

## Fluids in the metamorphic stage of Krivoy Rog iron deposit evolution, Ukraine

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Krivoy Rog deposit is situated in the Ukrainian crystalline shield and represents one of the biggest accumulations of iron ore within banded iron formation in Europe. Its complex evolution was initiated by sediment deposition in Early Proterozoic and formation of metaterrigenous-ferruginous complex that has undergone several episodes of ductile and brittle deformation as well as metamorphic and metasomatic events. Orogenic movements in Late Proterozoic ultimately determined the present shape of Krivoy Rog structure and completed the tectogenesis. Krivoy Rog iron deposit is classified as metamorphosed genetic type. Its origin is emphasized to be strictly associated with metamorphic processes that in majority influenced the iron ore formation. Metamorphic conditions determine extent of low-grade and high-grade iron ores. Samples, examined in the study, were collected from Skelevatske-Magnetitove deposit (Yugok open pit) in the interval of one year. The studied jaspilites (low-grade iron ore) belong to metaterrigenous-ferruginous complex corresponding to Saksaganskaya Suit of Kryvorizka Series in the local stratigraphy (Gurskiy, 2002). The rocks are composed of silicate, carbonate, magnetite and magnetite-martite bands. Circulation of residual metamorphic solutions during metamorphic stage was responsible for material migration within jaspilites. Fluids were generally transported along cracks and fractures. It resulted in formation of metamorphic veins, crosscutting iron ore bands. They contain fluid inclusion providing information about fluids present after peak metamorphic conditions. Studied veins are composed mainly of quartz, a younger style calcite and specularite assemblages. Fluid inclusions were observed in quartz veins excluding quartz bands in iron ore due to their small size. Fluid inclusions can be grouped in four

types: primary one-phase aqueous, secondary one-phase CO<sub>2</sub>, secondary two-phase or three-phase (CO<sub>2</sub>-H<sub>2</sub>O) and secondary three phase (CO<sub>2</sub>-H<sub>2</sub>O-nahcolite). Small in size (<1 μm), primary fluid inclusions are distributed in trails, parallel to the vein walls and may represent crystal growth surfaces. Their distribution indicates entrapment resulting from vein crack-seal mechanism. One-phase, liquid CO<sub>2</sub> inclusions are usually very irregular but in some cases they occur as negative crystal shaped, arranged in single trails. Some of the inclusions seem to be one-phase CO<sub>2</sub> but they may contain a thin aqueous rim, not always visible. This type often coexists with H<sub>2</sub>O-CO<sub>2</sub> inclusions, distributed along microfractures. Secondary CO<sub>2</sub>-H<sub>2</sub>O inclusions comprised of aqueous and liquid CO<sub>2</sub> phases may contain additional vapour CO<sub>2</sub> phase present at room temperature. Three-phase inclusions with an aqueous liquid, CO<sub>2</sub> liquid and a solid nahcolite phase are randomly scattered among two-phase inclusions. Elongated or oval crystals of solid phase occur entirely inside inclusion (Fig. 1) or crosscut its wall (Fig. 2). Laser Raman spectroscopy revealed that it is nahcolite (peaks at: 1046 cm<sup>-1</sup>, 685 cm<sup>-1</sup>, 659 cm<sup>-1</sup>), accidentally trapped during the inclusion formation. Veins that experienced more complex thermal history contain fluid inclusions grouped in decrepitation clusters and dense clouds indicating that part of inclusions had leaked due to the pressure increase in surrounding rock. It marks condition changes after vein formation and may indicate episodes of fracturing during late deformation events experienced by the rock. Two consistent data sets, corresponding to two quartz veins (vein1 and vein2), were obtained from microthermometry measurements. Studied two-phase inclusions were approximated by H<sub>2</sub>O-CO<sub>2</sub>-NaCl system, based on Raman spectroscopy that confirmed CO<sub>2</sub> and H<sub>2</sub>O

content. Salts were not detected but according to decreased clathrate melting temperatures,  $T_m(\text{cla}) = 6.0\text{--}8.6\text{ }^\circ\text{C}$ , salt is present in the aqueous solution. Properties of fluids were calculated using computer packages FLUIDS (Bakker, 2003). The total molar volume of inclusions ranges between 20.49 and 30.78  $\text{cm}^3/\text{mol}$  with mode close to 21.5  $\text{cm}^3/\text{mol}$ . Densities of carbon dioxide, fluctuating in the interval: 0.89–1.04  $\text{g}/\text{cm}^3$ , were determined from microthermometry data and from Raman spectroscopy, based on the splitting of the Fermi diad of  $\text{CO}_2$  (Fall et al., 2011). Carbon dioxide density in individual fluid inclusions appears to be independent in relation to  $\text{CO}_2$  volume fraction. This fact suggests that volume fractions diversity,  $\varphi^{\text{vap}} = 0.10$  to 0.30 is not the effect of reequilibration processes but rather result of heterogeneous fluid entrapment. Post-metamorphic leakage of aqueous solution from unmixed  $\text{CO}_2\text{--H}_2\text{O}$  fluids is excluded because there is no density decrease compared with carbon dioxide phase size (Hollister, 1990). Moreover, pure  $\text{CO}_2$  inclusions show higher densities than  $\text{CO}_2$  phase present in  $\text{CO}_2\text{--H}_2\text{O}$  inclusions. Generally low salinities of aqueous solution varying between 2.5 and 7.5 eq mass% NaCl are typical for metamorphic fluids and exclude influence of basinal brines. The most frequent salinity values assigned to each vein differ insignificantly. Clathrate melting temperatures are lower in inclusions from vein 2, indicating about 1 mass% higher salinities. Quartz veins were formed in aqueous-rich environment in accordance with primary fluid inclusion trails resulting from crack-seal mechanism. Early post-formation condition changes caused fracturing and formation of several inclusion generations. They are characterized by various compositions, as well aqueous-rich as carbon dioxide-rich. Heterogeneous entrapment implies that during fracturing event two different fluids and nahcolite solid phase were present. The most important source of carbon dioxide was probably decarbonation reactions during metamorphism of banded iron formation (Perry&Ahmad, 1981). Decomposition of calcite and siderite caused expulsion of  $\text{CO}_2$  during deformation. Each generation of secondary fluid inclusions represents different episodes in the thermal history of the

rock, after peak metamorphic conditions. Plotted isochores, constraining the possible fluid trapping conditions during retrograde metamorphism, overlap the greenschist and amphibolite facies on the P-T diagram. Fluid immiscibility of  $\text{H}_2\text{O--CO}_2$  system might have occurred during these facies during retrograde metamorphism (Hollister, 1990). Entrapped low saline fluid inclusions, containing 10 mol% of  $\text{CO}_2$ , resulted from trapping of retrogressive fluids that are predicted to be driven through jaspilites in metamorphic conditions of greenschist or lower amphibolite facies. Studied veins represent probably one of the late stages of Early Proterozoic orogeny.



Fig. 1. Nahcolite crystal enclosed within inclusion comprised of aqueous phase (aq), liquid  $\text{CO}_2$



Fig. 2. Three phase fluid inclusion comprised of aqueous phase (aq), liquid  $\text{CO}_2$  and nahcolite crystal

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