## Biogeochemistry of an Alpine-type zinc-lead mineralization

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Stable isotope and molecular biogeochemistry of kerogens and derived hydrocarbons (HCs) associated with sulfide mineralization are a clue to understand the formation of the organic matter-ore association. In this study we have performed isotopic (irm-EA-MS, irm-GC-MS) and molecular (GC-MS) analyses on the kerogens and bitumens from the ore and carbonate host rocks of the early diagenetic zinc-lead mineralization at Topla, Eastern Alps, Slovenia. Amorphous highly mature ( $R_o > 2.0\%$ ; Rock-Eval parameters) organic matter occurs in microbeds, microstylolite seams, fracture fillings, and disseminated around dolomite and sulfide crystals. The  $\delta^{13}C_{ker}$  (-29.4 to -25.0‰) and  $\delta^{15}N_{ker}$  (-2.5 to 6.8‰) values suggest contributions of continental organic matter to the marine planktonic/benthic organic matter. The differences in  $\delta^{13}$ C of bitumens and associated kerogens vary from insignificant (<-2‰) in barren and slightly mineralized samples to >+7‰ in highly mineralized (>5 wt.% Pb+Zn) samples, indicating the presence of variable amounts of locally migrated and (bacterially) reworked HCs. The extracted saturated-HC GCs are similar in all samples: dominated by nalkanes in the range  $n-C_{15}$  to  $n-C_{34}$ , maximizing at  $n-C_{19}$ - $n-C_{20}$ , moderate to large i-C18 to i-C21 isoprenoid peaks, pronounced unresolved naphthenic humps in the range  $n-C_{15}$  to  $n-C_{24}$ maximizing at n-C19-n-C23, and generally pristane/phytane ratios < 1. In most bitumens the individual *n*-alkanes have uniform  $\delta^{13}$ C values (-29 to -31‰) across the C-number range, suggesting a common phytoplanktonic source (algae and cyanobacteria) of the HCs. The highly mineralized samples are characterized by substantially higher amount of  $C_{27}$ - $C_{35}$  hopanes, presence of alkylcyclohexanes,  $C_{27}$ - $C_{29}$ steranes, lowest diasteranes/hopanes ratios, presence of a second naphthenic hump in the range of  $n-C_{24}$  to  $n-C_{34}$ maximizing at n-C<sub>26</sub> to n-C<sub>27</sub>, and C<sub>>17</sub> n-alkanes enriched in <sup>13</sup>C (up to 3‰), suggesting that they were probably formed from reduction of bacterial fatty acids. Such differences suggest that intense bacterial activity occurred during diagenesis under suboxic/anoxic conditions at the mineralization site. The bacterial degradation of organic matter using sulfate as electron acceptor, leads to high amounts of dissolved H<sub>2</sub>S in the shallow-water marine sediments. Mixing of the H<sub>2</sub>S-rich waters with a metal-rich brine caused precipitation of the ore sulfides.

## Monazite: Another Rosetta Stone?

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Petrologic studies (chemical zoning and textural analysis) coupled with differential thermodynamic modeling of monazite and xenotime from pelites from central New England, the Adirondack Mts., NY, and the Valhalla Complex, BC reveal several episodes of accessory phase growth and consumption, which have been correlated with specific P-T points, major-phase reactions, melting events, deformation events, and fabric production. Time of monazite growth has been determined from a combination of EMP and SIMS analysis to constrain major tectonic events in each terrane.

Central New England is composed of seven tectonic levels separated by major faults, each distinguished by different P-T histories. The deepest levels (domes of VT) enjoyed peak pressures of 8-10 kbar and clockwise P-T paths. Monazite within garnet records early metamorphism at 420 ±10 Ma. Monazite in garnet rims, and within kyanite and staurolite record growth at 390-370 Ma. Hydrothermal alteration of monazite rims occurred at 300-280 Ma. In contrast, the overlying Silurian-Devonian section in eastern VT experienced metamorphism from 370-340 Ma. In NH, the structurally highest (and highest grade - migmatitic) nappes record early contact metamorphism with at least three periods of monazite growth and subsequent regional low-P metamorphism at 410-390 Ma, whereas the structurally intermediate (and medium-grade) nappes were not metamorphosed until 360-340 Ma. Monazite in garnet and staurolite pseudomorphs within a major shear zone at the base of this zone yield ages of 300-290 Ma, suggesting the final assembly of the terrane occurred in the Alleghenian.

Metapelites from the Adirondacks record at least five periods of monazite growth. Small inclusions within garnet record 1227-1221 Ma ages and are likely detrital. Elzevirian (1174-1131 Ma) and Ottawan (1060-1050 Ma) ages are common in monazites that are found included in meltproduced garnet and in the matrix, requiring the main Ottawan melting to have occurred after 1050 Ma. Taconic (ca. 500 Ma) and Acadian (ca. 400 Ma) ages from monazite rims suggest fluid transport and hydrothermal monazite deposition at this time. Jurassic ages (155-144 Ma) from allanite alteration on monazite records additional fluid infiltration and may be related to normal faulting and uplift of the Adirondacks.

Monazite within garnet from the Valhalla complex records a 100-110 Ma contact metamorphism episode. In contrast, monazite recrystallized in post-melting fabrics records 63-60 Ma ages, which requires cooling rates in excess of 100 °C/Ma, probably associated with rapid tectonic emplacement of the complex onto cool basement.