Organometallic complexes from Ni-Mo-PGE black shales in South China – Combination of bioactivities, hydrothermal venting and phosphate deposition during global Cambrian biological explosion

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The study of organometallic complexes in ancient geological environments can explain mechanism of accumulation of metals and provide clues for the evolution of the earth life. For example, many synthesized complexes of aryl phosphines and aryl phosphites with platinum metals proved to have important mechanistic implications for homogeneous and heterogeneous catalysis.

Anomalous metal concentrations up to ore grade were reported from black shales that occur in different geological environments throughout the geological record. Besides major ore minerals and elevated metal concentrations in base metal sulfides, many authors suggested empirical relationship between various metals and organic matter.

Using HPCL-MS analysis, we found Co-, Cu-, Ni- and Pt-organometallic compounds in chloroform extract of organic matter from Ni-Mo polyelement sulfide ore bed hosted in lower Cambrian black shales whose organic matter was derived mainly from algae and cyanobacteria and whose formation coincided with the famous Cambrian biological explosion and world phosphate deposition. Beside organometallic compounds sulfur, polycyclic aromatic hydrocarbons and free-metal porphyrines were identified.

Our results demonstrate how biological activity was important for primary metal entrapment in hydrothermally enriched marine environment around medium temperature (< 300°C) hydrothermal vent in semi-restricted basin.

This work was financially supported by the EC in the frame of Bioshale European project (6th Framework program - NMP2-CT-2004-505710).

Re-Os study of the Polish Kupferschiefer: Implications for source and timing of metal enrichment

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The age and genesis of world-class copper deposits of the Kupferscheifer-type have been a subject of much debate with proposed synsedimentary to postdepositional models. The ^{187}Re- ^{187}Os isotope system has been successfully applied to generate whole rock isochrons in differently aged organic carbon-rich sediments.

Six samples of typically Cu-mineralized Upper Permian calcareous black shale and limestone of the Kupferschiefer type from the Lubin mining district (Poland) were studied for Re-Os isotopes, platinum group elements (PGE), and selected major and trace elements.

Mineralized black shales ($Cu_{avg.}$ = 4.9 wt.%, $Ag_{avg.}$ = 242 ppm, $Pb_{avg.}$ = 138 ppm and $Zn_{avg.}$ = 87 ppm) display low PGE values (Pt = <2 – 3.2 ppb, Pd = <2 – 2.8 ppb, Ru = <10 ppb, Rh = 0.4 – 5.2 ppb and Ir = <0.1 ppb) and c(Re) = 249.4 – 22174 ppb, c(Os) = 0.4831 – 1.0009 ppb and ^{187}Os/^{188}Os = 10.26 – 426.7. Lower base metal but comparable PGE, Re and Os values are typical for basal limestone. Calculated correlation coefficients indicate preferential Re affinity to Cu-sulfides and Os affinity to organic matter.

In a ^{187}Os/^{188}Os vs ^{187}Re/^{188}Os plot the entire data set defines an isochron corresponding to an age of 240 ± 3.8 Ma, which most likely reflect late diagenetic/epigenetic metal enrichment.

The initial ^{187}Os/^{188}Os ratio of 0.99 ± 0.22 is slightly less radiogenic but within the variation range of present-day seawater and excludes any significant contribution from hydrothermal/mantle or meteoritic PGE sources.

This work was financially supported by the EC in the frame of Bioshale European project (6th Framework program - NMP2-CT-2004-505710).