

Occurrence of native selenium in Yutangba of China

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Yutangba, located in northern part of Shuanghe Town of Enshi City in the SW of Hubei Province, China, is the unique location in the world where local villagers widely suffered from selenosis in 1963^[1]. In Yutangba, Se-rich rocks ("stone coal" named by local residents) are mainly carbonaceous siliceous rock and siliceous carbonaceous shale of the Lower Permian Maokou Formation. The rock samples have a maximum Se content of 84123mg/kg^[1], but little is known about the modes of occurrence of Se in Se-rich rocks.

The result of our studies by using SEM-EDX, electronic microprobe and X-ray diffraction shows that native Se, which varies morphologically due to different mechanisms, was found within the abandoned stone coal spoils and Se-rich carbonaceous siliceous rock. Genetically, native Se is mainly divided into three types, which are derived from natural burning of stone-coal, weathering and tectonic activity. But based on its occurring environments, native Se can be divided into five kinds. The first is produced near the subsurface of abandoned stone coal spoils with well developed crystal morphology and the grain size up to 28mm. The second is closely associated with quartz and carbonaceous matter with good crystal morphology but very small grain size as micro-needles. The third as micro-acicular crystals, found in the highly carbonaceous mudstone. The fourth is formed from weathering of Se-rich rocks, Se-bearing minerals (such as pyrite) and surface redox of the larger Se crystals. The fifth is elemental Se (Se⁰) or selenides with microorganism morphology, only found in the carbonaceous siliceous rock.

Native Se is first found in such a small landscape in China that Se crystals produced are so large in scale, and the occurrence of native Se in Yutangba would be helpful to further study mineralogy, environmental geochemistry of Se in stone coal and its effect on the local environment.

References

Yang G.Q., Wang S.Z., Zhou R.H. and Sun S.Z., (1983), *Am. J. Clin. Nutr.* 37, 872-881.

Spatial and temporal variations of transition metal isotopes in Oceans

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The transition metals Cu, Zn and Fe are present as trace elements in seawater, but are biologically utilised. It is anticipated that the isotope compositions of these elements in seawater will be a function of several factors including their source input, ocean circulation and biological processing. Isotopic variations of these elements may in turn be used to reconstruct details of these processes, particularly in relations to climate changes.

Samples selected for this study are Fe-Mn crusts from world-wide oceans. Hydrogenous Fe-Mn crusts has proved to provide excellent records of isotope compositions of dissolved metals in deep seawater (O'Nions et al., 1997; Zhu et al., 2000a). The investigation on transition metal isotopes was performed on surface samples and as depth-profiles (time series). Fe, Cu and Zn isotopes were measured using a Nu Instruments MC-ICPMS after chemical purification (Zhu et al, 2000b, 2002). Results are expressed in ϵ units which are deviations in parts per 10⁴ from the isotope reference materials.

The Fe, Cu and Zn isotopes of deep seawater deduced from the Fe-Mn crusts show both spatial and temporal variations. For Fe isotopes, an overall variation of ca. 20 $\epsilon^{57}\text{Fe}$ units has been observed from the surface samples. Whereas relatively large intra-ocean variation has been observed (e.g. Atlantic: $-13.9 \leq \epsilon^{57}\text{Fe}_{\text{IRMM14}} \leq 6.6$), the average Fe isotopes composition for each Ocean are remarkably similar. But they are significantly enriched in light isotopes relative to both the continental and oceanic crusts. Comparing with Fe isotopes, variations for Cu and Zn isotopes are much smaller. Like Fe isotopes, no inter-Ocean differences in Cu and Zn isotopes have been observed.

Besides the surfaces samples, a high resolution time-series of Fe, Cu and Zn isotopes has been obtained from a North Atlantic Fe-Mn crust, which demonstrates that the Fe, Cu and Zn isotope compositions in North Atlantic Deep Water have changed substantially over the last 6 Ma. Moreover, it has been observed that the Fe-isotope variations in the crust are closely correlated to those of Pb-isotopes, which indicates that the observed Fe-isotope variations predominantly reflect those of Fe input from terrigenous sources. But the profiles of Cu- and Zn-isotopes contrast greatly to those of Fe- and Pb-isotopes, whereas Cu- and Zn-isotopes themselves show remarkably similarity. This suggests that the recorded Cu and Zn isotope variations result predominantly from processing within Oceans themselves.

References

O'Nions, R.K. et al, (1997), *Earth Planet. Sci. Lett.* 155, 15-28.
 Zhu, X.K. et al, *Science* (2000a), 287, 2000-2002.
 Zhu, X.K. et al., (2000b), *Chem. Geol.* 163, 139-149.
 Zhu, X.K. et al., (2002), *Earth Planet. Sci. Lett.* 200, 47-62.