Os isotopes and Mo in Paleoproterozoic black shales at Talvivaara, Finland: implication for atmospheric evolution

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Black shales are variably enriched in redox-sensitive elements, such as U, V, Mo and Re, making them useful indicators of marine redox conditions and thereby of atmospheric evolution. We have studied the geochemistry of black shales from the Kuikkalampi Formation (Fm) and the underlying Ni-Zn-Cu black shale ore of the Talvivaara Fm[1]. Detrital zircon data suggest deposition close to ca. 1.92 Ga for the Kuikkalampi Fm and ca. 2.0 Ga for the Talvivaara Fm.

The Mo contents in the Kuikkalampi Fm reach values up to 326 ppm and average 167 ppm, being comparable to the level in some many Phanerozoic black shales. Mo correlates well with U, V and C_{org}. 16 whole-rock samples from the Kuikkalampi Fm give a Re-Os isochron age of 1985±29 Ma with a subchondritic initial $^{187}Os/^{188}Os$ ratio of 0.049±0.078. The older isochron age compared to zircon data is likely due to stratigraphic variation in initial $^{187}Os/^{188}Os$. The initial γOs (1.92 Ga) is variably radiogenic, ranging from +6 to +163, with three spatially closely related sample groups giving similar γOs within a group (56±13, n=6; 152±12, n=4; 131±13, n=4). Two samples of the Talvivaara Fm give an isochron age of 1966±25 Ma, with an age-corrected (1.97 Ga) γOs close to chondritic (+7 and +8).

The transition from the 1.97 Ga Talvivaara Fm to the 1.92 Ga Kuikkalampi Fm records a sharp chondritic-to-radiogenic change in the Os isotope composition together with a significant increase in the Mo, Re, V and U contents. This change indicates that the level of atmospheric oxygen at 1.92 Ga was sufficiently elevated to allow weathering of sulfides, including molybdenite, resulting in a higher influx of radiogenic Os from continental crust to the ocean. We suggest that the increase in atmospheric oxygen was related to burial of large amounts of organic carbon and pyrite during the global ca. 2.0 Ga Shunga Event.

[1] Kontinen, A. & Hanski, E. The Talvivaara black shale-hosted Ni-Zn-Cu-Co deposit, eastern Finland. In: Maier, W., O'Brien, H., Lahtinen, R. (Eds.) Ore Deposits of Finland. Elsevier, 557-612 (2015).