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REE-bearing epidotes in Mn-rich systems: new compounds and fO_2 controls

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The incorporation of trivalent rare-earth elements (REE) in the structure of epidote, A1 A2 M1 M2 M3 SiO₄ Si₂O₇ (O,F) OH, is achieved by replacement of Ca^{2+} in the large A2 site and charge-balanced by substitution of divalent Me^{2+} cations for Al^{3+} or Fe^{3+} in the octahedral M3 site. With Ca dominant in A1, and A1³⁺ dominant in M1 and in M2, these substitutions lead to allanite proper for Me = Fe and to dissakisite for Me = Mg. The case of Me = Mn, *i.e.* divalent Mn in M3, is considered here. Analyses of Mn-rich 'allanite', mostly from pegmatites, suggest that Mn^{2+} is primarily entering the A1 site in place of Ca, whereas Fe^{2+} is still the dominant charge-balancing cation in M3. Only in 'allanites' from extremely Mn-rich rock-compositions like metamorphosed manganese ore deposits does Mn^{2+} dominate the M3 site – in addition to the A1 site – provided the oxidation state also permits Mn^{3+} (in M1). This leads to the very Mn-rich end-member androsite, Mn²⁺REE³⁺ Mn³⁺AlMn²⁺ SiO₄ Si₂O₇ O OH ([1], with La as the dominant REE). In manganese-bearing sediments metamorphosed under a variety of pressure-temperature (P-T) conditions, we found new examples of Mn-rich REE-bearing epidote-group minerals extending the range of known compositions and leading to the definition of two new species, vanadoandrosite-(Ce) and androsite-(Ce), and two potentially new ones.

Androsite-(Ce) has dominant Mn^{3+} in the M1 site; it occurs at the Praborna manganese mine, Saint-Marcel, Aosta valley, Italy, in a Mesozoic eclogite-facies ophiolitic unit of the western Alps. Associated minerals are rhodochrosite and Mn-pyroxenoid, with minor calderite, spessartine, hematite and pyrophanite. The structural formula is ${}^{A1}[Mn^{2+}_{0.60} Ca_{0.40}] \sum_{=1} {}^{A2}[(Ce_{0.46} La_{0.23} Nd_{0.12} Sm_{0.01}) \sum_{REE \ge 0.82} Sr_{0.07}$ $Ca_{0.02}] \sum_{\geq 0.91} {}^{M1}[Mn^{3+}_{0.63} Fe^{3+}_{0.23} Ti_{0.10} Mg_{0.04}] \sum_{=1} {}^{M2}Al_{1.00} {}^{M3}[Mn^{2+}_{0.96} Ca_{0.96}]$ $Mn_{0.04}^{3+}]_{\sum=1} Si_2O_7SiO_4O(OH)$, ideally ^{A1}Mn²⁺ ^{A2}Ce ^{M1}Mn³⁺ ^{M2}Al ^{M3}Mn²⁺ Si₂O₇SiO₄ O(OH). Monoclinic, space group P2₁/m, a 8.901(2) Å, b 5.738(1) Å, c 10.068(2) Å, β 113.425(3)°, V 471.81 Å³, Z = 2. Biaxial positive, 2V = 80.6(1.5)°, n(calc) = 1.80, strong pleochroism: α light yellow, β orange brown, γ red brown.

Vanadoandrosite-(Ce) has dominant V³⁺ in M1. It occurs at the Vielle Aure mining district, central Pyrénées, France, in and around quartz–rhodochrosite–sulphide veinlets cross-cutting the rhodochrosite ore in greenschist-facies Lower Carboniferous radiolarite. Other associated minerals are vuorelainenite, chalcopyrite, vanadian spessartine, and friedelite. The structural formula of the most V-rich crystal is ${}^{A1}(Mn_{0.62}^{0+2}Ca_{0.38})_{\Sigma1.00} {}^{A2}[(Ce_{0.39}La_{0.15}Nd_{0.10}Sm_{0.02})_{\Sigma REE=0.66}Ca_{0.21}Sr_{0.11}]_{\Sigma0.98} {}^{M1}(V_{0.80}^{3+}Al_{0.16}Mg_{0.03}Ti_{0.01})_{\Sigma1.00} {}^{M2}Al_{1.00} {}^{M3}(Mn_{0.36}^{0+2}V_{0.31}^{3+}Fe_{0.23}^{2+}Fe_{0.10}^{3+})_{\Sigma1.00} (Si_{2}O_{7})(SiO_{4})O(OH), ideally {}^{A1}Mn^{2+} {}^{A2}Ce {}^{M1}V^{3+} {}^{M2}Al {}^{M3}Mn^{2+} Si_{2}O_{7}SiO_{4} O(OH). Monoclinic, space group P2_1/m, a 8.856(3) Å, b 5.729(2) Å, c 10.038(4) Å, <math>\beta$ 113.088(5)°, V 468.5 Å³, Z = 2. Biaxial, n(calc) = 1.82, strong pleochroism: yellow brown < red brown < dark greenish brown //b. The name applies to any epidote-group mineral in which REE are dominant in A2, Mn²⁺ in A1, V³⁺ in M1, A1 in M2 and in which Mn²⁺ is the dominant charge-compensating (i.e. divalent) cation in M3.

The compositional variations of REE-bearing epidotes and their phase relations with respect to Mn-rich V- or REE-bearing silicates (e.g. stavelotite [2]) are discussed as a function of Fe, Mn and V availability and oxidation state.

- [1] Bonazzi et al., 1996, Am. Mineral., 81, 735–743.
- [2] Bernhardt et al., 2005, Eur. J. Mineral., 17, 703-714.