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### Some secondary manganese minerals associated with the Mn-humites association in the Razoare Mn-Fe deposit, Preluca Mts, East Carpathians, Romania

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The Precambrian Razoare deposit is an example of a metamorphic Mn-Fe carbonate-silicate-oxide-sulphide type, which is characterized by the presence of manganooan fayalite and rhodochrosite. Minerals that formed during the first stage metamorphic event include: manganooan ferrosilite, manganooan fayalite, pyroxmangite, tephroite, Mn-bearing humites (MBH), rhodonite, spessartine-calderite and mangangrunerite. Primary minerals of the MBH association include: tephroite, sonolite/leucophoenicite, jacobsite, apatite/fluorapatite and rhodochrosite.

The presence of some sulphides, arsenides, tellurides and Bi-bearing phases in the MBH association could be linked with a local hydrothermal mineralization process. Indeed most of the over 130 different minerals that have been identified at Razoare are products of either this low temperature hydrothermal event, or later stage weathering products [1]. These secondary minerals include silicates, phosphates, arsenates, sulphates and oxides.

Beside bementite, neotocite, pennantite, and kellyite, the rare phyllosilicate tamaite,  $(Ca,K,Ba,Na)_3\text{-}_4\text{Mn}_{24}(\text{Si,Al})(\text{O,OH})_{112}\cdot 21\text{H}_2\text{O}$ , occurs in the MBH association as veinlets and nests. Its strongest lines in the X-ray powder diffraction pattern are: 12.73 (100), 3.13(80), 2.84(80), 2.69 (90), 2.60(80), 2.45(80), 2.38(50). Yoshimuraite, a complex barium titanium manganese sulphate-phosphate-silicate occurs associated with tephroite. Dravite occurs in the MBH association as an accessory mineral in local hydrothermal veinlets. Ericssonite,  $\text{BaFeMn}_2\text{O}(\text{Si}_2\text{O}_7)(\text{OH})$ , a rare Ba silicate, was determined on the basis of scanning electron microscope/EDS data. Secondary phosphates are hydroxylapatite and its arsenate analogue, johnbaumite,  $\text{Ca}_5(\text{AsO}_4)(\text{OH})$ . Johnbaumite has the X-ray powder pattern: 2.89 (100), 2.79(70), 2.68(50), 1.47(30). It occurs as grayish white grains with distinct cleavage and very low birefringence, in association with tephroite. Waterhouseite,  $\text{Mn}_7(\text{PO}_4)_2(\text{OH})$  was also determined, having the X-ray powder pattern: 3.62(100), 4.59(20), 2.71(20), 2.35(10). The arsenates show a wide variety; they contain Mn and Fe as the main cations, and formed from low temperature fluids at the expense of arsenide/sulfoarsenide (arsenopyrite, löllingite, rammelsbergite, skutterudite, etc). Arsenoclasite,  $\text{Mn}_5(\text{AsO}_4)_2(\text{OH})_4$ , has the X-ray powder pattern: 2.944 (100), 3.05(60), 4.925 (45), 4.539(70), 2.618(70),

2.303(50), 2.214(60), 1.631(5), 1.345(40) and cell data:  $a=9.31\text{\AA}$ ,  $b=5.75\text{\AA}$ ,  $c=18.29\text{\AA}$ ,  $Z=4$ ,  $V=979.11\text{\AA}^3$  [2]. Grishunite,  $\text{NaCa}_2\text{Mn}_5\text{Fe}^{3+}(\text{AsO}_4)_6 \cdot 2\text{H}_2\text{O}$  has the X-ray powder pattern: 2.84 (100), 2.94(60), 3.15(90). It occurs as brown red semitransparent microscopic grains closely associated with yellow micaceous tamaite in the MBH association.

Many other arsenates have been determined only via optical microscopy (sarkinite, eveite, etc). The sulphates present in the MBH association are manganooan barite and szmikite. The secondary carbonates are: rhodochrosite, manganooan calcite, manganooan witherite, holdawayite, aragonite and calcite. Hausmannite was exsolved from jacobsite during cooling under oxidizing conditions, and can be considered as a secondary oxide. The most oxidized areas of the MBH association are characterized by high grade manganese oxides such as birnessite, pyrolusite, todorokite, hollandite, cryptomelane and unidentified amorphous manganese oxides (AMO).

#### *References*

1. Hirtopanu P. and Udubasa G. 2015 Rom. J. Mineral Deposits 88 (1-2): 11-28.
2. Hirtopanu P., Udubasa G., Dumitras D. 2015 Acta Mineralogica-Petrographica, Abstract Series: 20.

