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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 SiO_4 Si_2O_7 (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 Al^{3+} 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, $Mn^{2+}REE^{3+}$ $Mn^{3+}AlMn^{2+}$ SiO_4 Si_2O_7 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 $^{A1}[\mathrm{Mn}^{2+}_{0.60}\ \mathrm{Ca}_{0.40}]_{\sum=1}$ $^{A2}[(\mathrm{Ce}_{0.46}\ \mathrm{La}_{0.23}\ \mathrm{Nd}_{0.12}\ \mathrm{Sm}_{0.01})_{\sum REE\geq 0.82}\ \mathrm{Sr}_{0.07}\ \mathrm{Ca}_{0.02}]_{\sum\geq 0.91}$ $^{M1}[\mathrm{Mn}^{3+}_{0.63}\ \mathrm{Fe}^{3+}_{0.23}\ \mathrm{Ti}_{0.10}\ \mathrm{Mg}_{0.04}]_{\sum=1}$ $^{M2}\mathrm{Al}_{1.00}$ $^{M3}[\mathrm{Mn}^{2+}_{0.96}$

$\mathrm{Mn}^{3+}_{0.04}]_{\sum=1}\ \mathrm{Si_2O_7SiO_4O(OH)}$, ideally $^{A1}\mathrm{Mn}^{2+}\ ^{A2}\mathrm{Ce}\ ^{M1}\mathrm{Mn}^{3+}\ ^{M2}\mathrm{Al}\ ^{M3}\mathrm{Mn}^{2+}\ \mathrm{Si_2O_7SiO_4}$ O(OH). Monoclinic, space group $P2_1/m$, a 8.901(2) Å, b 5.738(1) Å, c 10.068(2) Å, β 113.425(3)°, V 471.81 Å^3, 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 V^{3+} 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 $^{A1}(\mathrm{Mn}^{2+}_{0.62}\mathrm{Ca}_{0.38})_{\Sigma1.00}\ ^{A2}[(\mathrm{Ce}_{0.39}\mathrm{La}_{0.15}\mathrm{Nd}_{0.10}\mathrm{Sm}_{0.02})_{\Sigma REE=0.66}\mathrm{Ca}_{0.21}\mathrm{Sr}_{0.11}]_{\Sigma0.98}\ ^{M1}(\mathrm{V}^{3+}_{0.80}\mathrm{Al}_{0.16}\mathrm{Mg}_{0.03}\mathrm{Ti}_{0.01})_{\Sigma1.00}\ ^{M2}\mathrm{Al}_{1.00}\ ^{M3}(\mathrm{Mn}^{2+}_{0.36}\mathrm{V}^{3+}_{0.31}\mathrm{Fe}^{2+}_{0.23}\mathrm{Fe}^{3+}_{0.10})_{\Sigma1.00}$ $(\mathrm{Si_2O_7})(\mathrm{SiO_4})\mathrm{O(OH)}$, ideally $^{A1}\mathrm{Mn}^{2+}\ ^{A2}\mathrm{Ce}\ ^{M1}\mathrm{V}^{3+}\ ^{M2}\mathrm{Al}\ ^{M3}\mathrm{Mn}^{2+}\ \mathrm{Si_2O_7SiO_4}$ O(OH). Monoclinic, space group P2$_1$/m, a 8.856(3) Å, b 5.729(2) Å, c 10.038(4) Å, β 113.088(5)°, V 468.5 Å^3, 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, Mn^{2+} in A1, V^{3+} in M1, Al in M2 and in which Mn^{2+} 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.