Making sense of large sets of XANES spectra

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Natural materials are often heterogeneous, and must be sampled at many points to be understood. We demonstrate new PCA-based statistical techniques for estimating the number of end-member components required to describe a dataset. Also, we have developed a visualization tool which allows us to examine projections of the multidimensional dataset in such a way as to gain clues to the underlying statistical structure of the data. We show the example of the XANES analysis of Fe-bearing suspended marine particles from two regions, 214 spectra from particles collected in the Northwest Pacific, and 126 from the Southern Ocean. The data from the NW Pacific require more components to describe than those from the Southern Ocean. As shown in Figure 1, a well-chosen projection can let one identify distinct clusters of spectra having distinct features.

Figure1: Stereogram of 3D projection of the first 6 PCA components of the NW Pacific dataset, with groups of spectra colored in. Each dot represents one XANES spectrum, and nearby dots correspond to similar spectra.

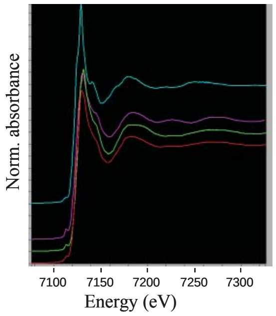

Figure 2: Averaged XANES spectra for the clusters shown above. The colors correspond to those in Figure 1.

Least-squares fits to the spectra shown in Figure 2 indicate clays+poorly-crystalline Fe oxyhdroxide (red), oxidized phyllosilicates (green), biotite+chlorite+clay (cyan) and magnetite+Fe^{2+} silicate+ Fe oxyhdroxide (purple).

Conclusion

Statistical tools can allow one to see patterns in data which would otherwise be invisible when examining spectra individually. We demonstrate how a complex XANES dataset can be simplified so that important characteristics such as dominant minerals and their distribution may be identified.

In situ Fe and multiple S isotope analyses of an Archean pyrite nodule

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Studies of Fe and multiple S isotope composition of sedimentary pyrites have placed important constraints on the chemistry and the redox evolution of the ocean and the atmosphere over the geological time [1,2,3]. Additionally, Fe isotopes have been explored as a proxy for microbial metabolism [2]. Pyrite in black shales is predominantly formed either in the water column or during early diagenesis close to the sediment-water interface and so potentially records chemical evolution of the ocean. Previous studies mostly used bulk samples, although individual pyrite nodules often show complex internal textures such as concentric lamination. Large isotopic variability within individual nodules has been shown for S isotopes [4] but not yet for iron isotopes.

We have performed coupled situ Fe and multiple S isotope analyses of a pyrite nodule hosted by c. 2.7 Ga black shale from Zimbabwe. This mm-size nodule is composed of pure pyrite. Fe isotopes were measured with ims 1270 ion probes at both UCLA and CRPG [5]. We also performed multiple S isotope measurements with the ion probe ims 1280 HR2 at CRPG. The measurements performed at CRPG and UCLA are in agreement with a reproducibility better than 0.2 ‰ (2σ) in δ^{56}Fe. Reproducibility for δ^{34}S is ~ 0.2 ‰ (2 σ) and ~ 0.1 ‰ (2 σ) for Δ^{33}S.

The mean δ^{34}S and δ^{56}Fe values of this nodule are +2.9 ± 0.5 ‰ and -1.08 ± 0.7 ‰, close to the bulk values of +3.2 ‰ and -1.46 ‰, respectively. Two profiles have been performed in one nodule and show large variations in both δ^{56}Fe (~ 2.5 ‰) and δ^{34}S (~5 ‰). The δ^{56}Fe profile shows ^{56}Fe enrichment in the rim relative to the core. The δ^{34}S profile shows large isotopic variation that have no systematic relationship with the location. Δ^{33}S values are negative in the core and positive in the rim. The pyrite nodule was likely formed in a closed system during diagenesis, under reducing conditions but also record some iron oxidation in the water column. S isotopes reflect mixing and different reactivity of two sulfides pools (sulfate and elemental sulfur photochemically produced in the atmosphere) in sediments. Coupled S and Fe isotope composition at µm-scale provides new insights into Archaean ocean chemistry.

[1] Rouxel et al. (2005) *Science*, **307**, 1088-1091, [2] Johnson et al. (2008) *Annu. Rev. Earth Planet. Sci.* **36,** 457-493, [3] Farquhar et al. (2000), *Science*, **298**, 756-758, [4] Kamber and Whitehouse (2007), *Geobiology*, **5,** 5-17, [5] Marin-Carbonne et al. (2011) *Chemical Geology*, **285**, 50-61