

Isotopic, organic and inorganic geochemistry of the Idrija mercury deposit, Slovenia: constraints on the formation of the Hg-PAH association

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Hydrothermal petroleum forms by geologically rapid maturation of sedimentary organic matter by hydrothermal fluids (60 to > 400°C) in submarine and continental systems. This process is similar to hydrous pyrolysis and produces among other hydrothermal petroleum rich in polycyclic aromatic hydrocarbons (PAH). This study aims to a better understanding of the formation mechanisms of highly aromatic hydrothermal petroleum and the nature of its association with mercury (Hg) at the Idrija world-class mercury deposit, western Slovenia (145,000 t Hg). In order to put constraints on the source and composition of the mineralizing fluids, the hydrothermal alteration of the host rocks and the associated organic matter, and the source and formation mechanisms of the Hg-associated PAH, an extensive inorganic and organic geochemical investigation included major and trace element litho-geochemistry and a combined molecular - stable isotopic (d13C, d15N, d18O, d34S) approach.

The deposit is hosted by Permocarboniferous to Middle Triassic sedimentary rocks of the Idrija graben, which were flushed with mercuriferous hydrothermal fluids (~ 250°C) during the Anisian-Ladinian intra-continental rifting and bimodal volcanism. The organic matter occurs as: (1) kerogen and bitumen in the host rocks and ore, (2) open space-filling black pyrobitumen, and (3) the solid PAH mixture idrialite intergrown with the ore.

The distribution of the 13Ccarb and 18Ocarb values and the elemental variations are indicative of a fracture-controlled hydrothermal system, with locally high fluid-rock ratios. Quantitative modeling of the 13C and 18O covariation for host carbonates during temperature dependent fluid-rock interaction, and concomitant precipitation of void-filling dolomite points to a slightly acidic hydrothermal fluid, which evolved during isotopic exchange with carbonates under low fluid to rock ratios. The 34S values of hydrothermal sulfides point to multiple sources of reduced sulfur including a deep-seated source and sulfates, thermochemically reduced by the organic matter, with a minor contribution of sedimentary sulfur.

The d13C and d15N values of kerogens and bulk bitumens reflects distinct primary organic sources in the different lithostratigraphic units, combined with a 13C-enrichment due to thermochemical degradation of local and migrated hydrocarbons during interaction with the mineralizing fluids. In bitumens extracted from the ore, the concentration of up to 7 rings PAH, sulfur containing heterocyclic compounds (S-PAH) and their alkylated homologues increases with the degree of mineralization. With the exception of the Paleozoic units, regional rocks contain no or only trace amounts of lower molecular weight PAH species. The compound-specific d13C values of n-alkanes, PAH and S-PAH are consistent with progressive thermal and oxidative degradation with increasing residence time of the organic phase in the hydrothermal fluid.

The observed molecular - isotopic patterns record the genetic link between the Hg mineralization and PAH, supporting the following mechanisms: 1) pyrolytic bond

cleavage in kerogen and free hydrocarbons produced free radicals and PAH precursors, 2) pericyclic reactions, annelation of benzene rings, dealkylation, and dehydrogenation led to the formation higher molecular weight aromatic compounds, and 3) these processes were sulfur-catalyzed, which is reflected by the high relative concentrations of S-PAH in the Hg ore. The results of this study show that hydrothermal petroleum was predominantly sourced by the Paleozoic sedimentary rocks and had an active role in the mineralization process in terms of enhancing mobility and concentration of mercury, increasing the availability of reduced sulfur species for the precipitation of ore sulfides, and inhibiting oxidation and remobilization of the Hg ore