The preservation of molybdenum isotope signatures in black shales

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The molybdenum isotope system has emerged as a promising new tool in the investigation of marine redox conditions in paleoenvironments (Barling et al., 2001). Mo isotopes are fractionated during adsorption to Mn-oxides, which accounts for the observation that Mo in marine ferromanganese oxides is about 2‰ lighter in $\delta^{97/95}$Mo than seawater (Barling et al., 2003). In contrast, there is little isotopic fractionation between modern seawater and the underlying organic-rich sediments in euxinic basins such as the Black Sea, presumably because of quantitative sequestration of molybdenum in such environments. It is likely that changes in the relative size of the oxic and anoxic sinks in the global marine mass balance for molybdenum can shift the $\delta^{97/95}$Mo value of seawater and that black shales may reflect the molybdenum isotopic composition of past global oceans and, thus, the extent of marine anoxia (Arnold et al., 2002).

In many instances, ancient black shales are altered by low-grade metamorphism and oxidative weathering. The affects on Mo isotopes are unknown., It is necessary to test if the molybdenum system is robust enough to preserve original isotopic signatures through such diagenesis and low grade alteration.

We are analyzing REE, Mo and Re in two sequences to examine the effects of weathering and low grade metamorphism. The sequences include three time-correlative cores in the Late Ordovician Utica Shale which vary in the level of hydrocarbon maturity, from pre-productive (20-50 deg C) through productive (~50 to 140 deg C) to post-productive (>200 deg C). We are also examining samples from a weathering profile in the Late Devonian Ohio Shale. The latter sequence has shown significant loss of organic carbon, Re, PGEs and radiogenic Os as weathering proceeds (Jaffe et al., 2002). Results will be presented at the conference.

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Hydrothermal Transfer of the Archean Oceanic Δ^{33}S Record to VMS Deposits

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Both photochemical experiments and measurements of sulfate minerals suggest the water-soluble component of the Archean sulfur cycle was mass-independent and uniformly negative throughout most of the Archean (Farquhar et al., 2000, 2001). The paucity of primary sulfate minerals in Archean rocks, however, makes this suggestion difficult to verify. Volcanogenic massive sulfide (VMS) deposits are common in nearly all Archean crustal successions, formed on the Archean seafloor, and may provide a unique way to constrain the multiple sulfur isotopic composition of the Archean oceanic sulfate reservoir. Ore sulfides from VMS deposits of the Superior Province of central Canada were recently reported to have δ^{34}S values between -5 to 5 ‰ with Δ^{33}S measurements of the same grains all ≤ 0 ‰ (Wing et al., 2002). These measurements provide qualitative support for both a mass-independent and negative character of Archean oceanic Δ^{33}S record but the direct assignment of mass-independently fractionated sulfur in VMS ore sulfides to the oceanic sulfate reservoir is not possible.

The sulfur isotope systematics of submarine ore deposits largely reflect a combination of hydrothermal reduction of seawater sulfate and the leaching of S from volcanic sulfides in the footwall rocks of the deposit (Ohmoto, 1972). We present calculations made with simple transport theory that describe the transfer of the mass-independent signature of Archean seawater sulfate to ore sulfides in a VMS deposit. The calculations are based on the physical and geochemical characteristics of the hydrothermal systems that drove VMS formation (e.g., thermal gradient, time-integrated fluid flux, mineral-fluid phase equilibria) and they provide a framework to constrain sulfate content of the local submarine environment from Δ^{33}S measurements. We demonstrate this framework with multiple-sulfur isotope measurements of ore sulfides from various Superior Province VMS deposits and combine the measurements with traditional stable isotopic data and physical scaling arguments to explore implications of the VMS Δ^{33}S record for the sulfate levels in the Archean ocean.

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