Cadmium isotope stratigraphy of Upper Permian shales

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Organic-rich shales from Greenland and Norway record establishment of oceanic anoxia prior to the Late Permian mass extinction [1]. Here, we discuss paleoredox and paleoproductivity changes during Late Permian shale deposition based on new Cd isotope data, pyrite framboid analyses, and organic and inorganic shale geochemistry.

The Cd content of shales, determined after inverse *aqua regia* digestion, varies between ~120 and ~5000 ng/g. The main sources of Cd are direct biologic contributions and authigenic Cd enrichments; detrital Cd is quantitatively insignificant. Redox-sensitive metals and Cd correlate positively with organic carbon and negatively with sulfur. These relations point to organic matter with/without micro sulfides, and not pyrite, as the likely host phase for metals.

The mean cadmium isotopic composition (IC) for these Upper Permian shales, relative to NIST SRM 3108, is $\delta^{114/110}$Cd = +0.16 ± 0.06 ‰ (1 SD, n=12). This is isotopically lighter than present-day seawater Cd by ~0.14 ‰ [2], and similar to the IC of today's main sources of Cd to the oceans [3, 4], and of modern Cd-lean suboxic sediments [5]. Variations in the IC between individual samples seem unrelated to the major changes in the Cd content, and are not statistically resolvable within analytical precision.

Assuming that biologic Cd fractionation in the Late Permian was similar to today (light isotopes favored), our data imply that authigenic Cd enrichments resulted from preferential uptake of isotopically lighter Cd compared to anoxic bottom waters or accumulated plankton biomass (both with $\delta^{114/110}$Cd ~ +0.30 ‰, [2]). The relatively invariable IC of shales with large differences in their Cd (and TOC) contents, suggests that paleoproductivity did not decline with the expansion of Late Permian bottom water euxinia.

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[1] Georgiev *et al* (2011), *EPSL*, **310**, 389-400 **[2]** Ripperger *et al* (2007), *EPSL*, **261**, 670-684 **[3]** Schmitt et al (2009) *EPSL*, **277**, 262-272 **[4]**; Lambelet *et al* (2013), *EPSL*, **361**, 64-73 **[5]** Horner *et al* (2013), *Min. Mag.* **77** (5), 1323