From many thousand tons to the laboratory balance pan

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ABSTRACT

We could define an unshakable optimist as someone who sincerely believes that the analysis of a few milligrams by micro-XRF, ICP-MS, or other sophisticated techniques may be representative of a several-thousand-ton ore block in a mountain or of a full shipment of any commodity traveling around the world. The many steps involved between the many orders of magnitude in weight changes are often dismissed as the steps that will totally ruin the analyst efforts. The assumption that the final analytical subsample is representative of the bulk from which it originated is an audacious one and extreme precautions involving theory and practice must be taken. Unfortunately, many important steps are too often casually addressed at best and the ultimate fault is too often attributed to the incompetence of the analyst, disregarding causes arising out of improper sampling and subsampling. Furthermore, at the laboratory, the most probable assay result is not independent of the weight of the selected subsample analyzed. Case histories are summarized. Solutions borrowed from the well-established Theory of Sampling are suggested. Appropriate sampling and subsampling diagrams providing good visual indicators are recommended. Precautions for the development of Standard Reference Materials are also listed.

The Upper Pennsylvanian Hushpuckney Black Shale Member from the Swope Formation in Kansas: Rhenium – Osmium Isotope Systematics, and the Highly Siderophile Elements.

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The Pennsylvanian Hushpuckney "core" black shale of the Midcontinent USA has been well studied geochemically and stratigraphically, but lacks Re, Os, and other HSE (Ir, Ru, Pt, and Pd) data. We studied eleven samples from interpreted anoxic and euxinic intervals of four cores and found highly uniform chondrite-normalized HSE patterns. The concentrations are as follows: Os (0.27-9.8), Ir (0.02-0.07), Ru (0.04-0.31), Pt (3.0-11.3), Pd (0.32-13.3), and Re (34.6–1,827), in parts per billion. The Re-Os data show significant scatter on a $^{187}Re/^{188}Os$ versus $^{187}Os/^{188}Os$ isochron plot but give the expected early Kasimovian (Missourian) age of 306 Ma. The HSEs and Mo were used to consider geological processes that might have influenced the Re-Os systematics, and caused the extraordinary spread in $^{187}Re/^{188}Os$ (713-9122). Chondrite-normalized HSE patterns are similar to that of seawater, but with slightly higher relative Re and slightly lower relative Os, consistent with the interpretation that the Midcontinent Seaway had a fairly unrestricted opening to the global ocean. Rhenium and Mo show a positive correlation that suggests sulfidic conditions were, in part, responsible for Re enrichment.

It has been suggested that high Re concentrations from late Permian black shales reflect the unusual conditions during that interval, including warming deep water temperatures and increasing ocean acidity, which were linked to the deterioration of environmental conditions at the end of the Permian[1]. The Re concentrations and $^{187}Re/^{188}Os$ from the Hushpuckney black shale are higher than any reported from the late Permian, suggesting environmental deterioration is not the only reason for late Permian Re enrichment (Fig.1). More data from across the interval that represents the time of unification of Pangea (Early Carboniferous to Late Permian) may offer further insight into processes that control availability of HSE in black shales.

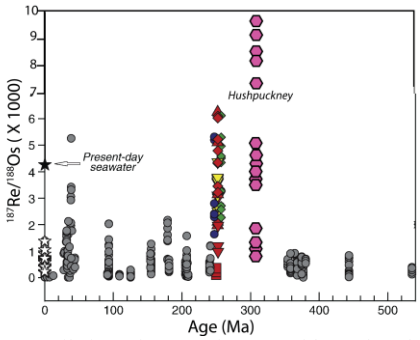

Figure 1: Compilation of Re-Os data [1] with Hushpuckney data shown for comparison.

[1] S. Georgiev *et al.* (2011) *EPSL* **310**, 389-400.