molybdenum (Mo) isotopes variations through the section.

All RSTE measured present similar behaviour, with a low background level contrasted by maxima in concentrations within the Selli level. A relatively good correlation is observed between total organic carbon (TOC) values and RSTE accumulation, suggesting well-developped anoxia. However, Mo isotopes show surprisingly negative values through the section. An increasing trend in $\delta^{98/95}$Mo is observed before the Selli interval, with values ranging from -0.89 up to 0.06 ‰. Then, $\delta^{98/95}$Mo values remain more or less constant fluctuating around -0.23 ‰, but with a shift towards more negative values within the Selli level. This trend is interrupted by a positive peak to 0.13 ‰, corresponding to samples with the highest Mo content (up to 94 ppm).

The RSTE behaviour indicates variations in the oxygenation state of the western Tethys, reaching anoxic/euxinic conditions during OAE 1a. However, the light $\delta^{98/95}$Mo values suggest that the redox conditions may not have been fully euxinic. Iron speciation measurments will be performed to further investigate the redox conditions during the deposition of the Selli interval, and its relationship to sedimentary Mo isotope evolution.

[1] Pancost, R. *et al.* (2004). *Journal of the Geological Society* 161, 353–364. [2] van Breutel *et al.* (2007). *Paleoceanography* 22, PA1210.

Melting and melt/rock reaction of sulphides in Middle Atlas spinel peridotite xenoliths

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The major and siderophile and chalcophile trace element composition (n=25) in sulphides (58 analyses) and Fe-hydroxides (7 analyses) of seven spinel-facies peridotite xenoliths from the Moroccan Middle Atlas was determined at the University of Erlangen by electron microprobe and in-situ LA-ICP-MS. The sulphide assemblage comprises monosulphide solid solution, pentlandite and minor isocubanite. Sulphides occur as: (i) inclusions (eu- to subhedral) in primary silicates, usually associated with sulphide melt trails; (ii) anhedral grains on silicate grain boundaries, and (iii) within silicate glass in discrete melt pockets formed during the ascent of the xenoliths. Variably pervasive alteration of sulphides to hydroxides is generally associated with cracks in the peridotite matrix. Three PGE patterns were identified – often within the same sample and irrespective of the petrographic occurrence: [a] IPGE > PPGE; [b] no PGE fractionation and [c] PPGE > IPGE. Hydroxides show nearly identical PGE patterns with similar PGE abundances to their host sulphides. Relatively incompatible chalcophile elements correlate with the degree of PGE fractionation. The presence of such PGE fractionation ([a] & [c]) on thin-section scale is consistent with mantle melting experiments [1], which predict residual IPGE-rich sulphides and (trapped) PPGE-rich melt blebs. The close proximity of interstitial and enclosed grains with these patterns suggests contemporaneous sulphide-silicate crystallisation due to melt-rock reaction of olivine and pyroxene, hence trapping sulphide melt as inclusions and leaving potentially earlier residual IPGE-rich sulphides intact. Whole rock major and siderophile trace elements and Os isotopes are also in accordance with coupled sulphide-silicate introduction [2]. Our results allow deciphering the mobility and transport of upper mantle sulphide melts, which is a crucial prerequisite for understanding the generation of crustal noble metal deposits.

[1] Bockrath *et al.* (2004) *Science* **305**, 1951-1953. [2] Wittig *et al.* (2010) *Lithos* **115**, 15-26.