

Organic geochemical records of hydrothermal alteration at Idrija mercury deposit, Slovenia

Organski geokemični zapisi hidrotermalnih sprememb v rudišču živega srebra Idrija, Slovenija

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Abstract

A combined molecular and stable isotopes (C, N) investigation of the organic matter associated to the Idrija mercury deposit is being used to track the pathway of the mineralizing hydrothermal fluids and their interaction with the organic matter. The studied samples include regional barren rocks, and host rocks and ore from the mine. The Rock-Eval parameters indicate that the organic matter disseminated in regional and mine rocks is mature to post mature. The bitumens from mineralized samples are depleted in aliphatic hydrocarbons and enriched in polycyclic aromatic hydrocarbons (PAH), aromatic sulfur compounds (S-PAH) and hydrogenated PAH. The isotopic compositions of kerogens, bitumens, and individual hydrocarbons point to thermal and oxidative degradation of indigenous and migrated bitumens during mineralization and later evolution of the Idrija deposit.

Kratka vsebina

Kombinirana molekularna in stabilno izotopska (C, N) raziskava organske snovi Idrijskega živosrebrovega rudišča je bila uporabljena za sledenje poti hidrotermalnih raztopin in njihovega vpliva na organsko snov. Preiskani vzorci zajemajo regionalne kamnine ter prikamnino in rudo iz Idrijskega rudnika. Parametri Rock-Eval kažejo na zrelost do prezrelost organske snovi, ki je razpršena v idrijskih in okolnih kamninah. Bitumni iz mineraliziranih vzorcev nakazujejo zmanjšane vsebnosti nasičenih ogljikovodikov ter povečane koncentracije policikličnih aromatskih ogljikovodikov (PAH), aromatskih žveplovih spojin (S-PAH) in hidrogeneranih PAH. Izotopske sestave kerogenov, bitumnov in posameznih ogljikovodikov pričajo o termični in oksidativni degradaciji prvotnih in migriranih bitumnov med mineralizacijo in poznejšim razvojem idrijskega rudišča.

Introduction

The Idrija world-class mercury deposit is located in western Slovenia, about 50 km west of Ljubljana (Fig. 1). As the world second largest mercury mine after Almadén (Spain), Idrija has produced more than 12.7 Mt ore with 145,000 t Hg since 1490 (Mlakar, 1974). In 1988 the Idrija mine stopped production and initiated a shutdown program, which shall finish in 2006.

The geology and the genesis of the Idrija deposit were described in numerous studies (e.g. Mlakar, 1967; Mlakar & Drovenik, 1971; Placer, 1982; Čar, 1975, 1990). The geochemical investigations include trace element concentrations in host rocks (Čadež et al., 1981) and cinnabar (Berce, 1958;

Drovenik et al., 1980), mercury contents at deposit scale (Berce, 1965), stable isotopic studies of ore and host rocks (Ozerova et al., 1973; Drovenik et al., 1976, 1991), and mineralogical, molecular and isotopic characterization of the polycyclic aromatic hydrocarbon (PAH) mineral *idrialite* associated to the Idrija ore (Strunz & Contag, 1965; Blumer, 1975; Wise et al., 1986; Spangenberg et al., 1999). However, in order to better understand the mineralization process and in its relationship with the organic matter, further geochemical investigations are necessary. The ongoing organic and inorganic geochemical study includes trace elements of the host rocks, the isotopic composition of carbonate and sulfur minerals ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$), and molecular and iso-

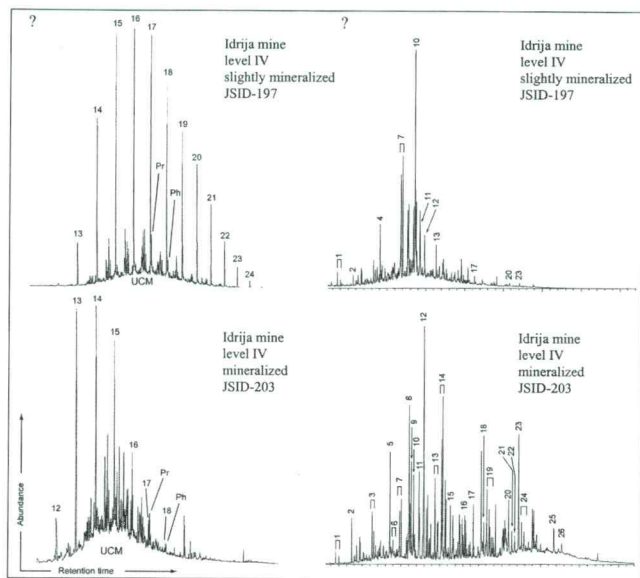


Figure 1. Gas chromatograms of (a) aliphatic and (b) aromatic hydrocarbons extracted from the Upper Scythian dolostone. The *n*-alkanes are indicated by their carbon numbers. Pr = pristane; Ph = phytane; UCM = unresolved complex mixture. Compounds corresponding to numbered peaks are listed in Table 1

Slika 1. Plinski kromatogrami (a) nasičenih in (b) aromatskih ogljikovodikov iz zgornjeskitskega dolomita. Normalni alkani so označeni s številkami, ki pomenijo število ogljikovih atomov Pr = pristane; Ph = fitan; UCM = nerazločena kompleksna mešanica. Spojine, ki ustrezajo oštevilčenim kromatogramskim vrhovom, so navedene v tabeli 1

topic (δD , $\delta^{13}C$, $\delta^{15}N$) composition of the associated organic matter (e.g. Lavrič & Spangenberg, 2001, 2002). Here we present Rock-Eval pyrolysis parameters, $\delta^{13}C$ and $\delta^{15}N$ of the kerogens (insoluble organic matter), $\delta^{13}C$ and the molecular composition of the bitumens (extractable organic matter), $\delta^{13}C$ of the individual *n*-alkanes, and $\delta^{13}C$ of pyrobitumen. These data provide insights into the nature of the hydrothermal alteration and remobilization of the Idrija organic matter, and help to constrain the ore fluids pathway.

Geological setting and mineralization

The stratigraphic succession at the Idrija deposit comprises about 5,500 m of sedimentary rocks of Permocarboneous to Eocene age, from which the lowermost 800 m host the mineralization (Mlakar & Drovenik, 1971). The Idrija structure developed as a part of an E-W extending failed rift (Idrija graben) during the Middle Triassic intra-continental rifting (Placer & Čar, 1977). The host rocks were affected by two main post-ore deformation episodes: (1) an Early Tertiary folding and thrusting of about 30 km toward SSW, and (2) a Late Tertiary dextral NW-SE strike-slip faulting, with a horizontal displacement of up to 2.5 km (Mlakar, 1969; Placer, 1982).

The mineralization took place in two phases during the Scythian-Ladinian rifting and bimodal volcanism from near neutral mercuriferous hydrothermal fluids channeled by a system of deep subvertical faults within the Idrija graben (Mlakar & Drovenik, 1971). The ore occurs as syngenetic stratiform bodies in the Upper Ladinian Skonca beds and the overlying tuffs, and as epigenetic open space filling and replacement in fault zones in Permocarboneous to Upper Ladinian beds. The ore consists of cinnabar and native mercury, with minor pyrite, marcasite and metacinnabar. Up to 1.5 m thick lenses of evaporites (gypsum and anhydrite) occur in the Upper Permian and Lower Scythian dolostones (Čadež, 1977). The main gangue minerals are quartz, calcite and dolomite, with rare barite and fluorite (Mlakar & Drovenik, 1971). Three distinct types of organic matter occur at Idrija: (1) kerogen and bitumen in the host rocks and ore, (2) open-space filling black solid pyrobitumen, and (3) *idrialite* intergrown with the mercury ore.

Sampling

Permocarboneous to Upper Ladinian barren and mineralized lithologies were sampled at outcrops up to 6 km from the deposit ($n = 56$), and from the mine walls at

different levels of the Idrija mine ($n = 125$). The hydrothermal alteration and flow direction of the mineralizing fluids on mine scale were investigated in profiles across mineralized and barren zones. The largest part of the host rock and ore samples ($n = 111$) was collected in seven profiles at level IV.

Analyses

Rock powders of selected regional ($n = 18$) and mine ($n = 45$) samples were submitted to the determination of total organic carbon (TOC) and Rock-Eval pyrolysis. The organic matter was studied following the procedures described in Spangenberg & Macko (1998). The C and N stable isotopic composition of the kerogens, and the $\delta^{13}\text{C}$ of bulk bitumens and pyrobitumens were determined by using a Carlo Erba 1108 elemental analyzer connected to a Thermo Finnigan Delta S isotope ratio mass spectrometer (EA/IRMS). The isotopic data are reported in the delta (δ) notation as the per mil (‰) deviations relative to the VPDB and AIR for carbon and nitrogen, respectively. The reproducibility of the EA/IRMS measurements for carbon and nitrogen is better than ± 0.1 and ± 0.3 ‰ (1s), respectively. The aliphatic and aromatic fractions of the bitumens were chemically characterized by an Agilent Technologies 6890 gas chromatograph coupled to a 5973N mass selective detector (GC/MSD). The C stable isotopic composition of the individual n -alkanes was determined in triplicate by using the GC coupled to the Delta S IRMS by a combustion (C) interface III (GC/C/IRMS). The reproducibility of the GC/C/IRMS analyses of the Idrija n -alkanes ranges between 0.1 and 1.0‰.

Results

Bulk organic geochemical and isotopic data

The TOC content for mine samples ranges from 0.01 to 1.47 wt%, with median values of 0.45 wt% for the Permian dolostone, 0.25 wt% for the Upper Permian dolostone, 0.13 wt% for the Lower Scythian to Anisian dolostones, and 0.85 wt% for the Upper Ladinian Skonca beds. For regional samples the TOC ranges from 0 to 1.75 wt%, with median values of 0.61 wt% for the Permian dolostone, 0.31 for the Up-

per Permian dolostone, 0.03 wt% for the Lower Scythian to Anisian dolostones, and 0.98 wt% for the Upper Ladinian Skonca beds. The Rock-Eval S_1 and S_2 peaks are generally small (< 0.2 mg HC/g) or absent, which indicates a low petroleum-generative potential, and makes the S_2 -derived temperatures (T_{max}) unreliable (Peters, 1986). Exceptions are one regional and one mine sample of the Upper Ladinian Skonca shale, having S_2 peaks of 0.27 and 0.41 mg HC/g, and T_{max} values of 524 and 504°C, respectively. The samples have low hydrogen and high oxygen indices ($HI < 29$ mg HC/g TOC, $OI < 267$ mg CO_2 /g TOC), which is typical of highly recycled and oxidized kerogens. An additional decrease of the HI, and increase of the OI due to the mineral matrix effect have to be taken into account for samples with TOC < 1.5 wt% (e.g. Hunt, 1996). The C and N isotopic compositions of the kerogens ($n = 12$) range from -29.0 to -23.1 ‰ and from -1.2 to $+4.6$ ‰, respectively. The kerogens of mineralized samples are enriched in ^{15}N (up to ~ 1 ‰) and in ^{13}C (up to 3.6 ‰) compared to barren or slightly mineralized samples. In both mineralized and barren mine samples the kerogens are isotopically lighter (-29.0 to -23.1 ‰, median = -26.3 ‰) compared to the associated bitumens (-27.7 to -22.8 ‰, median = -25.2 ‰). The pyrobitumens are isotopically heavier ($\delta^{13}\text{C} \approx -23.0$ ‰), reflecting their origin from thermally altered migrated hydrocarbons.

Molecular organic geochemistry

The main resolvable compounds in the aliphatic hydrocarbons (HC) fraction of the Idrija bitumens are unimodally-distributed n -alkanes in the C_{12} to C_{30} range and the acyclic isoprenoids pristane (Pr) and phytane (Ph). Trace amounts of the biomarker hydrocarbons hopanes and steranes are present. Regional samples and barren mine samples have higher concentrations of aliphatic HC as the mineralized samples. The mineralized samples show a larger hump of unresolved complex mixture (UCM) of light hydrocarbons moieties, and higher concentrations of lower molecular weight n -alkanes compared to barren samples (Fig. 1). The molecular parameters Pr/Ph (0.36 to 3.94), Pr/ $n\text{-C}_{17}$ (0.10 to 1.83), and Ph/ $n\text{-C}_{18}$ (0.06 to 3.31) are highly variable, and independent of the degree of mineralization. Two distinct trends of the $\delta^{13}\text{C}$ values of the individual n -

Peak	Compound	Peak	Compound
1	Methylnaphtalene	17	Pyrene
2	Biphenyl	18	Tetrahydrobenzofluorene
3	Methylbiphenyl	19	Benzofluorene
4	Bibenzyl	20	Benzonaphtothiophene
5	Fluorene	21	Tetrahydrobenzanthracene
6	Dimethylbiphenyl	22	Tetrahydrochrysene
7	Dimethylmethylphenylbenzene	23	Chrysene/Triphenylene
8	Dihydroanthracene	24	Methylbenzonaphtothiophene
9	Methylfluorene	25	Benzofluoranthene
10	Dihydrotrimethylphenylindene	26	Perylene
11	Dibenzothiophene	27	Cyclohexylbenzene
12	Phenanthrene/Anthracene	28	Ethenylnaphtalene
13	Methyldibenzothiophene	29	Cyclohexylmethylbenzene
14	Methylphenanthrene	30	Dimethyldibenzothiophene
15	Tetrahydrofluoranthene	31	Dimethylphenanthrene
16	Fluoranthene		

Table 1. Aromatic hydrocarbons identified in Figures 1 and 2

Tabela 1. Aromatski ogljikovodiki, identificirani v slikah 1 in 2

alkanes were observed. In mineralized samples the $C_{=17}$ *n*-alkanes are up to 3‰ lighter compared to the longer C-chain homologues, whereas in barren and slightly mineralized samples short and long-chain *n*-alkanes are enriched in ^{13}C (1–27‰), with the lowest values at *n*- C_{18} and *n*- C_{19} (~–33‰).

The aromatic fraction of bitumens from mineralized samples is characterized by up to 5-rings polycyclic aromatic hydrocarbons (PAH), aromatic sulfur compounds (S-PAH; e.g. dibenzothiophene, benzonaphtothiophene) and their alkylated homologues (Table 1). Furthermore, the mineralized samples contain substantial concentrations of hydrogenated PAH (e.g., dihydroanthracene, tetrahydrochrysene), which occur in smaller concentrations or are not detected in barren mine samples and regional samples (Fig. 1). The PAH content increases with the degree of mineralization. Regional and barren mine samples have lower content in aromatic hydrocarbons which are mainly represented by lower molecular weight compounds (e.g. benzenes, naphtalenes). Exceptions are the barren samples from the Permocarboneous shale and the Upper Permian dolostone which show substantial PAH concentrations (Fig. 2).

Discussion

The TOC and Rock-Eval data indicate that the Idrija host rocks, which were sub-

jected to prolonged hydrothermal activity, burial and extensive tectonic deformation, are organic-lean (TOC < 1 wt. %). The T_{max} of the Upper Ladinian Skonca shale samples (504 and 557°C) suggest that they are post mature and may have been heated at temperatures of up to ~ 190°C (e.g. Hunt, 1996). This is in line with the homogenization temperatures of fluid inclusions in single quartz crystals from the Gruebler orebody of Idrija deposit (160 to 218°C; Palinkaš et al., 2001).

The relatively wide scatter of the kerogen C and N isotopic compositions can be attributed to (1) distinct primary organic sources in the different lithostratigraphic units, and (2) different degrees of alteration. The overall ^{13}C enrichment of bitumens, associated to isotopically lighter kerogens, can be explained by a combination of thermal maturation and oxidative degradation of the indigenous HC on deposit scale during and after mineralization. A contribution of migrated solid bitumen (pyrobitumen) explains the additional ^{13}C enrichment in the mineralized samples of the different lithostratigraphic units. The variations of the hydrocarbons distribution (Pr/Ph, Pr/*n*- C_{17} , Ph/*n*- C_{18}) and $\delta^{13}C$ values of the individual *n*-alkanes indicate different maturation degrees and enhanced thermal alteration (e.g. cracking of longer chain *n*-alkanes, water washing) along the hydrothermal fluids pathways.

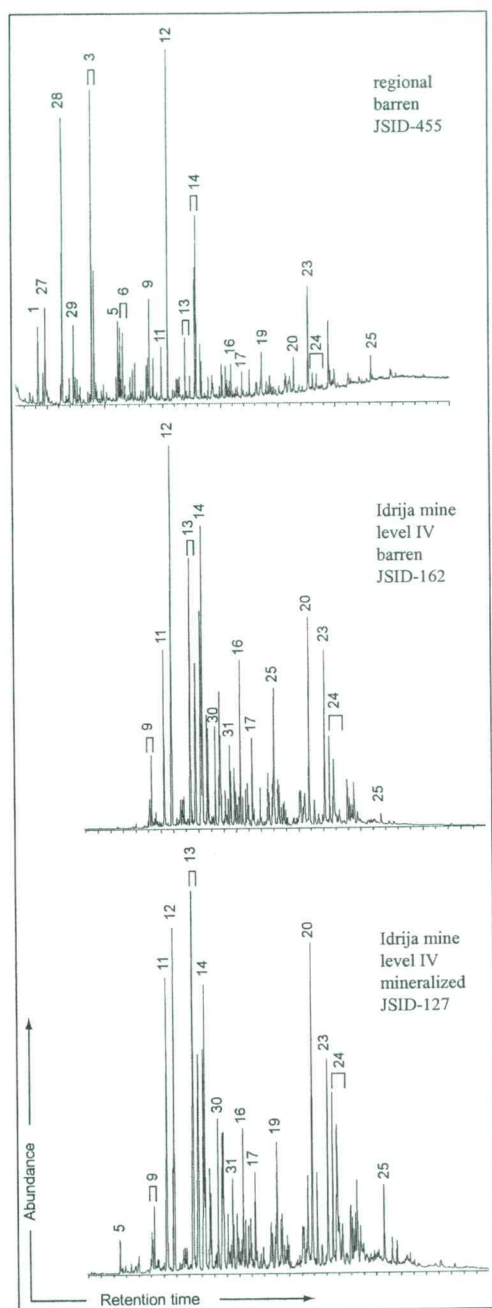


Figure 2. Gas chromatograms of the aromatic hydrocarbons extracted from Upper Permian dolostone. Compounds corresponding to numbered peaks are listed in Table 1

Slika 2. Plinski kromatogrami aromatskih ogljikovodikov iz zgornjepermškega dolomita. Spojine, ki ustrezajo oštevilčenim kromatogramskim vrhovom, so navedene v tabeli 1

PAH at Idrija hydrothermal system may have been formed through: (1) pyrolytic fragmentation of organic compounds followed by reformation (cyclization, aromatization, annelation), and (2) transformation of biologic precursors (e.g. saturated cyclic compounds) through dehydrogenation and dealkylation (e.g. McCollom et al., 1999). The efficiency of both processes increases with temperature. Further aromatization of Idrija hydrocarbons may be related to S-catalyzed reactions (e.g. Hunt, 1996) during thermochemical sulfate reduction which was one of the processes involved in the precipitation of cinnabar (Lavrič & Spangenberg, 2002). The high content of PAH in the barren Permian carboniferous shales and Upper Permian dolostones suggest that these rocks most likely were the source of the aromatic petroleum staining Idrija ore and host rocks. Hydrous pyrolysis experiments showed that PAH could be hydrogenated at elevated temperatures (330°C) in an aqueous environment (McCollom et al., 1999). Thus, the occurrence of hydrogenated PAH in the Idrija ore samples indicates the degree of alteration and pathway of the hydrothermal fluids. The S-PAH are incorporated into the sedimentary organic matter during early diagenesis (e.g. Orr & Sinninghe Damsté, 1990). In hydrothermal deposits a part of the sulfur can be incorporated in the PAH structure during mineralization (e.g. Landaïs & Gize, 1997). Thus, the high concentrations of S-PAH in Idrija mineralized samples were formed during mineralization, probably related to thermally mediated reduction of sulfate by organic matter (Fig. 2)

Conclusions

The molecular and isotopic characteristics of the Idrija organic matter reflect migration, thermal maturation, and oxidation, which were enhanced by the mineralizing hydrothermal and post-ore fluids in the mineralized zones. The abundance and distribution patterns of hydrocarbons indicate that the organic matter in the Permian carboniferous shales and Upper Permian dolostones was the main source of the aromatic hydrothermal petroleum associated to the Idrija ore. The organic geochemistry confirms the fracture-controlled nature of the

Idrija hydrothermal system, previously established by the inorganic geochemical and isotopic patterns.

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