Detecting total dissolved sulfide anomalies in marine sediments using XRF core scanner

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X-Ray flurorescence core scanning (XRF-CS) allows the rapid, non-destructive, and semi-quantitative determination of high-resolution geochemical profiles along split sections of marine sediment cores. Over the last decade, XRF-CS has provided a wealth of information on past changes in the accumulation of biogenic and terrigenous material in sediment records.

Here, we show that XRF-CS can be used to detect Total Dissolved Sulfide anomalies in sediment cores. A series of cores collected at cold seeps from the Niger Delta area (as part of a joint project between TOTAL and IFREMER; ERIG-3D) was analysed on-board by XRF-CS (Aavatech), immediately upon core opening. Prior to analysis, sediment surfaces were covered with a thin utralene film (4µm thick) to prevent contamination, oxidation and drying. Selected sediment samples were also processed for quantitative WD-XRF (both oxidised and total sulfur contents) and pore water analyses: Total Dissolved Sulfide contents (by colorimetry, on board) and dissolved sulfate (ion chromatography).

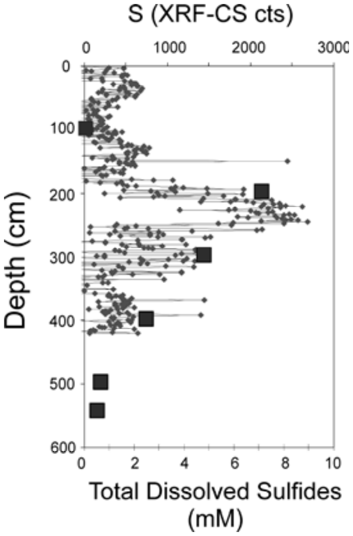

Figure 1: Example of the correlation between XRF-core scanner S and pore water TDS (infilled squares) data versus depth.

Taken together, the XRF-CS, WD-XRF and pore water data indicate that the S signal measured by XRF-CS in our studied cores is mainly driven by the presence of total dissolved sulfides in pore waters. The potential of XRF core scanning for detecting pore water signals in marine sediment cores will be further discussed.

Copper speciation and partitioning between vapor and liquid phases in sulphuric solution: An XAS study

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To understand the role of sulphur in copper transport and vapour-liquid partitioning in hydrothermal fluids, the solubility of copper(I) sulphide (Cu_2S) and the structure of copper species in hydrothermal sulphuric solutions at 25-600°C and 180-600 bar were measured using the synchrotron X-ray absorption spectroscopic (XAS) techniques. This study provides the first *in situ* evidence of solubility of copper sulphides and structure the predominant copper species in sulphuric fluids at high temperature. We find that either linear bisulfide complexes (e.g., $[HS\text{-}Cu\text{-}SH]^-$ or $[H_2O\text{-}Cu\text{-}HS]^0$) predominate in alkaline solutions, which indicates that aqueous Cu-S complexing at high temperature and pressure is simpler than ambient conditions where various types of multi-nuclear species have been identified (Helz *et al.* [1]).

The Cu_2S solubility we observed in this study show remarkable agreement with solubility calculations using available thermodynamic data for copper hydrosulphide complexes (mainly $Cu(HS)_2^-$) from Mountain & Seward [2] and Akinfiev & Zotov [3], suggesting those data are reasonable and can be used for modelling of copper transport in hydrothermal sulphuric fluids.

The phase separation data from this study shows that significant amount of copper can be partitioned to vapour phase, with apparent partitioning coefficients around 0.3-0.8. However, these experimental data are still not sufficient to explain the preferential partition of copper into the vapour phase observed in many natural fluid inclusions from porphyry copper deposits.

[1] Helz *et al.* (1993) *Geochim. Cosmochim. Acta* **57,** 15-25. [2] Mountain & Seward (1999) *Geochim. Cosmochim. Acta* **63,** 11-29. [3] Akinfiev & Zotov (2001) *Geochem. Int.* **39**, 990-1006.