The alteration of oil during formation of the low-temperature MVT Zn-Pb sulfide ore deposit at Tres Marias, Chihuahua, Mexico

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The ore body in the Tres Marias Mine in Mexico is exceptionally rich in germanium and occurs in a carbonate collapse breccia. It consists of two major ore types reflecting the history of the ore deposit formation: The primary Zn-Pb-sulfide ore deposit and a secondary sulfide poor oxidized ore body with Zn silicates, carbonates and other oxide minerals (Saini-Eidukat et al., 09).

Within the primary sulfide ore body, there is an intimate association of the type I Zn-sulfide crystals with abundant bitumen (fig. 1). Common modes of bitumen occurrence include vein fillings in the host rock or sulfide ore, masses within vugs associated with sulfides, as fluid and solid inclusions in sphalerite, and as small stalagmites or seeps in the mine stopes. At some places the texture of the Zn-sulfide crystals seem to indicate the growth of the ore into an oil-rich fluid.

The sulfur isotopic values of the Zn,Pb-sulfide samples cluster between +4.8 to +8.3 ‰ and confirm the invoked low-temperature Mississippi Valley type origin for the primary ore deposit. For this type of deposits a major source of the sulfide could be provided by thermochemical sulfate reduction concomitant with alteration of hydrocarbons in the vicinity.

To elucidate the timing of the oil emplacement, its role for the ore deposit formation – and perhaps the importance for the unusual enrichment of some elements as germanium, cadmium and arsenic - bitumen from the primary ore body has been analyzed with GC-FID, GC-MS, Py-GC-MS and EA-irmMS. The samples investigated include bitumen extracted from small closed vugs, bitumen from whole ore extraction, aliphatic and aromatic fractions as well as separated asphaltene fractions.

The microscopic investigations clearly indicate that the bitumen was in place before the ore formation has commenced. The bitumen content in the whole ore samples ranges from 0.2 to 1.8%. The organic geochemical analyses depict an increasing level of alteration on the compound class and molecular level. Clear indications of alteration of oil include the increase of the percentage of the asphaltenes, an increase in the aromatic/aliphatic ratio, the progressive removal of n-alkanes and isoprenoids (fig. 2), ring-opening of some terpenoids, progressive incorporation of S into the bitumen as indicated by pyrolysis products, and depletion of hydrogen in the bitumen. It is interesting to note that most of the observed bitumen alteration patterns could be caused by both abiotic as well as biotic alteration of the oil – which is further discussed in the contribution with its implications for the ore formation/oxidation.

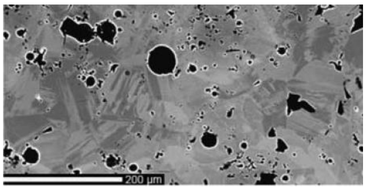

Fig. 1: Backscattered micrographs of minerals (Zn-sulfides: dark/light grey) of the primary ore body with bitumen (black) in vugs..

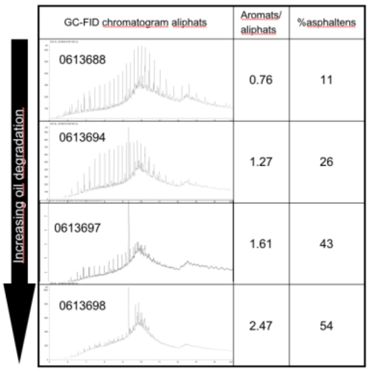

Fig. 2: Examples of observed changes during alteration of bitumen.

References

[1] Saini-Eidukat, B.; Melcher, F.; Lodziak, J. Miner. Deposita 44: 363-70.

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