



Article

Ferriandrosite-(Ce), a new member of the epidote supergroup from Betliar, Slovakia

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Abstract

A new member of the epidote supergroup, ferriandrosite-(Ce), ideally $\text{MnCeFe}^{3+}\text{AlMn}^{2+}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$, was found at the Július manganese ore occurrence near Betliar, Rožňava Co., Košice Region, Slovakia. It occurs as subhedral grains and polycrystalline aggregates, up to 0.3 mm in size, enclosed in pyroxmangite. Other associated minerals are spessartine, rhodochrosite, quartz, baryte and pyrosmalite-(Mn). Ferriandrosite-(Ce) is dark brown, with a light brown streak and vitreous lustre. The Mohs hardness is $\sim 6\frac{1}{2}$ to 7 and tenacity is brittle with no observable cleavage or fracture. The calculated density is 4.321 g cm^{-3} . Ferriandrosite-(Ce) is optically biaxial (+), with weak pleochroism, high surface relief and the mean calculated refractive index is 1.832. The empirical structural formula of ferriandrosite-(Ce), based on 13 anions per formula unit, is $\text{Al}_{1.00}^{M3}(\text{Mn}_{0.75}^{2+}\text{Fe}_{0.22}^{2+}\text{Mg}_{0.03})_{\Sigma 1.00}^{T1-3}\text{Si}_{3.00}\text{O}_{11}^{O4}(\text{O}_{0.67}\text{F}_{0.33})(\text{OH})$, where REE* are minor rare earth elements. Ferriandrosite-(Ce) is monoclinic, space group $P2_1/m$, $a = 8.8483(4)\text{ \AA}$, $b = 5.7307(3)\text{ \AA}$, $c = 10.0314(5)\text{ \AA}$, $\beta = 113.3659(15)^\circ$, $V = 466.95(4)\text{ \AA}^3$ and $Z = 2$. The crystal structure of ferriandrosite-(Ce) was refined to a final $R_1 = 0.0210$ for 1910 reflections with $F_o > 4\sigma(F_o)$ and 127 refined parameters. Structural features of ferriandrosite-(Ce) are discussed and compared with other members of the androsite-series.

Keywords: ferriandrosite-(Ce); new mineral; epidote supergroup; allanite group; crystal structure; manganese mineralisation; Betliar, Slovakia

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Introduction

The epidote supergroup is composed of mixed-anion silicates with the general formula $A_2M_3[T_2O_7][TO_4](\text{O,F})(\text{OH},\text{O})$ (Armbruster *et al.*, 2006). Currently, this supergroup is represented by 33 monoclinic species, divided into the allanite group (17 species), clinozoisite group (11), and dollaseite group (4); åskagenite-(Nd) is an additional member of this supergroup with O dominant over (OH) at the O10 site. Members of the allanite group are phases rich in rare earth elements (REE), with the following valences at key sites: $A1 = M^{2+}$, $A2 = M^{3+}$, $M1 = M^{3+}$, $M2 = M^{3+}$, $M3 = M^{2+}$, $O4 = O^{2-}$, and $O10 = (\text{OH})^-$ (Armbruster *et al.*, 2006).

During examination of the mineral assemblage of the Július manganese ore occurrence, near Betliar, in Slovakia, a new allanite-group mineral was identified, corresponding to the ideal composition $\text{MnCeFe}^{3+}\text{AlMn}^{2+}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$. Such a composition was reported previously by Girtler *et al.* (2013) and

Kolitsch *et al.* (2021) from some occurrences of metamorphosed Mn ores in Austria but no formal proposal for its approval was submitted to the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC). On the basis of the Slovak occurrence, this mineral has been named ferriandrosite-(Ce), in accordance with the existing nomenclature scheme for the epidote-supergroup minerals (Armbruster *et al.*, 2006). The root-name ‘androsite’ was first used by Bonazzi *et al.* (1996) for a REE-rich member from the Andros Island, Greece, having Mn^{2+} as the dominant cation at the A1 and M3 sites and the M1 site occupied by Mn^{3+} ; the prefix ‘ferri’ indicates the dominance of Fe^{3+} at the M1 site for the specimen from the Július manganese ore occurrence. The suffix, indicating the dominant cation at the A2 site, agrees with the nomenclature for REE mineral species (Bayliss and Levinson, 1988). The new mineral and its name have been approved by the IMA-CNMNC (IMA2023–022, Števkó *et al.*, 2023). The approved mineral symbol of ferriandrosite-(Ce) is Fea-Ce. The holotype specimen of ferriandrosite-(Ce) (polished section Be-5) is deposited in the collections of the Department of Mineralogy and Petrology, National Museum in Prague, Cirkusová 1740, 19300 Praha 9, Czech Republic under the catalogue number PIP 2/2023 and the grain used for the single-crystal X-ray diffraction study is kept in the

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collections of the Museo di Storia Naturale of the Università di Pisa, Via Roma 79, Calci (PI), Italy under catalogue number 20063.

Occurrence and physical properties

Occurrence

Ferriandrosite-(Ce) was found at the Július metamorphosed manganese ore occurrence, which is located on the NE slopes of the Turecká hill (953 m a.s.l.), ~1.4 km WSW of the Betliar village, Rožňava Co., Košice Region, Slovak Republic. Samples with ferriandrosite-(Ce) were collected on September 17, 2019, by one of the authors (MS) from the dump of the main exploration adit (48°41'53.3"N, 20°29'20.1"E).

The Július manganese ore occurrence is situated in the Spišsko-gemerské rudohorie Mts. Small bodies and lenses of metamorphosed carbonate–silicate manganese ore mineralisation are known from several localities in the Spišsko-gemerské rudohorie Mts. (e.g. Čučma-Čierna baňa, Smolník-Hekerová, Betliar-Július), and are hosted in Lower Palaeozoic black phyllites and lydites of the Gelnica Group (Gemic Unit), metamorphosed in greenschist-facies conditions (Kantor, 1954; Bajanič et al., 1983; Faryad, 1994; Grecula et al., 1995; Rojkovič, 2001; Peterec and Ďuďa, 2003). According to Rojkovič (2001), mineral associations composed of Mn carbonates and silicates in the Spišsko-gemerské rudohorie Mts., mainly represented by rhodochrosite, rhodonite, pyroxmangite, spessartine, tephroite and magnetite, were formed during Variscan metamorphism of sedimentary–diagenetic manganese proto-ores. Subsequent metamorphic–hydrothermal veinlets with quartz, calcite and sulfides represent younger mineralisation stages, probably related to the Alpine orogeny. Ore mineralisation at the Július occurrence was explored in a small scale for manganese and iron in the second half of the 19th century (Maderspach, 1875). In contrast with the nearby and very similar Čučma-Čierna baňa or Smolník-Hekerová manganese deposit, the mineralogy of the small Július manganese ore occurrence was never studied in detail. Maderspach (1875) briefly mentioned rhodonite, rhodochrosite, magnetite, pyrite, 'wad' and 'psilomelane' as principal ore minerals. Ferriandrosite-(Ce) was discovered in a large block of rhodochrosite–spessartine–pyroxmangite–magnetite ore, cut by abundant younger veinlets consisting mainly of coarse crystalline pyroxmangite and spessartine, with minor amounts of quartz, rhodochrosite, baryte and pyrosmalite-(Mn). It occurs rarely as aggregates embedded in pyroxmangite–spessartine veinlets together with rhodochrosite, quartz, baryte and pyrosmalite-(Mn). Its origin is probably due to an Alpine metamorphic–hydrothermal event, favouring the remobilisation of Mn and REE in the Július manganese ore deposit.

Physical and optical properties

Ferriandrosite-(Ce) occurs as subhedral grains and polycrystalline aggregates up to 0.3 mm in size (Figs 1, 2), enclosed in pyroxmangite–spessartine matrix. Ferriandrosite-(Ce) is dark brown, with a light-brown streak and vitreous lustre and it is non-fluorescent in shortwave and longwave ultraviolet light. The Mohs hardness is estimated at ~6½ to 7 based on analogy to other members of the allanite group. It is brittle, with no observable cleavage or fracture. A density of 4.321 g·cm⁻³ was calculated using the unit-cell volume refined from the single-crystal X-ray diffraction data and empirical chemical formula.



Figure 1. Dark brown aggregate of ferriandrosite-(Ce) enclosed in pyroxmangite (light pink)–spessartine (light yellow) matrix. Field of view is 2.06 mm. Photo L. Hrdlovič. Holotype material (P1P 2/2023, polished section Be-5).

Ferriandrosite-(Ce) is optically biaxial (+), with weak pleochroism and high surface relief. Other optical properties were not measured because of relatively strong compositional zoning of the studied aggregates and the presence of intimate intergrowths between the two distinct members of the epidote supergroup. In agreement with Armbruster et al. (2006), it is recognised that optical data can be ambiguous and have some limitations in identifying some chemically complex minerals like those belonging to the allanite group. The mean refractive index of ferriandrosite-(Ce), obtained from the Gladstone–Dale relationship (Mandarino, 1979, 1981) using ideal end-member formula and calculated density is 1.832.

Chemical composition

Quantitative chemical (wavelength dispersive spectroscopy) analyses of ferriandrosite-(Ce) were carried out using a JEOL-JXA850F electron microprobe (Earth Science Institute, Slovak Academy of Sciences, Banská Bystrica, Slovakia). The following conditions were applied: accelerating voltage 15 kV, probe current 20 nA, counting time 20s on peak and 10s for background. The diameter of the electron beam ranged from 2–4 µm; ZAF correction was used. The following standards, X-ray lines and crystals were used: diopside (CaKα, PETL and MgKα, TAP); UO₂ (UMβ, PETL); orthoclase (KKα, PETL and SiKα, TAP); thorianite (ThMα, PETL); tugtupite (ClKα, PETL); crocoite (PbMβ, PETL); YPO₄ (YLα, PETL); fluorite (FKα, LDE1); albite (NaKα, TAP and AlKα, TAP); LaPO₄ (LaLα, LIFH); CePO₄ (CeLα, LIFH); NdPO₄ (NdLα, LIFH); PrPO₄ (PrLβ, LIFH); EuPO₄ (EuLα, LIFH); SmPO₄ (SmLβ, LIFH); TbPO₄ (TbLα, LIFH); GdPO₄ (GdLβ, LIFH); ErPO₄ (ErLα, LIFH); TmPO₄ (TmLα, LIFH); DyPO₄ (DyLβ, LIFH); YbPO₄ (YbLα, LIFH); HoPO₄ (HoLβ, LIFH); LuPO₄ (LuLα, LIFH); hematite (FeKα, LIF); rhodonite (MnKα, LIF); Cr₂O₃ (CrKα, LIF); ScVO₄ (VKα, LIF); and rutile (TiKα, LIF). The detection limit (1σ) of every element ranged from 61–881 ppm. REE interferences were solved by overlap corrections as well as F / Fe and F / Ce X-ray line coincidences.

As shown by back-scattered electron images (Fig. 3), the sample studied is chemically zoned. Four different chemical domains were identified. One of them corresponds to the chemical domain

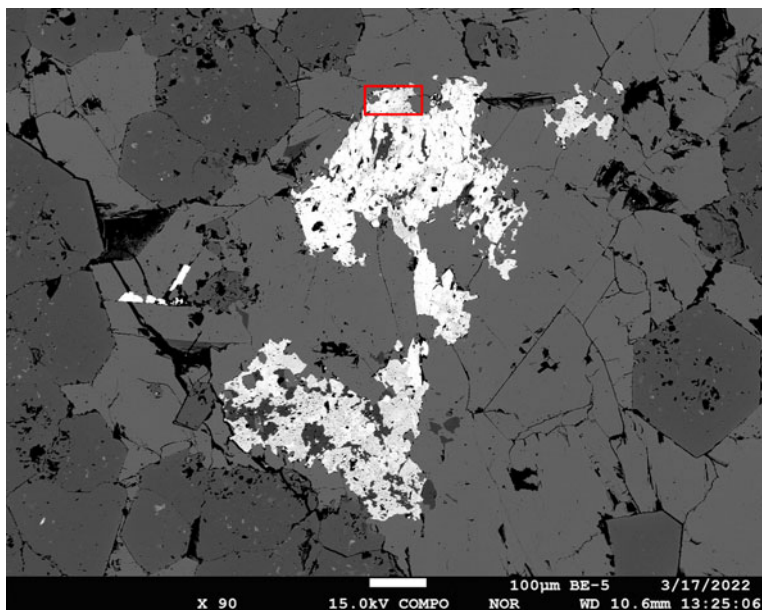


Figure 2. Aggregates and subhedral grains of ferriandrosite-(Ce) (white) enclosed in pyroxmangite (light grey) associated with euhedral crystals of spessartine (dark grey). The red box indicates the area where the grain used for single-crystal X-ray diffraction was picked up. Back-scattered electron (BSE) photo T. Mikuš. Holotype material (P1P 2/ 2023, polished section Be-5).

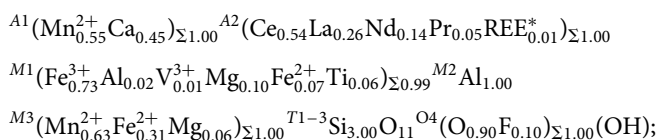
(‘domain A’) characterised through single-crystal X-ray diffraction and its chemical data are given in Table 1 (average of 4 spot analyses). The content of Fe₂O₃ and FeO and the amount of H₂O were recalculated in order to achieve 8 (A+M+T) atoms per formula unit (pfu). If the full oxidation of Fe is not sufficient, then Mn is also partially oxidised.

The empirical formula of ferriandrosite-(Ce), based on 13 anions pfu, distributing the chemical constituents among different structural sites, in agreement with the crystal structure refinement (see below), is (with rounding errors and REE* corresponding to minor REE) $A^1(Mn_{0.63}^{2+}Ca_{0.35}Ce_{0.02})_{\Sigma 1.00} A^2(Ce_{0.53}La_{0.27}Nd_{0.14}Pr_{0.05}REE^*_{0.01})_{\Sigma 1.00} M^1(Fe_{0.41}^{3+}Al_{0.12}V_{0.01}^{3+}Mg_{0.40}Ti_{0.05})_{\Sigma 0.99} M^2Al_{1.00} M^3(Mn_{0.75}^{2+}Fe_{0.22}^{2+}Mg_{0.03})_{\Sigma 1.00} T^{1-3}Si_{3.00}O_{11}^{O^4}(O_{0.67}F_{0.33})(OH)$. It corresponds to a ideal formula of ferriandrosite-(Ce) of MnCeFe³⁺AlMn²⁺(Si₂O₇)(Si₄O₄)O(OH).

Table 1 also reports the average compositions of the other three domains (B, C, and D). The crystal chemical formulae for

these three domains are the following:

domain B:



domain C:

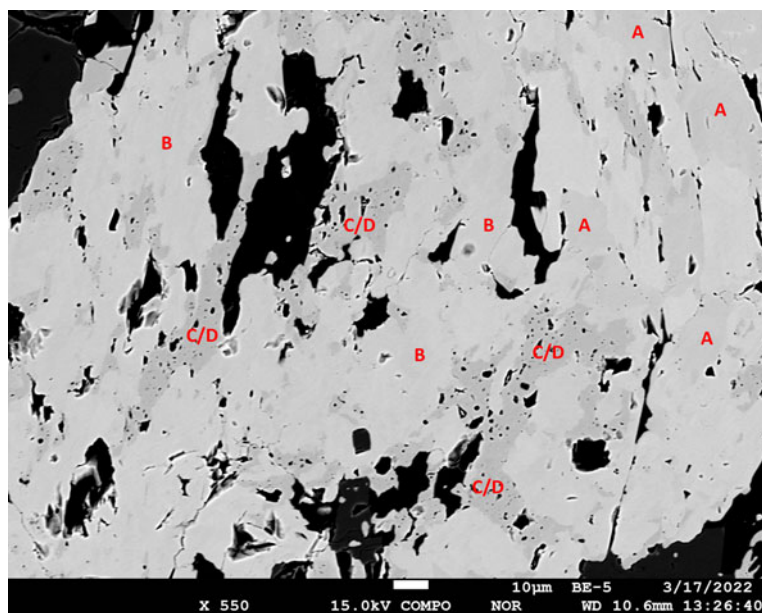
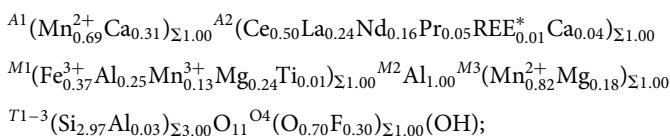


Figure 3. Back-scattered electron (BSE) image showing the chemical inhomogeneity of the material studied. Different chemical domains are shown. Domains C/D are hardly distinguishable in BSE, owing to similar grey hues. BSE photo T. Mikuš.

Table 1. Electron microprobe data (in wt.%) of ferriandrosite-(Ce) (domains A–C) and associated vielleaureite-(Ce) (domain D).

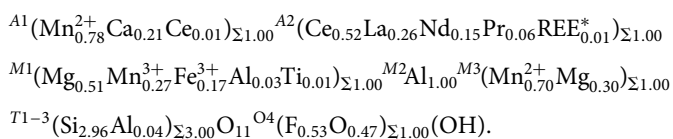
Domain	A			B	C	D
	Mean	Range n = 4	e.s.d.	wt.% n = 8	wt.% n = 2	wt.% n = 2
SiO ₂	29.43	29.29–29.52	0.10	29.02	29.57	29.62
TiO ₂	0.67	0.44–0.92	0.21	0.80	0.17	0.17
ThO ₂	0.02	0.00–0.04	0.02	0.04	–	–
Al ₂ O ₃	9.29	8.70–9.56	0.40	8.39	10.82	9.05
V ₂ O ₃	0.14	0.09–0.19	0.04	0.18	–	–
Cr ₂ O ₃	0.02	0.00–0.09	0.04	0.01	–	0.06
Y ₂ O ₃	0.01	0.00–0.03	0.01	0.02	0.04	0.04
La ₂ O ₃	7.14	7.04–7.22	0.08	6.92	6.36	7.09
Ce ₂ O ₃	14.86	14.74–14.93	0.08	14.27	13.73	14.58
Pr ₂ O ₃	1.43	1.28–1.60	0.14	1.30	1.39	1.53
Nd ₂ O ₃	3.80	3.62–3.95	0.17	3.85	4.40	4.30
Eu ₂ O ₃	0.14	0.11–0.17	0.03	0.16	0.21	0.13
Dy ₂ O ₃	–	–	–	0.04	–	–
Ho ₂ O ₃	0.05	0.00–0.19	0.10	–	0.04	–
Er ₂ O ₃	0.07	0.00–0.14	0.08	0.07	–	0.03
Tm ₂ O ₃	0.01	0.00–0.05	0.02	0.01	0.04	0.03
Yb ₂ O ₃	–	–	–	0.01	–	–
Lu ₂ O ₃	0.01	0.00–0.05	0.02	–	0.03	0.04
Fe ₂ O _{3(tot)}	8.20	7.84–8.43	0.26	14.23	4.85	2.31
Fe ₂ O ₃ ¹	5.40	–	–	9.40	–	–
FeO ¹	2.52	–	–	4.35	–	–
MgO	2.84	2.28–3.32	0.43	1.05	2.84	5.46
CaO	3.21	2.91–3.58	0.28	4.03	3.23	1.94
MnO _{tot}	16.00	15.16–17.07	0.80	13.52	19.32	20.67
MnO ¹	16.00	–	–	13.52	17.77	17.52
Mn ₂ O ₃ ¹	–	–	–	–	1.73	3.50
PbO	0.01	0.00–0.03	0.01	0.01	–	–
F	1.01	0.86–1.26	0.17	0.32	0.95	1.68
Cl	0.01	0.00–0.01	0.01	0.01	0.02	0.02
H ₂ O _{calc} ²	1.47	–	–	1.45	1.49	1.50
O = –(F,Cl)	–0.43	–	–	–0.14	–0.40	–0.71
Total	99.13	–	–	99.06	99.28	99.89

Notes: e.s.d. = estimated standard deviation. The symbol ‘–’ indicates that the chemical constituent was below the detection limit.

¹Calculated to yield 8 (A+M+T) cations.

²Calculated to yield 1 OH group per formula unit.

domain D:



Domains B and C correspond to the end-member formula $\text{MnCeFe}^{3+}\text{AlMn}^{2+}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$, i.e. to ferriandrosite-(Ce), however domain D leads to end-member formula $\text{MnCeMgAlMn}^{2+}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{F}(\text{OH})$ and corresponds to a recently approved new member of the dollaseite group, vielleaureite-(Ce) (Ragu *et al.*, 2023). The domains A and B can be easily distinguished in back-scattered electron images, whereas C and D domains have similar grey hues. In the material studied, there is a clear positive correlation between Mg and F contents, in agreement with the substitution ${}^{M1}\text{Fe}^{3+} + \text{O}^4\text{O}^{2-} = {}^{M1}\text{Mg}^{2+} + \text{O}^4\text{F}^-$ (Fig. 4).

X-ray crystallography

X-ray diffraction study and structural refinements

Single-crystal X-ray intensity data were collected using a Bruker D8 Venture four-circle diffractometer equipped with an air-cooled

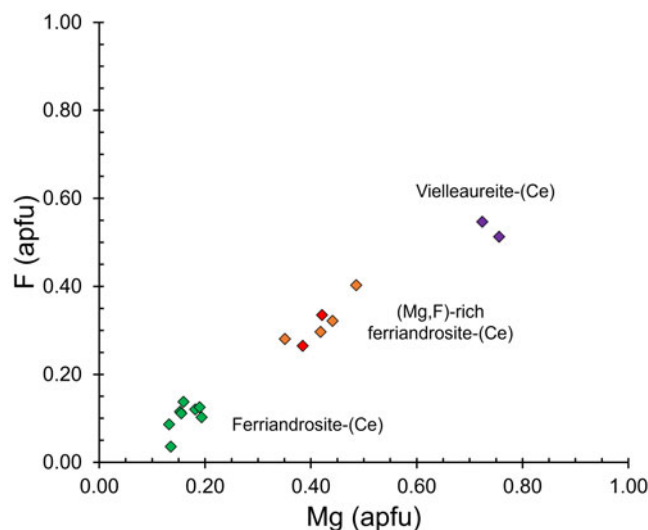


Figure 4. Relationship between F and Mg atoms per formula unit (apfu). Different colours correspond to the chemical homogenous domains: A = orange, B = green, C = red and D = violet.

Photon III detector, and microfocus MoK α radiation. The detector-to-crystal distance was set to 38 mm. Data were collected using φ scan modes, in 0.5° slices, with an exposure time of 30 s per frame. A total of 1644 frames were collected and they were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for Lorentz-polarisation, absorption, and background using the package of software Apex4 (Bruker AXS, 2022). Unit-cell parameters were refined on the basis of the XYZ centroids of 9895 reflections above 20 σ_1 with $7.898^\circ < 2\theta < 66.315^\circ$. Ferriandrosite-(Ce) is monoclinic, space group $P2_1/m$ (#11), with the following unit-cell parameters: $a = 8.8483(4)$ Å, $b = 5.7307(3)$ Å, $c = 10.0314(5)$ Å, $\beta = 113.3659(15)^\circ$, $V = 10.0314(5)$ Å³ and $Z = 2$.

The crystal structure of ferriandrosite-(Ce) was refined using *Shelxl-2018* (Sheldrick, 2015) starting from the atomic coordinates of ferriakasaite-(Ce) (Biagioni *et al.*, 2019). The position of the H atoms was located through the difference-Fourier map. The following scattering curves for neutral atoms, taken from the *International Tables for Crystallography* (Wilson, 1992), were used: Mn vs. Ca at A1, Ce vs. Ca at A2, Fe vs. Mg at M1, Al vs. Fe at M2, Mn vs. Mg at M3, Si at T1–T3 sites, H at the H10 site, and O at all the O sites but the O4 position, whose site occupancy was modelled using the scattering curves of O vs. F. Refinement of the O/F atomic ratio pointed to $\text{O}_{0.65(6)}\text{F}_{0.35(5)}$, in agreement with the electron microprobe data. The anisotropic structural model (only H was refined isotropically) converged to $R = 0.0210$ for 1910 reflections with $F_o > 4\sigma(F_o)$ and 127 refined parameters.

Details of data collection and refinement are given in Table 2. Fractional atom coordinates and equivalent isotropic or isotropic displacement parameters are reported in Table 3. Table 4 reports selected bond distances, whereas Table 5 compares observed and calculated mean atomic numbers at the A1, A2 and M1–M3 sites of ferriandrosite-(Ce). Finally, Table 6 gives the weighted bond-valence calculations obtained using the bond-valence parameters of Brese and O’Keeffe (1991). The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Table 2. Crystal and experimental data for ferriandrosite-(Ce).

Crystal data	
Crystal size (mm)	0.115 × 0.055 × 0.040
Cell setting, space group	Monoclinic, $P2_1/m$
a (Å)	8.8483(4)
b (Å)	5.7307(3)
c (Å)	10.0314(5)
β (°)	113.3659(15)
V (Å ³)	466.95(4)
Z	2
Data collection and refinement	
Radiation, wavelength (Å)	MoK α , 0.71073
Temperature (K)	293(2)
$2\theta_{\max}$ (°)	66.314
Measured reflections	11900
Unique reflections	1921
Reflections with $F_o > 4\sigma(F_o)$	1910
R_{int}	0.0302
$R\sigma$	0.0204
Range of h, k, l	$-11 \leq h \leq 13$ $-8 \leq k \leq 8$ $-15 \leq l \leq 14$
$R [F_o > 4\sigma(F_o)]$	0.0210
R (all data)	0.0211
wR (on F_o^2)*	0.0533
Goof	1.326
Number of least-squares parameters	127
Maximum and minimum residual peak ($e^- \text{ \AA}^{-3}$)	1.46 (at 1.27 Å from A2) -0.67 (at 0.75 Å from A2)

$$*w = 1/[\sigma^2(F_o^2) + (1.6608P)^2].$$

Owing to the inhomogeneous nature of the material studied, powder X-ray diffraction data were collected only on the same crystal used for single-crystal X-ray diffraction, simulating a Gandolfi-like pattern using a Bruker D8 Venture single-crystal diffractometer equipped with a Photon III area detector and microfocused CuK α radiation. The observed X-ray diffraction pattern is reported in Table 7. Unit-cell parameters refined for the monoclinic space group $P2_1/m$ from the powder data using the method of Holland and Redfern (1997) on the basis of 19 unequivocally indexed reflections are as follows: $a = 8.889(2)$ Å,

Table 3. Sites, fractional coordinates and isotropic (*) or equivalent isotropic displacement parameters (in Å²) for ferriandrosite-(Ce).

Site	x/a	y/b	z/c	$U_{\text{eq}}/U_{\text{iso}}^*$
A1	0.76127(8)	3/4	0.15277(6)	0.01271(15)
A2	0.59206(2)	3/4	0.42861(2)	0.01022(6)
M1	0	0	0	0.0093(2)
M2	0	0	1/2	0.0076(3)
M3	0.31659(7)	1/4	0.20660(6)	0.01323(17)
Si1	0.34794(11)	3/4	0.03373(10)	0.00853(18)
Si2	0.69473(11)	1/4	0.28300(10)	0.00785(18)
Si3	0.19079(11)	3/4	0.32318(10)	0.00731(18)
O1	0.2426(2)	0.9904(3)	0.03055(18)	0.0130(3)
O2	0.3157(2)	0.9723(3)	0.36055(18)	0.0106(3)
O3	0.8047(2)	0.0126(3)	0.33408(19)	0.0123(3)
O4	0.0584(3)	1/4	0.1394(3)	0.0130(6)
O5	0.0487(3)	3/4	0.1569(3)	0.0115(4)
O6	0.0803(3)	3/4	0.4219(3)	0.0099(4)
O7	0.5151(3)	3/4	0.1758(3)	0.0139(5)
O8	0.5573(4)	1/4	0.3492(3)	0.0190(6)
O9	0.6010(3)	1/4	0.1060(3)	0.0140(5)
O10	0.0922(3)	1/4	0.4334(3)	0.0100(4)
H10	0.065(9)	1/4	0.334(8)	0.041(19)*

$b = 5.7356(16)$ Å, $c = 10.0262(17)$ Å, $\beta = 113.504(17)^\circ$, $V = 468.75(12)$ Å³ and $Z = 2$.

Crystal structure description

Ferriandrosite-(Ce) is isotypic with the other members of the epidote supergroup (e.g. Dollase, 1968). The crystal structure can be described as formed by single chains of edge-sharing M2-centered octahedra and zig-zag chains of M1-centered octahedra with M3-centered octahedra attached on alternate sides along b . Octahedral chains are bonded to Si₂O₇ and SiO₄ groups. In this octahedral-tetrahedral framework, two kinds of structural cavities occur, i.e. the smaller cavity hosting the nine-fold coordinated A1 site and the larger one where the ten-fold coordinated A2 site is located.

Cation sites

In ferriandrosite-(Ce), the A1 site has a mixed (Mn,Ca) site occupancy, with a Mn/(Mn+Ca) atomic ratio of 0.65. Mean atomic number (Table 5) and weighted bond-valence sum (Table 6) agree with this occupancy. As discussed by previous authors (e.g. Bonazzi *et al.*, 1996; Nagashima *et al.*, 2010, 2013, 2015), the replacement of Ca²⁺ by Mn²⁺ promotes a decrease in the coordination number of the A1 site that can be described as six-fold coordinated. This coordination number decrease is related to the shift of the O6 and O9 atoms away from the A1 site, whereas O3 and O1 get closer to the cation site; O5 and O7 are unaffected by these changes. If one defines the difference between the bond distances A1–O6 and A1–O5 (with O6 and O5 being the seventh and sixth ligands of A1, respectively) as δ_{7-6} , a direct relation between the Mn²⁺ content at A1 and the δ_{7-6} value can be observed (e.g. Bonazzi *et al.*, 1996; Nagashima *et al.*, 2010, 2013, 2015; Biagioni *et al.*, 2019). In ferriandrosite-(Ce), this difference is 0.508 Å, to be compared with the theoretical value of 0.502 Å calculated on the basis of the regression line given by Bonazzi *et al.* (1996). Moreover, a decrease in the $^{[6]}<A1-O>$ can be observed and indeed, ferriandrosite-(Ce) shows the low value of 2.314 Å, to be compared with 2.320, 2.322, 2.310 and 2.335 Å reported for manganiandrosite-(La), manganiandrosite-(Ce), vanadoandrosite-(Ce) and ferriandrosite-(La), respectively (Bonazzi *et al.*, 1996; Cenki-Tok *et al.*, 2006; Nagashima *et al.*, 2015).

The shift of the O9 site away from the cation located at the A1 position is associated with a reduction of the Si1–O9–Si2 bond angle that is related not only to the occupancy at the A1 site but also to the average bond length at M3 (e.g. Cenki-Tok *et al.*, 2006). In ferriandrosite-(Ce), O9 is at 3.148 and 3.227 Å from A1, with a Si1–O9–Si2 bond angle of 137.6(2)°; this angle is similar to those reported by Cenki-Tok *et al.* (2006) for manganiandrosite-(Ce) and vanadoandrosite-(Ce), i.e. 137.4(6) and 137.4(8)°, respectively, and slightly smaller than that given by Nagashima *et al.* (2015) for ferriandrosite-(La), i.e. 139.4(2)°; however, it is smaller than those reported by Biagioni *et al.* (2019) in manganiakasakaite-(La) and ferriakasakaite-(Ce), i.e. 140.88(19) and 144.47(14)°, respectively.

The A2 site of ferriandrosite-(Ce) is a REE-bearing site, with Ce as the dominant element. Bonazzi *et al.* (1996) observed a relationship between the ratio of the cell parameters c/V and the REE content in species belonging to the series piemontite – ‘androsite’, as well as between the amount of REE and the β angle. In ferriandrosite-(Ce), the c/V ratio is 0.0215, and the β angle is 113.37°. On the basis of the relationship given by Bonazzi *et al.*

Table 4. Selected bond distances (in Å) in ferriandrosite-(Ce).

A1–O3	2.2463(18) ×2	A2–O7	2.351(3)	M1–O4	1.9242(16) ×2	M2–O3	1.8846(17) ×2
A1–O7	2.279(3)	A2–O2	2.5104(17) ×2	M1–O5	2.0439(18) ×2	M2–O10	1.8966(16) ×2
A1–O1	2.2911(19) ×2	A2–O10	2.580(2)	M1–O1	2.0694(18) ×2	M2–O6	1.9010(16) ×2
A1–O5	2.527(3)	A2–O2	2.5969(17) ×2	<M1–O>	2.012	<M2–O>	1.894
A1–O6	3.035(2)	A2–O3	2.8710(19) ×2				
A1–O9	3.1487(11) ×2	A2–O8	2.9572(7) ×2				
A1–O9	3.227(3)	<A2–O>	2.680				
<A1–O>	2.644						
M3–O8	2.041(3)	Si1–O7	1.596(3)	Si2–O8	1.600(3)	Si3–O2	1.6301(18) ×2
M3–O4	2.110(2)	Si1–O9	1.634(3)	Si2–O3	1.6303(18) ×2	Si3–O5	1.643(3)
M3–O2	2.2196(18) ×2	Si1–O1	1.6413(18) ×2	Si2–O9	1.635(3)	Si3–O6	1.644(3)
M3–O1	2.2586(19) ×2	<Si1–O>	1.628	<Si2–O>	1.624	<Si3–O>	1.637
<M3–O>	2.185						

Table 5. Refined site scattering vs. calculated site scattering (in electrons) and site population (in apfu) at the A and M sites in ferriandrosite-(Ce).

Site	Refined site scattering	Proposed site population	Calculated site scattering
A1	23.16	Mn _{0.65} Ca _{0.35}	23.25
A2	56.29	Ce _{0.55} La _{0.25} Nd _{0.15} Pr _{0.05}	58.10
M1	18.30	Fe _{0.41} Al _{0.12} V _{0.01} Mg _{0.41} Ti _{0.05}	18.47
M2	13.27	Al _{1.00}	13.00
M3	24.95	Mn _{0.75} Fe _{0.22} Mg _{0.03}	24.83

(1996), considering $\Sigma\text{REE} = 1$ atom per formula unit (apfu), one should have $c/V = 0.0213$ and $\beta = 113.4^\circ$, in agreement with observed values. Actually, as stressed by Nagashima *et al.* (2015), the value of the β angle is also affected by the Mn²⁺ at the A1 site. The value observed in ferriandrosite-(Ce) can be compared with those reported for other ‘androsites’, i.e. 113.88° in manganiandrosite-(La) (Bonazzi *et al.*, 1996), 113.84° in ferriandrosite-(La) (Nagashima *et al.*, 2015), 113.42° in manganiandrosite-(Ce), and 113.09° in vanadoandrosite-(Ce) (Cenki-Tok *et al.*, 2006).

Among the three independent M sites, cation assignments were based on refined mean atomic numbers (Table 5) and bond-valence sums (Table 6). M2 hosts Al only; a possible minor replacement of Al by Fe³⁺ (~2 at.%) or Ti⁴⁺ (~3 at.%) cannot be discarded, as observed in other samples, e.g. in manganiandrosite-(La) by Bonazzi *et al.* (1996) who reported

4% Fe³⁺ in M2 and in ferriandrosite-(La) by Nagashima *et al.* (2015) who hypothesised the presence of 0.04 Ti at the M2 site. The <M2–O> distance is 1.894 Å, to be compared with those observed in other androsites, i.e. 1.892 Å in manganiandrosite-(La) (Bonazzi *et al.*, 1996), 1.902 and 1.894 Å in manganiandrosite-(Ce) and vanadoandrosite-(Ce), respectively (Cenki-Tok *et al.*, 2006), and 1.902 Å in ferriandrosite-(La) (Nagashima *et al.*, 2015). The M3 site is occupied mainly by Mn²⁺, with minor Fe²⁺ and trace Mg²⁺. This occupancy is in keeping with the large observed <M3–O>, 2.185 Å. This average distance is larger than that observed in manganiandrosite-(La) (i.e. 2.159 Å, where 0.28 M³⁺ apfu occur), and similar to those reported by Cenki-Tok *et al.* (2006) for M3 sites in manganiandrosite-(Ce) (2.197 Å) and vanadoandrosite-(Ce) (2.195 Å), where only Mn²⁺ occurs. The slight contraction observed in ferriandrosite-(Ce) is probable due to the minor Fe²⁺–Mn²⁺ replacement, in agreement with the smaller ionic radius of ^{VI}Fe²⁺ (0.78 Å) with respect to that of ^{VI}Mn²⁺ (0.83 Å), according to Shannon (1976). The M1 site has a complex chemistry, with mainly Fe³⁺ and Mg²⁺, minor Al and Ti, and trace amounts of V. Whereas Fe³⁺ and Mg²⁺ occur in the same amount (0.41 apfu), the sum of trivalent cations (Fe³⁺ + Al + V) is larger than those of divalent ones (Mg), i.e. 0.54 vs. 0.41, with Fe³⁺ as the dominant constituent of the dominant valence (e.g. Bosi *et al.*, 2019a, 2019b). The average bond distance is 2.012 Å, similar to those observed in other androsites, i.e. 2.010, 2.019, 2.011 and 2.002 Å for manganiandrosite-(La), manganiandrosite-(Ce),

Table 6. Weighted bond-valence balance (in vu) in ferriandrosite-(Ce).

	A1	A2	M1	M2	M3	Si1	Si2	Si3	Σ anions
O1	0.31 ^{1×2}		0.39 ^{1×2}		0.27 ^{1×2}	0.95 ^{1×2}			1.92
O2		0.38 ^{1×2} 0.30 ^{1×2}			0.30 ^{1×2}			0.98 ^{1×2}	1.96
O3	0.35 ^{1×2}	0.14 ^{1×2}		0.53 ^{1×2}			0.98 ^{1×2}		2.00
O4*			2x→0.54 ^{1×2}		0.37				1.45
O5	0.17		2x→0.42 ^{1×2}					0.95	1.96
O6	0.04			2x→0.51 ^{1×2}				0.95	2.01
O7	0.32	0.58				1.08			1.98
O8		2x→0.11 ^{1×2}			0.49		1.07		1.78
O9	2x→0.03 ^{1×2}					0.97	0.97		2.00
O10*		0.31		2x→0.51 ^{1×2}					1.33
Σ cations	1.91	2.75	2.70	3.10	2.00	3.95	4.00	3.86	
Theoretical	2.00	3.00	2.64	3.00	2.00	4.00	4.00	4.00	

Notes: left and right superscripts indicate the number of equivalent bonds involving anions and cations, respectively. For sites with mixed occupancy, the bond valences have been weighted according to site populations given in Table 5.

*Anion positions involved in the hydrogen bond O10–H...O4 [d (O10...O4) = 2.843(4) Å]. According to Ferraris and Ivaldi (1988), the bond-valence sum (BVS) of such a bond is 0.17 vu. Consequently, the corrected BVS at O4 and O10 sites are 1.62 and 1.16 vu, respectively.

Table 7. Powder X-ray diffraction data (d in Å) for ferriandrosite-(Ce).

l_{obs}	d_{obs}	l_{calc}	d_{calc}	hkl
w	9.3	25	9.21	0 0 1
w	8.2	21	8.12	1 0 0
m	7.8	21	7.82	$\bar{1}$ 0 1
vw	5.17	19	5.16	1 0 1
vw	4.92	7	4.93	$\bar{1}$ 0 2
w	4.69	19	4.683	1 1 0
vw	4.62	10	4.604	0 0 2
vw	3.935	2	3.911	$\bar{2}$ 0 2
w	3.743	11	3.738	$\bar{1}$ 1 2
vw	3.584	11	3.589	0 1 2
ms	3.511	44	3.499	$\bar{2}$ 1 1
w	3.323	14	3.316	2 1 0
vw	3.268	11	3.268	2 0 1
		100	2.888	$\bar{1}$ 1 3
vs	2.895	21	2.887	$\bar{3}$ 0 2
		41	2.865	0 2 0
		14	2.839	2 1 1
		11	2.708	3 0 0
m	2.704	32	2.706	0 1 3
		34	2.702	1 2 0
		54	2.610	$\bar{3}$ 1 1
s	2.615	26	2.580	2 0 2
vw	2.486	5	2.489	$\bar{1}$ 0 4
vw	2.381	11	2.373	$\bar{3}$ 1 3
w	2.316	13	2.311	$\bar{2}$ 2 2
vw	2.261	4	2.265	$\bar{2}$ 1 4
m	2.177	22	2.172	4 0 1
		18	2.155	2 2 1
		19	2.109	$\bar{2}$ 2 3
mw	2.112	14	2.095	0 2 3
		2	2.034	$\bar{3}$ 2 2
w	2.032	3	2.031	4 1 1
		2	1.958	2 1 3
vw	1.963	2	1.955	4 0 4
vw	1.917	16	1.917	2 2 2
w	1.872	10	1.869	$\bar{2}$ 2 4
w	1.8291			
w	1.7721			
w	1.7251			
mw	1.657	13	1.659	$\bar{1}$ 3 3
		10	1.631	$\bar{1}$ 0 6
mw	1.600	21	1.615	4 2 4
		12	1.600	$\bar{3}$ 3 1

Notes: Intensity and d_{hid} were calculated using the software *PowderCell* 2.3 (Kraus and Nolze, 1996) on the basis of the structural model given in Table 3. Only the reflections with $l_{\text{calc}} > 10$ are given, if not observed. Intensities were visually estimated: vs = strong; s = strong; ms = medium-strong; m = medium; mw = medium-weak; w = weak; vw = very weak. 1These reflections correspond to more than two calculated reflections with $l < 10$.

vanadoandrosite(Ce) and ferriandrosite-(La), respectively (Bonazzi *et al.*, 1996; Cenki-Tok *et al.*, 2006; Nagashima *et al.*, 2015). As discussed by Cenki-Tok *et al.* (2006), the occurrence of Mn^{3+} at the M1 site increases the difference between the distances M1–O1 and M1–O4, owing to the Jahn–Teller effect shown by this cation; this difference is 0.231 and 0.227 Å in manganiandrosite-(La) and manganiandrosite-(Ce), respectively (Bonazzi *et al.*, 1996; Cenki-Tok *et al.*, 2006), whereas in vanadoandrosite-(Ce) and ferriandrosite-(La) this difference is smaller, i.e. 0.161 and 0.137 Å, respectively (Cenki-Tok *et al.*, 2006; Nagashima *et al.*, 2015). In ferriandrosite-(Ce), a difference of 0.145 Å was observed, in agreement with the absence of Mn^{3+} at the M1 site.

Three independent Si-centred tetrahedra occur in ferriandrosite-(Ce). Si1 and Si2 are bonded, sharing the O9 atom and forming Si_2O_7 groups; as discussed above, the Si1–O9–Si2 bond angle is sensitive to the occupancy at the A1 and

the bond length at the M3 site. Si3 forms an isolated SiO_4 group. Average bond distances range between 1.624 and 1.637 Å, with bond-valence sums between 3.86 and 4.00 valence units (vu).

Anion sites

Ten independent anion sites occur in ferriandrosite-(Ce). Among them, eight are four-fold coordinated, with bond-valence sums ranging between 1.78 and 2.01 vu; these sites are occupied by O^{2-} . Two sites, namely O4 and O10, are three-fold coordinated and are underbonded, with bond-valence sums of 1.45 and 1.33 vu, respectively. The crystal-structure refinement allowed us to locate a residual maximum that was interpreted as a H atom located at 0.95(9) Å from O10. Moreover, the O10...O4 distance, 2.841(4) Å, agrees with a H bond, corresponding to a bond strength, calculated according to Ferraris and Ivaldi (1988), of 0.17 vu. In this way, the correct bond-valence sums at O4 and O10 are 1.62 and 1.16 vu, respectively. These values agree with the mixed nature (O,F) of the O4 site, with an O/(O+F) atomic ratio close to 0.65 (in accord with both chemical and structural data) and the occurrence of (OH) at O10. Moreover, it is worth noting that the O10...O4 is similar to those observed in manganiandrosite-(Ce), ferriandrosite-(La), and vanadoandrosite-(Ce) (ca. 2.87 Å – Cenki-Tok *et al.*, 2006; Nagashima *et al.*, 2015), and shorter than that reported by Bonazzi *et al.* (1996) in manganiandrosite-(La), i.e. 2.94 Å. This difference may be explained considering that the O4 site is bonded to two M1 and one M3 sites; in all the known species belonging to the androsite series but manganiandrosite-(La), the M3 site has a virtually pure M^{2+} occupancy. On the contrary, the latter species has 0.28 M^{3+} apfu, and consequently the bond strength on O4 is higher than in the other cases, thus favouring an elongation (= a weakening) of the H bond.

Relations with other epidote supergroup minerals

Ferriandrosite-(Ce) is a new member of the allanite group, composed, after the addition of this new species, of 18 minerals (Table 8). Five root-names, based on different combinations of cations at the A1 and M3 sites, are currently known: allanite ($\text{A1} = \text{Ca}^{2+}$, $\text{M3} = \text{Fe}^{2+}$), akasakaite ($\text{A1} = \text{Ca}^{2+}$, $\text{M3} = \text{Mn}^{2+}$), androsite ($\text{A1} = \text{Mn}^{2+}$, $\text{M3} = \text{Mn}^{2+}$), dissakisite ($\text{A1} = \text{Ca}^{2+}$, $\text{M3} = \text{Mg}^{2+}$), and uedaite ($\text{A1} = \text{Mn}^{2+}$, $\text{M3} = \text{Fe}^{2+}$).

The name ‘androsite’ was first introduced by Bonazzi *et al.* (1996) on the basis of a sample from a small metamorphic Mn ore body in the Andros Island, Cyclades, Greece. The new species was named ‘androsite-(La)’, later renamed manganiandrosite-(La) by Armbruster *et al.* (2006), owing to the dominance of Mn^{3+} at the M1 site. Later, Cenki-Tok *et al.* (2006) described the Ce-analogue manganiandrosite-(Ce) from the Praborna mine (Aosta Valley, Italy), along with the new species vanadoandrosite-(Ce), that has V^{3+} as the dominant cation at the M1 position, from a Mn ore deposit located near Vielle-Aure, Hautes-Pyrénées, France. Finally, Nagashima *et al.* (2015) identified the Fe^{3+} -analogue of manganiandrosite-(La), i.e. ferriandrosite-(La) from a Mn deposit in the Mie Prefecture, Japan. The Ce-analogue of this latter species, ferriandrosite-(Ce), is now added to this series. As reported in the Introduction, samples corresponding to this species were reported by Girtler *et al.* (2013) and Kolitsch *et al.* (2021). In particular, the former authors

Table 8. Valid mineral species belonging to the allanite group.

Species	A1	A2	M1	M2	M3	Reference
Allanite-(Ce)	Ca	Ce	Al	Al	Fe ²⁺	Thomson (1811)
Allanite-(La)	Ca	La	Al	Al	Fe ²⁺	Orlandi and Pasero (2006)
Allanite-(Nd)	Ca	Nd	Al	Al	Fe ²⁺	Škoda et al. (2012)
Allanite-(Y)	Ca	Y	Al	Al	Fe ²⁺	Nel et al. (1949)
Dissakisite-(Ce)	Ca	Ce	Al	Al	Mg	Grew et al. (1991)
Dissakisite-(La)	Ca	La	Al	Al	Mg	Tumiati et al. (2005)
Ferriakasaite-(Ce)	Ca	Ce	Fe ³⁺	Al	Mn ²⁺	Biagioni et al. (2019)
Ferriakasaite-(La)	Ca	La	Fe ³⁺	Al	Mn ²⁺	Nagashima et al. (2015)
Ferriallanite-(Ce)	Ca	Ce	Fe ³⁺	Al	Fe ²⁺	Kartashov et al. (2002)
Ferriallanite-(La)	Ca	La	Fe ³⁺	Al	Fe ²⁺	Kolitsch et al. (2012)
Ferriandrosite-(Ce)	Mn ²⁺	Ce	Fe ³⁺	Al	Mn ²⁺	This work
Ferriandrosite-(La)	Mn ²⁺	La	Fe ³⁺	Al	Mn ²⁺	Nagashima et al. (2015)
Manganiakasaite-(La)	Ca	La	Mn ³⁺	Al	Mn ²⁺	Biagioni et al. (2019)
Manganiandrosite-(Ce)	Mn ²⁺	Ce	Mn ³⁺	Al	Mn ²⁺	Cenki-Toc et al. (2006)
Manganiandrosite-(La)	Mn ²⁺	La	Mn ³⁺	Al	Mn ²⁺	Bonazzi et al. (1996)
Uedaite-(Ce)	Mn ²⁺	Ce	Al	Al	Fe ²⁺	Miyawaki et al. (2008)
Vanadoallanite-(La)	Ca	La	V ³⁺	Al	Fe ²⁺	Nagashima et al. (2013)
Vanadoandrosite-(Ce)	Mn ²⁺	Ce	V ³⁺	Al	Mn ²⁺	Cenki-Toc et al. (2006)

first used the name ‘ferriandrosite-(Ce)’ without approval by the IMA-CNMNC.

The partial replacement of Mn²⁺ by Ca²⁺ at the A1 site in androsite-series minerals is in keeping with the possible solid solution between members of this series and those of the akasaite series, as suggested, for instance, by Biagioni et al. (2019), who described strongly zoned grains containing ferriakasaite-(Ce), manganiandrosite-(Ce), and the potential ‘androsite-(Ce)’ end-member in samples from the Mn mineralisation of Monte Maniglia, Piedmont, Italy.

As shown in Fig. 4, the occurrence of the ‘dollaseite-type’ substitution is effective in the androsite series, as previously reported by Cenki-Tok et al. (2006). This led to the appearance of a species having end-member composition MnCeMgAlMn²⁺(Si₂O₇)(SiO₄)F(OH). Such a composition would correspond to the Mn-analogue of khristovite-(Ce), a species defined by Pautov et al. (1993) as MnCeMgAlMn²⁺(Si₂O₇)(SiO₄)F(OH) and recently described by Ragu et al. (2023) as a new mineral, vielleaureite-(Ce). Actually, as discussed by Cenki-Tok et al. (2006), there are some doubts about the actual definition of khristovite-(Ce) as the structural data, reported by Sokolova et al. (1991), suggests the dominance of Mn²⁺ at the A1 site.

Conclusions

Ferriandrosite-(Ce), Mn²⁺CeFe³⁺AlMn²⁺(Si₂O₇)(SiO₄)O(OH), is a new member of the epidote supergroup and another REE-bearing epidote first identified from Mn ore deposits. In this kind of occurrence, epidote-supergroup minerals can host REE and variable amounts of Fe and Mn, showing different oxidation states reflecting the *f*₀₂ conditions occurring during the geological evolution of the Mn-rich assemblages.

The possibility of extracting high-quality crystal-chemical information from micrometre-sized volumes of matter, as exemplified by the results obtained on the strongly zoned grains of ferriandrosite-(Ce), opens interesting future scenarios for unravelling the evolution of Mn ore deposits and the ability to

shed further light on the complex geological processes shaping our planet.

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