A NEW OCCURRENCE OF MANGANILVAITE CaFe²⁺Fe³⁺(Mn²⁺, Fe²⁺)[Si₂O₇]O(OH) AT DOGNECEA, SOUTHWESTERN BANAT, ROMANIA: CHEMICAL COMPOSITION, CRYSTAL STRUCTURE AND CATION ORDERING

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Samples of ilvaite systematically exceeding 0.5 *apfu* Mn (in formula normalized on the basis of 6 cations) and suggesting the presence of the recently discovered mineral manganilvaite (ZOTOV *et al.*, 2005; BONEV *et al.*, 2005) were identified in the skarn deposit at Dognecea, where they occur in association with Mn-hedenbergite and magnetite. A number of 14 EDS chemical analyses of such ilvaites resulted in the following ranges of variation: (in weight percents; numbers in parentheses read as average values and standard deviations, respectively): **Si**: 13.39–14.09 (13.92; 0.15), **Al**: 0.00–0.27 (0.09; 0.11), **Fe**: 32.88–34.53 (34.62; 0.64), **Mn**: 7.30–9.17 (7.85; 0.54), **Mg**: 0.00–0.26 (0.07; 0.10), **Ca**: 9.86–10.64 (10.26; 0.22). Atomic proportions of Fe^{2+} and Fe^{3+} for a chemical formula unit normalized for 6 cations, were calculated as $Fe^{2+} = 2 - Mn^{2+}$ and $Fe^{3+} = Fe_{total} - Fe^{2+}$. The variation domains of Fe^{2+}, Fe^{3+} and Mn^{2+} atomic proportions were the following: 1.34–1.48 (average 1.44; standard deviation 0.04), 0.98–1.04 (1.01; 0.021) and 0.52–0.66 (0.56; 0.04), respectively. Other varieties of Mn-poorer ilvaites were identified, too.

Manganilvaite from Dognecea is a $P2_1/a$ polymorph (a = 13.014 Å, b = 8.846 Å, c = 5.848 Å and β = 90.34°) with significant ordering of Fe^{2+} and Fe^{3+} among *Me*11 and *Me*12 structural sites. The single crystal structure determination of manganilvaite – based on 1509 unique reflections, was refined down to a final R = 5.41% (with single generic metals – Fe or Mn – in *Me*11, *Me*12 and *Me*2 positions). The crystal structure data allowed the calculation of interatomic and per-polyhedra average distances for all relevant cation-oxygen pairs and the evaluation of Fe^{2+} and $Fe3^+$ occupancies in *Me*11 and *Me*12 structural sites. Statistical Fe^{x+} occupancies were calculated on the basis of two classic atomic radii models, *i.e.* GHOSE (1966) – (G) and SHANNON (1976) – (S). Thus, *Me*11 structural site is 53% (G) or 84% (S) occupied by Fe^{2+} (normalized values for *Me*11 + *Me*12 = 100%). Fe^{3+} occupancy in *Me*11 and Fe^{2+} occupancy in *Me*12 site is complementary to these values. The corresponding ordering parameter (TAKEUCHI *et al.*, 1983) was 0.34 (G) or 0.47 (S). Same calculations concerned the *Me*2 structural site and allowed indirect evaluation of Mn^{2+} occupancy *vs.* complementary Fe^{2+}. Calculation of Mn occupancy in *Me*2 based on a simple linear variation of *Me*2–O Shannon distances be-

tween 2.18 Å (Fe^{2+}–O) and 2.23 Å (Mn–O), resulted in 42% Mn^{2+} whereas the empirical model of Carrozzini (1994) yielded 52% Mn^{2+}. Similar discrepancies between the Shannon and Carrozzini models may be described in the case of the type manganilvaite from Ossikovo (BONEV *et al.*, 2005). The refinement of the structure with split *Me*2 position (Mn and Fe) resulted in a slightly lower R = 5.33%. Attempts to refine the structure with Mn in Ca, *Me*11 or *Me*12 position have failed, suggesting that Mn is confined to the *Me*2 position.

The experimental β value is slightly discrepant with regard to the ones calculated on the basis of correlated ordering parameter and degree of monoclinicity (TAKEUCHI *et al.*, 1983 (T); FINGER & HAZEN, 1987 (FH)): 90.16° (T) and 90.27° (FH).

Local paragenetical relations and various published correlations between the ordering parameter and the temperature of formation, suggest that Mn-ilvaite from Dognecea represents a reaction product of 6 hed + 4 mgt + 3 $H_2O \rightarrow$ 6 ilvaite + ½ O_2, formed at temperatures not exceeding 300 °C, and in conditions of relatively low fO_2.

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