

Sample digestion methods for trace element measurement: Paleoredox proxies under scrutiny

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Trace elements in marine shales (e.g. U, Mo, Re, V, Ni) are employed to probe paleoenvironmental conditions. They have either a lithogenous or a seawater source. The lithogenous contribution is often modeled from bulk-sediment analyses. Using bulk trace element ratios as paleoredox proxies, however, presents limitations [1]. In this study, we compare three different methods of digestion using Middle Triassic black shales (1.4 <TOC <8.1 %) from Svalbard (Botneheia Fm) and the Svalis Dome on the Barents shelf (Steinkobbe Fm) [2]. Multi-acid digestions yield the whole-rock shale composition. *Aqua regia* and inverse *aqua regia* digestions release trace metals from organic matter, sulfides and carbonates, but do not digest the detrital silicate component. Thus, *aqua regia* digestions provide an approximation of the hydrogenous (seawater) component.

Svalis Dome shales have whole-rock major-element compositions (Al, Fe, Mg, Ca, Na, K, P) akin to the World Shale Average whereas Svalbard shales have slightly lower Al, much lower Fe, and higher Ca. Trace-metal concentrations and their ratios derived from *aqua regia* and inverse *aqua regia* dissolutions agree within 10%. For Svalbard, bulk-rock analyses have similar abundances for Co, Ni, Mo, Cu, Zn, Mn and Pb, and similar V/Cr and Ni/Co ratios when compared to *aqua regia* analyses. In contrast, for Svalis Dome, Mo and V/Cr by *aqua regia* are only 40-85% of the bulk rock values. When normalized to whole-rock values, Cr, V, U, V/Mo and V/Sc by *aqua regia* are very different for Svalbard and Svalis Dome shales, respectively.

We conclude that: (1) trace metals released by *aqua regia* or inverse *aqua regia* better represent the hydrogenous (seawater) components, and thus have value as paleoredox proxies, (2) differences between trace element compositions from whole-rock and *aqua regia* dissolutions depend on the major element composition and are different for different elements, and (3) values for trace metal ratios (such as Th/U, V/Sc, V/(V+Ni)) based on whole-rock compositions and commonly used to infer redox conditions are not globally applicable, as these ratios reflect *both* detrital and hydrogenous components.

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[1] Piper & Calvert (2009) *Earth-Science Reviews* **95**, 63–96

[2] Xu *et al.* (2009) *EPSL* **288**: 581-587

Constraining cooling paths using T_C estimates from Lu – Hf and Sm – Nd

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Lu – Hf and Sm – Nd dating of garnets has been undertaken on twenty one samples of pelites, granulites, amphibolites and eclogites from the Scottish Northern Highlands. A wide variety of inclusions in the garnets can affect Sm – Nd and Lu – Hf systematics, but as each is affected by different inclusion mineralogy, the use of both systems provides much stronger age constraints. The difference between ages achieved from the two systems varies dramatically throughout the samples dated. For example several of the samples from the northern part of the terrane show Sm – Nd and Lu – Hf ages that are very close to each other, often within analytical error. This most likely indicates that these samples were subjected to temperatures higher than the closure temperatures for both systems and cooled relatively quickly. Samples from further south have wide differences between Lu – Hf and Sm – Nd, of up to 200 Ma. One sample has Lu – Hf core and rim ages of 947 Ma and 942 Ma respectively but Sm – Nd ages of 951 Ma and 773 Ma respectively. This most likely shows that the garnet was subjected to temperatures higher than the apparent Sm – Nd closure temperature in the rim, but not necessarily in the core. The Lu – Hf ages probably date the prograde metamorphism. Using this information and the commonly used expression of closure temperature, derived by Dodson (1973) [1] is it possible to give estimations of pressure, temperature paths and cooling histories.

[1] Dodson, M. H. (1973) 'Closure temperature in cooling geochronological & petrological systems.' *Contributions to Mineralogy & Petrology* **40**(3), 259–274.