Speciation of platinum in marine ferromanganese oxides using wavelength-dispersive XAFS

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X-ray absorption Fine Structure analysis in fluorescense mode (FL-XAFS) has played a crucial role in speciation of trace elements in various environmental samples. However, this method does not nessecerily work well for precious metals in ore deposits because high concentrations of coexisting elements can cause serious interference. Here, we report high-sensitivity speciation of platinum (Pt) in marine ferromanganese oxides by the application of the wavelength-dispersive XAFS method. This method places a Bent Crystal Laue Analyzer (BCLA) in front of the detector[1], which enables the selective extraction of fluorescence X-rays of Pt.

Marine ferromanganese oxides are aggregates of Fe and Mn (oxyhydr)oxides that accumulate a variety of elements from seawater, including ~1.8 ppm of Pt (Lα: 9.443 keV) and ~1000 ppm of Zn (Kβ: 9.572 keV)[2]. Introduction of BCLA in front of the detector succesfully reduced the spectral background by about 100 times compared with conventional FL-XAFS; this allowed us to find the white line of Pt L_3-XANES of natural ferromanganese oxides for the first time. Although spectal quality was still poor for the determination of its host phase by EXAFS analysis, the white lines in XANES region clearly indicated that Pt is present as a tetravalent species coordinated by O atoms, which is different from the tetrachloro complex of P(II) dissolved in seawater. Two opposite mechanisms for Pt accumulation have previously been proposed: (i) oxidation to insoluble form of Pt(IV) on the solid surface or (ii) reduction to the insoluble metal phase. Direct evidence for the oxidative Pt accumulation, obtained from natural samples, provides significant progress applied to the future exploration of Pt-rich ferromanganse oxides in the marine environment.

[1] Kashiwabara et al. (2010) *Chem. Lett.* **39**, 870-871.
[2] Hein et al. (2016) *Deep-sea Res. I*, **110**, 1-19.