

Cerchiarait-(Fe) and cerchiarait-(Al), two new barium cyclosilicate chlorides from Italy and California, USA

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ABSTRACT

The ideal formula for members of the cerchiarait group is $Ba_4M_4(Si_4O_{12})O_2(OH)_4Cl_2[Si_2O_3(OH)_4]$, where M represents Mn^{3+} , Fe^{3+} or Al in the octahedral site. A suffix-based naming scheme is used in which the original cerchiarait is renamed cerchiarait-(Mn) and two new minerals are named cerchiarait-(Fe) and cerchiarait-(Al). The type localities for cerchiarait-(Fe) are the Cerchiarait mine, Liguria, Italy and the Esquire No. 7 and No. 8 claims, Big Creek, Fresno County, California, USA. The type localities for cerchiarait-(Al) are the Esquire No. 1 claim, Rush Creek, Fresno County, California, USA and the Esquire No. 7 and No. 8 claims noted above. At the Cerchiarait mine, cerchiarait-(Fe) occurs in small fractures and veinlets in a Jurassic ophiolitic sequence. It is of secondary hydrothermal origin and occurs as tan to brown thin prisms and matted fibres. Cerchiarait-(Fe) and cerchiarait-(Al) from the Esquire No. 1, No. 7 and No. 8 claims occur in parallel-bedded quartz-sanbornite vein assemblages which formed as a result of fluid interaction along the margin of the vein. At the Esquire No. 1, No. 7 and No. 8 claims, both cerchiarait-(Fe) and cerchiarait-(Al) occur as subparallel aggregates of blue to bluish green irregular prisms. Both minerals are transparent with a vitreous lustre, Mohs hardness $\sim 4\frac{1}{2}$, brittle tenacity, irregular fracture and no cleavage. The calculated density of cerchiarait-(Fe) is 3.710 g cm^{-3} ; the measured density of cerchiarait-(Al) is $3.69(3)\text{ g cm}^{-3}$ and the calculated density is 3.643 g cm^{-3} . Cerchiarait-(Fe) is uniaxial (+), with $\omega = 1.741(2)$ and $\epsilon = 1.768(2)$; it is weakly pleochroic and O is colourless and E is yellow. Cerchiarait-(Al) is uniaxial (-), with $\omega = 1.695(2)$ and $\epsilon = 1.677(2)$; it is strongly pleochroic and O is colourless and E is blue. Electron-microprobe analyses yielded empirical formulae ranging from $(Ba_{3.82}Na_{0.02}Ca_{0.04})_{\Sigma 3.88}(Fe_{3.42}Ti_{0.27}Al_{0.25}Mn_{0.04}Mg_{0.02})_{\Sigma 4.00}Si_{5.62}O_{15.47}(OH)_{9.31}Cl_{2.22}$ (Cerchiarait mine) to $Ba_{4.00}(Al_{2.40}Fe_{1.12}Mg_{0.15}Fe_{0.12}Mn_{0.06})_{\Sigma 3.85}Si_{5.78}O_{15.34}(OH)_{8.75}Cl_{2.91}$ (Esquire No. 1 claim). Cerchiarait is tetragonal with $Z = 2$ and crystallizes in space group $I4/mmm$. The cell parameters for cerchiarait-(Fe) are $a = 14.3554(12)$, $c = 6.0065(5)$ Å and $V = 1237.80(5)$ Å³; those for cerchiarait-(Al) are $a = 14.317(4)$, $c = 6.0037(18)$ Å and $V = 1230.6(6)$ Å³. In the cerchiarait-(Fe) structure, Si_4O_4 tetrahedra share corners forming a four-membered Si_4O_{12} ring. The ring is corner-linked to an edge-sharing chain of $Fe^{3+}O_6$ octahedra running parallel to c . A Cl site alternates along c with the Si_4O_{12} ring. A large channel in the framework contains Ba atoms around its periphery and statistically distributed Si_2O_7 silicate dimers and Cl atoms. The strong blue pleochroic colour is attributed to $Fe^{2+}-Fe^{3+}$ intervalence charge transfer along the octahedral chain.

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KEYWORDS: cerchiaraita-(Fe), cerchiaraita-(Al), cerchiaraita-(Mn), new mineral, crystal structure, cyclosilicate, electron microprobe analysis, intervalence charge transfer, Big Creek – Rush Creek, Fresno County, California, USA, Cerchiar mine, Liguria, Italy.

Introduction

THE sanbornite deposits which are located along Big Creek and Rush Creek (Walstrom and Leising, 2005) in Fresno County and at Trumbull Peak (Dunning and Cooper, 1999) in Mariposa County, California, USA, have yielded a wealth of exotic minerals, including 17 new species. The first of these, sanbornite, was described by Rogers (1932) from Trumbull Peak; fencooperite was described from the same locality by Roberts *et al.* (2001). Seven of the new species, namely fresnoite, krauskopfit, macdonaldite, muirite, traskite, verplanckite and walstromite, were described from Big Creek and Rush Creek by Alfors *et al.* (1965), these were followed by alforsite (Newberry *et al.*, 1981), titantaramellite (Alfors and Pabst, 1984), bigcreekite (Basciano *et al.*, 2001a), kampfite (Basciano *et al.*, 2001b), devitoite (Kampf *et al.*, 2010) and ferroericssonite (Kampf *et al.*, 2011). In this paper, we report the two new minerals, cerchiaraita-(Fe) and cerchiaraita-(Al), from Big Creek and Rush Creek.

When they were discovered at the deposits along Big Creek and Rush Creek by one of the authors (REW) in the mid-1960s, the new minerals described herein were thought to be a single phase, which was referred to as ‘mineral 10’. Following the description of cerchiaraita from the historic Cerchiar mine in the northern Apennines, Italy, by Basso *et al.* (2000), the similarity of ‘mineral 10’ to cerchiaraita was recognized by comparing their X-ray powder diffraction data. Subsequent investigations have demonstrated that ‘mineral 10’ corresponds to two species with identical frameworks, the Fe³⁺- and Al-analogues of cerchiaraita. The research has also shown that the Fe³⁺-analogue occurs at the Cerchiar mine.

The cerchiaraita group is therefore made up of three species and in accordance with Mills *et al.* (2009) they have been named using a suffix-based scheme in which cerchiaraita is the root name and the single suffix corresponds to the dominant cation (Mn, Fe or Al) in the octahedral site. The original cerchiaraita described by Basso *et al.* (2000) is renamed cerchiaraita-(Mn) and the two new minerals, described herein, are cerchiaraita-(Fe) and cerchiaraita-(Al). The new minerals (IMA 2012-012 and IMA 2012-011, respectively),

their names and the new name for the original cerchiaraita have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association.

The descriptions of the new minerals are based upon five cotype specimens deposited at the Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, USA. A specimen from the Esquire No. 1 claim, which contains crystals with compositions that are all in the Al-dominant range, has been assigned catalogue number 63519 and is referred to as ‘Esq1’. Specimens from the Esquire No. 7 and No. 8 claims, which contain crystals representing both Fe- and Al-dominant compositions, have been assigned catalogue numbers 63517 and 63518 and are referred to as ‘Esq7’ and ‘Esq8’, respectively. Specimens from the Cerchiar mine have been assigned catalogue numbers 63517 and 63518 and are referred to as ‘Cer1’ and ‘Cer2’, respectively. Crystals from Cer1 have compositions close to the Fe endmember; crystals from Cer2, are Fe-dominant and exhibit significant substitution of Mn for Fe.

Occurrence and paragenesis

Cerchiaraita-(Fe) occurs at the Cerchiar mine, Borghetto Vara, Vara Valley, La Spezia Province, Liguria, Italy and at the Esquire No. 7 and No. 8 claims, Big Creek, eastern Fresno County, California, USA. The locations of the claims are as follows: Esquire No. 7 is at SE¼ SE¼, Section 27, T11S., R25E., Mount Diablo Meridian, 36°56′40″N, 119°14′28″W; Esquire No. 8 is at SE¼ SW¼, Section 22, T11S., R25E., Mount Diablo Meridian, 36°56′42″N, 119°14′12″W. Cerchiaraita-(Al) occurs at the Esquire No. 1 claim, Rush Creek, eastern Fresno County, California, USA [which is located at NE¼ NW¼, Section 16, T11S., R25E., Mount Diablo Meridian, 37°05′N, 119°16′20″W] and also at the Esquire No. 7 and No. 8 claims, noted above. These are considered to be the type localities.

At the Cerchiar mine, cerchiaraita-(Fe) occurs in small fractures and veinlets within the metacherts of a Jurassic ophiolitic sequence. Associated minerals include aegirine, calcite,

Mn-bearing diopside (variety schefferite), hematite, K-feldspar, norrishite and quartz. The occurrence is very similar to that of cerchiarait-(Mn), which is described in detail by Basso *et al.* (2000). The new mineral is of secondary hydrothermal origin, related to re-equilibration of the ophiolitic sequences during tectonometamorphic overprinting (~80 Ma) in prehnite-pumpellyite facies conditions ($P = 2-3$ kbar, $T = 250-300^{\circ}\text{C}$) (Lucchetti *et al.*, 1988). The occurrence of cerchiarait-(Fe) in metapelites in the cherts suggests a sedimentary and/or diagenetic barium enrichment, followed by hydrothermal mobilization and concentration processes along fractures (Cabella *et al.*, 1993).

The samples of cerchiarait-(Fe) and cerchiarait-(Al) from the Esquire No. 1, No. 7 and No. 8 claims were collected during the mid-1960s by one of the authors (REW). The mineral is found in parallel-bedded quartz-sanbornite vein assemblages. At the Esquire No. 1 claim, cerchiarait-(Al) is associated with bazirite, diopside, goethite, opal, quartz, sanbornite, titantaramellite, traskite and witherite. At the Esquire No. 7 claim, cerchiarait-(Fe) and cerchiarait-(Al) are associated with bazirite, diopside, muirite, pyrrhotite, Ba-rich tobermorite, traskite and witherite. At the Esquire No. 8 claim, they are associated with bazirite, calcite, diopside, pyrrhotite, titantaramellite and Ba-rich tobermorite. A description of the mineralogy of the sanbornite deposits located along Big Creek and Rush Creek in eastern Fresno County, California is provided by Walstrom and Leising (2005). The mineral formed on the margins of quartz-sanbornite veins as a result of fluid interactions. The environment in which the cerchiarait phases occur at the Esquire No. 1, No. 7 and No. 8 claims appears to have been less oxidizing than at Cerchiar mine, based upon the pleochroic blue colour of the Esquire crystals (see below).

The new minerals have also been found at Trumbull Peak, Mariposa County, California, USA (Dunning and Cooper, 1999), the Baumann prospect, Chickencoop Canyon, Tulare County, California, USA (Walstrom and Dunning, 2003) and the Gunn claim, MacMillan Pass, Yukon Territory, Canada (the type locality for pellyite; Montgomery *et al.*, 1972). Material from all three localities has compositions between the Fe and Al endmembers, although all of the samples tested thus far from Trumbull Peak fall into the Fe-dominant range. Material from the Gunn claim has been referred to as 'mineral C'.



FIG. 1. Cerchiarait-(Fe) with hematite (upper right) from the Cerchiar mine (specimen Cer1); field of view is 3 mm.

Physical and optical properties

At the Cerchiar mine, cerchiarait-(Fe) occurs as tan to brown thin prisms with square cross-sections. Near-endmember cerchiarait-(Fe) (Cer1) occurs as matted aggregates of very thin tan fibres (Fig. 1); more Mn-rich cerchiarait-(Fe) (Cer2) occurs as coarser brown crystals reaching 2 mm in length and 0.1 mm across. The streak varies from nearly colourless to tan. At the Esquire No. 1, No. 7 and No. 8 claims, both cerchiarait-(Fe) and cerchiarait-(Al) occur as blue, greenish blue and bluish green irregular prisms in subparallel crystal aggregates which are generally less than 1 mm across (Figs 2 and 3). The streak is pale green-blue.

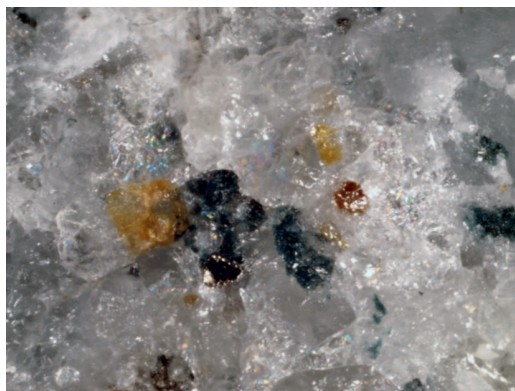


FIG. 2. Cerchiarait-(Fe)–cerchiarait-(Al) with pyrrhotite (brown metallic), muirite (yellow), traskite (orange) and diopside (nearly colourless) embedded in witherite from the Esquire No. 7 claim; field of view is 3 mm.

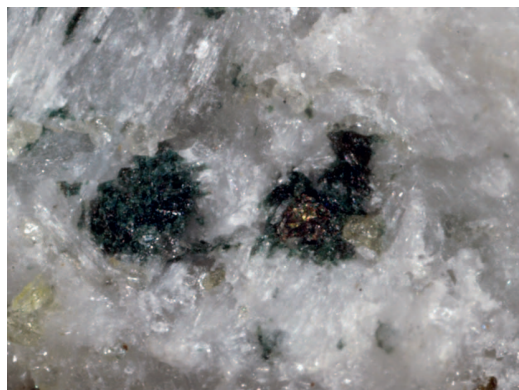


FIG. 3. Cerchiaraites-(Fe)—cerchiaraites-(Al) with pyrrhotite (brown metallic), tobermorite (white silky) and diopside (pale yellow) embedded in calcite from the Esquire No. 8 claim; field of view is 3 mm.

Cerchiaraites-(Fe) and cerchiaraites-(Al) crystals are transparent and have a vitreous lustre. They do not fluoresce in long-wave or short-wave ultraviolet light. Their Mohs hardness is about $4\frac{1}{2}$, their tenacity brittle, their fracture irregular and they exhibit no cleavage. The density of the near-endmember cerchiaraites-(Fe) crystals on Cer1 could not be measured because of difficulty in working with the very thin fibres. The calculated density for these crystals is 3.710 g cm^{-3} , based on the empirical formula and the unit-cell dimensions determined by single-crystal X-ray diffraction. The density of cerchiaraites-(Al) crystals on specimen Esq1 determined by the sink–float technique in an aqueous solution of sodium polytungstate is $3.69(3) \text{ g cm}^{-3}$; the calculated density is 3.643 g cm^{-3} , based on the empirical formula and unit-cell dimensions refined from powder-diffraction data.

The optical properties of cerchiaraites-(Fe) and cerchiaraites-(Al) were measured in white light. Cerchiaraites-(Fe) is uniaxial (+), with $\omega = 1.741(2)$ and $\varepsilon = 1.768(2)$; it is weakly pleochroic, with O colourless and E yellow. Cerchiaraites-(Al) is uniaxial (–), with $\omega = 1.695(2)$ and $\varepsilon = 1.677(2)$; it is strongly pleochroic with O colourless and E blue.

Chemical composition

Chemical analyses were carried out on a Cameca SX-50 electron microprobe (EMP) fitted with four wavelength-dispersive spectrometers operating in WDS mode at 15 kV, 10 nA with a $5 \mu\text{m}$ beam

diameter. The acquisition times were 10 s on the peak and 5 s on the low and high background positions. Data were reduced, with a ZAF matrix correction (Armstrong, 1988), using *Probe for Windows* software. A variety of natural and synthetic minerals and metals were used as standards.

Insufficient material was available for a direct determination of H_2O , which was calculated by stoichiometry based upon 27 anions ($\text{O} + \text{Cl} = 27$) such that there were no more than four cations in either the large cation sites ($\text{Ba} + \text{Na} + \text{Ca} = 4$) or the octahedral site ($\text{Fe} + \text{Al} + \text{Mn} + \text{Mg} + \text{Ti} = 4$). Analytical data for samples Cer1, Cer2, Esq1, Esq7 and Esq8 and the corresponding empirical formulae are given in Table 1. The presence of a small amount of Fe^{2+} in samples from the Esquire claims is revealed by the strong blue pleochroism of the crystals. On the basis of bond-valence analysis (see below) Fe in the structure was allocated as 90% Fe^{3+} and 10% Fe^{2+} . The presence of Fe^{2+} indicates that all of the Mn must be Mn^{2+} in the Esquire samples. The low analytical total for Cer1 is due to the very limited thickness of the crystals.

The atom percentages of Mn, Fe and Al in the studied specimens, and in cerchiaraites-(Mn) (labelled Cer0; Basso *et al.*, 2000), are plotted in Fig. 4. The composition of cerchiaraites from the Cerchiar mine varies between the Mn and Fe endmembers and contains relatively little Al. The compositions from the three Esquire claims are low in Mn and cover a broad range on either side

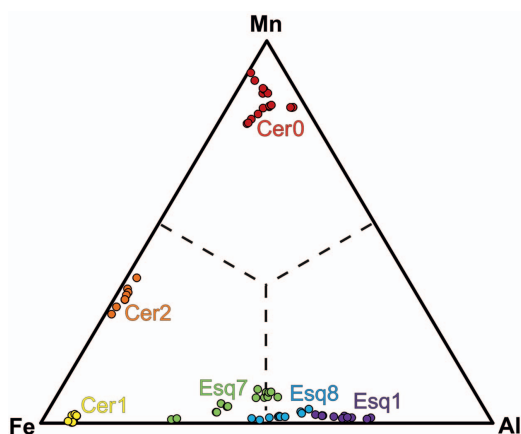


FIG. 4. Ternary plot of cerchiaraites compositions based upon atom% Mn, Fe and Al. The compositions labelled 'Cer0' correspond to those of the original Mn-dominant cerchiaraites of Basso *et al.* (2000).

TABLE 1. Analytical data for cercharraite-(Fe) and cercharraite-(Al).

Const.	Cer1 [10 analyses (wt.%)]			Cer2 [8 analyses (wt.%)]			Esq1 [11 analyses (wt.%)]			Esq7 [18 analyses (wt.%)]			Esq8 [11 analyses (wt.%)]		
	Mean	Range	SD	Mean	Range	SD	Mean	Range	SD	Mean	Range	SD	Mean	Range	SD
Na ₂ O	0.05	0.00–0.13	0.05	0.09	0.00–0.21	0.08	44.82	43.75–46.91	0.95	43.85	41.89–45.75	1.08	44.84	43.21–46.09	0.99
BaO	40.81	39.13–42.08	1.10	41.65	39.81–44.17	1.69	0.43	0.35–0.59	0.08	0.12	0.06–0.18	0.04	0.21	0.12–0.31	0.06
CaO	0.17	0.03–0.42	0.13	0.03	0.00–0.05	0.02	0.30	0.20–0.44	0.07	1.09	0.18–1.69	0.50	0.38	0.16–0.74	0.17
MgO	0.06	0.00–0.13	0.05	0.02	0.01–0.04	0.01	(7.27)	5.58–8.25	0.88	(11.44)	9.62–14.99	1.76	(9.90)	8.63–11.49	0.90
MnO*							0.65			1.08			0.89		
Mn ₂ O ₃	0.22	0.04–0.46	0.18	6.96	5.74–8.03	0.68	6.55			10.30			8.91		
Fe ₂ O ₃	19.03	18.25–20.26	0.59	13.82	12.77–14.46	0.57	8.94	8.12–9.79	0.59	5.74	3.77–6.81	0.92	7.22	6.40–8.14	0.60
FeO*															
Fe ₂ O ₃ *															
Al ₂ O ₃	0.87	0.74–0.94	0.66	0.28	0.18–0.34	0.06	25.38	25.25–26.22	0.29	24.90	24.29–25.37	0.30	25.15	24.61–26.14	0.50
TiO ₂	1.51	0.52–2.25	0.17	1.02	0.68–1.20	0.17	7.53	7.35–7.94	0.18	6.89	6.50–7.41	0.31	6.73	6.48–6.92	0.18
SiO ₂	23.51	23.26–23.83	0.26	25.16	24.10–25.82	0.62	–1.70			–1.55			–1.52		
Cl	5.47	5.13–5.98	1.05	5.07	4.77–5.36	0.18	5.76			5.81			6.24		
O=Cl	–1.23			–1.14											
H ₂ O	5.84			5.07			98.66			98.23			99.05		
Total	96.31			98.03											

* The presence of a small amount of Fe²⁺ in samples from the Esquire claims is indicated by the strong blue pleochroism; based upon the bond-valence analysis Fe has been allocated as 90% Fe³⁺ and 10% Fe²⁺; furthermore, the presence of Fe²⁺ indicates that all Mn must be present as Mn²⁺.

Empirical formulae (based on 27 anions):

Cer1: (Ba_{3.82}Na_{0.02}Ca_{0.04})Σ_{3.88}(Fe_{3.42}Ti_{0.27}Al_{0.25}Mn_{0.04}Mg_{0.02})Σ_{4.00}Si_{5.62}O_{15.47}(OH)_{9.31}Cl_{2.22}

Cer2: (Ba_{3.88}Na_{0.04}Ca_{0.01})Σ_{3.93}(Fe_{2.47}Mn_{1.26}Ti_{0.18}Al_{0.08}Mg_{0.01})Σ_{4.00}Si_{5.98}O_{16.92}(OH)_{8.04}Cl_{2.04}

Esq1: Ba_{4.00}(Al_{15.4}Fe_{3.12}Mg_{0.15}Fe_{2.12}Mn_{0.06})Σ_{3.85}Si_{5.78}O_{15.34}(OH)_{8.75}Cl_{2.91}

Esq7: Ba_{4.00}(Fe_{1.80}Al_{11.57}Fe_{0.21}Mn_{0.21}Mg_{0.04})Σ_{3.83}Si_{5.80}O_{15.26}(OH)_{9.02}Cl_{2.72}

Esq8: Ba_{4.00}(Al_{11.94}Fe_{1.53}Fe_{0.17}Mn_{0.07}Mg_{0.07})Σ_{3.78}Si_{5.73}O_{14.92}(OH)_{9.48}Cl_{2.60}

of the boundary between the Fe and Al endmembers; they do not approach the endmember compositions, extending between Fe:Al ratios of 75:25 and 25:75.

The ideal formula for members of the cerchiarite group is $Ba_4M_4(Si_4O_{12})O_2(OH)_4Cl_2 [Si_2O_3(OH)_4]$, in which M represents the cation in the octahedral site, which can be Mn, Fe or Al. The endmember formula for cerchiarite-(Fe) requires BaO 43.19, Fe_2O_3 22.49, SiO_2 25.38,

H_2O 5.07, Cl 4.99, O=Cl -1.13; total 100.00 wt.%. The endmember formula for cerchiarite-(Al) requires BaO 47.01, Al_2O_3 15.63, SiO_2 27.63, H_2O 5.52, Cl 5.43, O=Cl -1.23; total 100.00 wt.%. Note that Basso *et al.* (2000) reported an ideal formula for cerchiarite-(Mn) with only one Cl, even though their empirical formula included 1.54 Cl atoms per formula unit (a.p.f.u). All of our empirical formulae for cerchiarite-(Fe) and cerchiarite-(Al) (Table 1)

TABLE 2. Powder X-ray data for cerchiarite-(Fe) (sample Cer1).

I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{calc}	hkl	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{calc}	hkl
25	10.23	10.1366	40	110					
17	7.21	7.1677	30	200	11	1.7439	{ 1.7384	6	820
21	5.57	5.5466	39	101	16	1.6818	{ 1.7369	11	413
7	5.09	5.0683	7	220			{ 1.6811	8	552
5	4.56	4.5332	9	310	19	1.6552	{ 1.6584	24	642
26	4.403	4.3866	42	211			{ 1.6431	18	503
9	3.751	3.7415	11	301	9	1.6016	{ 1.6027	5	840
19	3.593	3.5838	38	400			{ 1.5956	7	732
		3.3789	7	330			{ 1.5831	5	910
48	3.327	3.3168	73	321			{ 1.5397	5	901
18	3.214	3.2055	38	420	23	1.5062	{ 1.5054	7	761
		3.0102	100	411			{ 1.5038	13	004
70	3.016	{ 3.0075	19	002			{ 1.4936	9	543
8	2.887	{ 2.8833	8	112	8	1.4755	{ 1.4733	7	851
		{ 2.8114	12	510			{ 1.4730	4	662
16	2.788	{ 2.7733	21	202			{ 1.4335	4	860
		{ 2.5881	59	501			{ 1.4147	17	941
100	2.595	{ 2.5864	76	222	43	1.4107	{ 1.4049	14	723
		{ 2.5342	38	440			{ 1.4009	13	912
8	2.470	{ 2.4585	11	530			{ 1.3924	6	950
		{ 2.2666	4	620			{ 1.3866	5	404
29	2.258	{ 2.2465	35	332			{ 1.3614	4	424
		{ 2.1933	5	422			{ 1.3159	4	871
18	2.107	{ 2.0982	33	541	29	1.2980	{ 1.3047	4	772
		{ 2.0538	9	512			{ 1.2941	16	10·0·2
19	2.034	{ 2.0273	11	550			{ 1.2932	11	444
		{ 2.0137	6	631			{ 1.2735	5	10·2·2
		{ 1.9880	4	640	14	1.2609	{ 1.2635	8	952
		{ 1.9857	5	103			{ 1.2540	6	11·2·1
		{ 1.9136	7	213			{ 1.2540	9	10·5·1
20	1.907	{ 1.9035	4	532	7	1.2162	{ 1.2171	3	10·4·2
		{ 1.8823	17	730			{ 1.2110	4	853
26	1.880	{ 1.8714	34	721	17	1.1796	{ 1.1784	7	12·2·0
		{ 1.8708	9	602			{ 1.1779	9	943
		{ 1.8101	42	622			{ 1.1749	6	734
39	1.8118	{ 1.7919	15	800					
		{ 1.7903	10	323					

Only calculated lines with intensities of 4 or greater are listed, unless they correspond to observed lines. The calculated powder data are based on the structure refinement for Esq8.

have between two and three Cl a.p.f.u. We did not observe any evidence that Cl migration, such as that reported for F and Cl in apatite by Stormer *et al.* (1993), produced higher than actual Cl values in the EMP analyses. In the crystal structure (see below), one Cl a.p.f.u. is located at a fully occupied Cl site (Cl1) at the origin [0;0;0]. The additional Cl is located at a partially occupied channel site (Cl2) 0.8 Å from the partially occupied O5 site of the channel silicate group, leading to the conclusion that both the channel Cl and the silicate group cannot be locally present at the same time. Those samples that provide close to the ideal six Si a.p.f.u., Cer0 and Cer2, have 1.54 and 2.04 Cl a.p.f.u., respectively, leading us

to propose two Cl a.p.f.u. (and 27 total anions) for the ideal formula. The other samples, Cer1, Esq1, Esq7 and Esq 8, exhibit significant deficiencies in Si and excesses of Cl.

The Gladstone–Dale compatibility indices, $1 - (K_p/K_c)$, for Cer1 and Esq1 are 0.010 and 0.007, respectively; both of these are in the superior range (Mandarino, 1981).

X-ray crystallography and structure refinement

Powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with mono-

TABLE 3. Powder X-ray data for cerchiarait-(Al) (sample Esq1).

I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{calc}	hkl	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{calc}	hkl
39	10.15	10.1237	41	110					
9	7.16	7.1585	9	200					
33	5.555	5.5365	39	101	68	1.880	1.9101	7	213
13	5.066	5.0618	18	220			1.9005	4	532
							1.8799	20	730
							1.8689	28	721
39	4.407	{ 4.5274	9	310			1.8679	6	602
		4.3795	33	211			1.8455	3	303
8	3.736	3.7358	7	301			1.8074	26	622
16	3.584	3.5793	23	400	33	1.8004	1.7896	10	800
		3.3746	6	330			1.7871	8	323
77	3.316	3.3119	80	321			1.7362	3	820
24	3.201	3.2014	27	420	15	1.7395	1.7339	7	413
							1.6786	8	552
100	3.009	{ 3.0058	100	411	10	1.6816	1.6560	15	642
		3.0018	24	002			1.6403	18	503
13	2.870	2.8779	8	112	29	1.6473	1.5933	7	732
							1.5811	5	910
15	2.779	{ 2.8078	11	510	17	1.5920	1.5377	3	901
		2.7682	10	202			1.5034	4	761
							1.5009	9	004
93	2.580	{ 2.5845	56	501	13	1.4995	1.4912	7	543
		2.5819	51	222			1.4713	4	851
11	2.527	2.5309	25	440			1.4128	14	941
16	2.463	2.4553	13	530	21	1.4764	1.4027	14	723
3	2.407	2.4309	2	521			1.3989	11	912
2	2.368	2.3862	6	600			1.3906	5	950
9	2.306	2.3000	7	402	54	1.4031	1.3142	4	871
							1.3029	5	772
38	2.244	{ 2.2637	6	620			1.2922	13	10-0-2
		2.2428	36	332			1.2910	8	444
21	2.097	2.0953	33	541			1.2618	7	952
							1.2524	9	10-5-1
		2.0506	9	512			1.2524	4	11-2-1
43	2.029	{ 2.0247	10	550	22	1.3013	1.2910	8	444
		2.0110	8	631			1.2618	7	952
							1.2524	9	10-5-1
		1.9819	5	103			1.2524	4	11-2-1
		1.9349	4	442	37	1.2570			

Only calculated lines with intensities of 3 or greater are listed, unless they correspond to observed lines. The calculated powder data are based on a whole-pattern-fitting Rietveld structure refinement for Esq1.

chromatic MoK α radiation. In the powder-diffraction studies, the observed d -spacings and intensities were determined by profile fitting using *JADE 2010* software. Powder data are presented for samples Cer1 (Table 2) and Esq1 (Table 3), as these have the closest compositions to endmember cerchiaraitite-(Fe) and cerchiaraitite-(Al), respectively. Unit-cell parameters refined from the powder data using *JADE 2010* software with whole pattern fitting are as follows: $a = 14.3554(12)$, $c = 6.0065(5)$ Å with $V = 1237.80(5)$ Å³ for Cer1 and $a = 14.317(4)$, $c = 6.0037(18)$ Å with $V = 1230.6(6)$ Å³ for Esq1. The unit-cell parameters refined from the powder data should be considered the most definitive as they were obtained from material closest to the endmember compositions.

Single-crystal structure data were obtained from cerchiaraitite-(Fe) from specimen Esq8. The Rigaku *CrystalClear* software package was used to process these data, including the application of

an empirical absorption correction. The structure was solved by direct methods using *SIR2004* (Burla *et al.*, 2005) and refined with *SHELXL-97* (Sheldrick, 2008). Most of the fully occupied sites in the structure were located by direct methods; the remaining sites, including those with partial occupancies, were located in difference-Fourier maps. The occupancy of the octahedral site refined to an Fe:Al ratio of 0.596:0.404, indicating that the crystal used was cerchiaraitite-(Fe), rather than cerchiaraitite-(Al).

The analysis showed the Ba site on the periphery of the channel to be fully occupied; however, all of the other channel sites are partially occupied. In the structure of cerchiaraitite [now cerchiaraitite-(Mn)], Basso *et al.* (2000) reported the Si2 tetrahedron to be statistically distributed in the channel and to exhibit a high degree of distortion. We found the same to be true of the Si2 tetrahedron in cerchiaraitite-(Fe). For the Si2, O4 and O5 sites of the channel silicate group,

TABLE 4. Data collection and structure refinement details for crystal from Esq8 corresponding to cerchiaraitite-(Fe).

Diffractionmeter	Rigaku R-Axis Rapid II
X-ray radiation; power	MoK α ($\lambda = 0.71075$ Å); 50 kV, 40 mA
Temperature	298(2) K
Structural Formula	Ba ₄ Fe _{2.38} ³⁺ Al _{1.62} Si _{6.04} Cl _{2.70} O _{25.17} H _{8.88}
Space group	<i>I4/mmm</i>
Unit-cell dimensions	$a = 14.3554(12)$ Å $c = 6.0065(5)$ Å
<i>Z</i>	2
<i>V</i>	1237.80(18) Å ³
Density (for above formula)	3.765 g cm ⁻³
Absorption coefficient	8.373 mm ⁻¹
<i>F</i> (000)	1295.6
Crystal size	70 × 40 × 40 μm
θ range	3.68 to 25.03°
Index ranges	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-7 \leq l \leq 7$
Reflections collected/unique	10,966/343 [$R_{\text{int}} = 0.0646$]
Reflections with $F_o > 4\sigma F$	329
Completeness to $\theta = 25.03^\circ$	98.0%
Refinement method	Full-matrix least-squares on F^2
Parameters refined	59
GoF	1.134
Final <i>R</i> indices [$F_o > 4\sigma F$]	$R_1 = 0.0253$, $wR_2 = 0.0557$
<i>R</i> indices (all data)	$R_1 = 0.0269$, $wR_2 = 0.0566$
Largest diff. peak / hole	+0.883 / -0.799 e Å ⁻³

$$R_{\text{int}} = \frac{\sum |F_o^2 - F_o^2(\text{mean})|}{\sum [F_o^2]}$$

$$\text{GoF} = S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$$

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

$$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } a \text{ is } 0.0213, b \text{ is } 17.7504 \text{ and } P \text{ is } [2F_c^2 + \text{Max}(F_o^2)]/3.$$

Basso *et al.* (2000) assigned occupancies of $\frac{1}{4}$, $\frac{1}{4}$ and $\frac{1}{2}$, respectively. Our refined occupancies for these sites are 0.255(11), 0.24(3) and 0.52(7), respectively. In addition, we found a significant residual peak 0.80 Å from the O5 site. This peak is only 1.42 Å from Si2, which is too close for a Si–O bond; however, the peak is at an appropriate distance from the Ba site (3.10 Å) to correspond to a partially occupied Cl site and was assigned as such.

The details of the data collection and structure refinement are provided in Table 4, the final atom coordinates and displacement parameters in Table 5, selected interatomic distances and angles in Table 6 and bond-valence summations in Table 7. Lists of observed and calculated structure factors have been deposited with *Mineralogical Magazine* and can be downloaded from http://www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Description of the structure

The crystal structure of cerchiarait-(Fe) (Fig. 5) is essentially identical to that reported by Basso *et al.* (2000) for cerchiarait [now cerchiarait-(Mn)]. In the structure, SiO₄ tetrahedra share corners to form a four-membered Si₄O₁₂ ring about the fourfold axis [0,0,z]. The ring is corner-linked to an edge-sharing chain of Fe³⁺O₆ octahedra that runs parallel to *c*. The framework thereby created contains a large channel centred about the 4₂ screw axis [0,½,z] with Ba atoms positioned around its periphery. Two silicate dimers, Si₂O₃(OH)₄, p.f.u. are statistically distributed within the channel. One fully occupied Cl site is located on the fourfold axis, alternating along *c* with Si₄O₁₂ rings. A feature not reported by Basso *et al.* (2000) is an additional partially occupied Cl site (Cl2) in the channel, which accounts for approximately one Cl a.p.f.u. if there are two silicate dimers p.f.u., but which can accommodate more Cl if there are less than two silicate dimers. Note that the very low bond-valence sum of 0.33 vu for Cl2 is likely to be augmented by two hydrogen bonds from the O2 OH groups.

Crystals from the Esquire No. 8 claim (and also from the Esquire No. 1 and No. 7 claims) exhibit a strongly pleochroic blue colour parallel to *c*, which corresponds to the direction of the edge-sharing octahedral chains. The

TABLE 5. Atom coordinates and displacement parameters (Å²) for cerchiarait-(Fe).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ba	0.21637(5)	0	0	0.0275(2)	0.0349(4)	0.0222(4)	0.0254(4)	0	0	0.000
<i>M</i>	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.0190(6)	0.0207(7)	0.0207(7)	0.0156(9)	0.0001(5)	0.0001(5)	–0.0075(7)
Si1	0.38855(13)	0.38855(13)	0	0.0165(6)	0.0164(8)	0.0164(8)	0.0167(13)	0	0	–0.0010(10)
Si2	0.4183(6)	0.1121(5)	0	0.027(3)	0.041(6)	0.019(5)	0.023(5)	0	0	0.006(4)
Cl1	0	0	0	0.0279(12)	0.0240(16)	0.0240(16)	0.036(3)	0	0	0
Cl2	$\frac{1}{2}$	0.1388(15)	0.118(9)	0.082(13)	0.037(10)	0.073(10)	0.14(3)	–0.042(12)	0	0
O1	0.3460(2)	0.3460(2)	0.2268(7)	0.0218(10)	0.0254(15)	0.0254(15)	0.015(2)	0.0018(14)	0.0018(14)	–0.005(2)
O2	0.1766(4)	0.3076(4)	0	0.0293(12)	0.026(3)	0.039(3)	0.024(3)	0	0	–0.009(2)
O3	0.3686(5)	$\frac{1}{2}$	0	0.0256(16)	0.037(4)	0.011(3)	0.028(4)	0	0	0
O4	0.394(2)	0	0	0.036(13)	0.04(2)	0.016(18)	0.05(3)	0	0	0
O5	$\frac{1}{2}$	0.126(3)	0.247(9)	0.139(18)	0.22(4)	0.10(2)	0.09(3)	–0.074(19)	0	0

* Refined occupancies are *M* (Fe/Al): 0.596/0.404(12); Si2: 0.255(11); Cl2: 0.21(3); O4: 0.24(3); O5: 0.52(7).

TABLE 6. Selected bond distances (Å) and angles (°) in cerchiarite-(Fe).

Ba–O4	2.55(3)	Si1–O1 (×2)	1.612(5)	Si2–O4	1.646(11)
Ba–O5 (×2)	2.73(2)	Si1–O3 (×2)	1.626(2)	Si2–O2	1.839(10)
Ba–O2 (×2)	2.854(5)	<Si1–O>	1.619	Si2–O5 (×2)	1.90(4)
Ba–O1 (×4)	2.895(3)			<Si2–O>	1.821
Ba–Cl2 (×2)	3.10(4)	O1–Si1–O1	115.3(4)		
Ba–Cl1	3.1061(7)	O1–Si1–O3 (×4)	107.80(15)	O2–Si2–O4	108.0(13)
<Ba–φ>*	2.897	O3–Si1–O3	110.3(6)	O2–Si2–O5 (×2)	118.8(6)
				O4–Si2–O5 (×2)	103.3(15)
				O5–Si2–O5	103(2)
M–O1 (×2)	1.955(5)				
M–O2 (×4)	2.012(4)				
<M–O>	1.993				

* Occupancies for partially occupied O and Cl atoms (O4, O5 and Cl2) have been used for calculating <Ba–φ>.

colour is clearly attributable to Fe^{2+} – Fe^{3+} intervalence charge transfer (IVCT). The <M–O> of 1.993 Å is consistent with the site being predominantly occupied by Al and Fe^{3+} . Furthermore, using a bond-valence parameter in

accord with the refined site occupancy of Fe^{3+} :Al = 0.595:0.405, the bond-valence sum (BVS) for the site is 2.84 vu, confirming the dominance of trivalent cations. The somewhat low BVS (for a trivalent cation) is consistent with a small

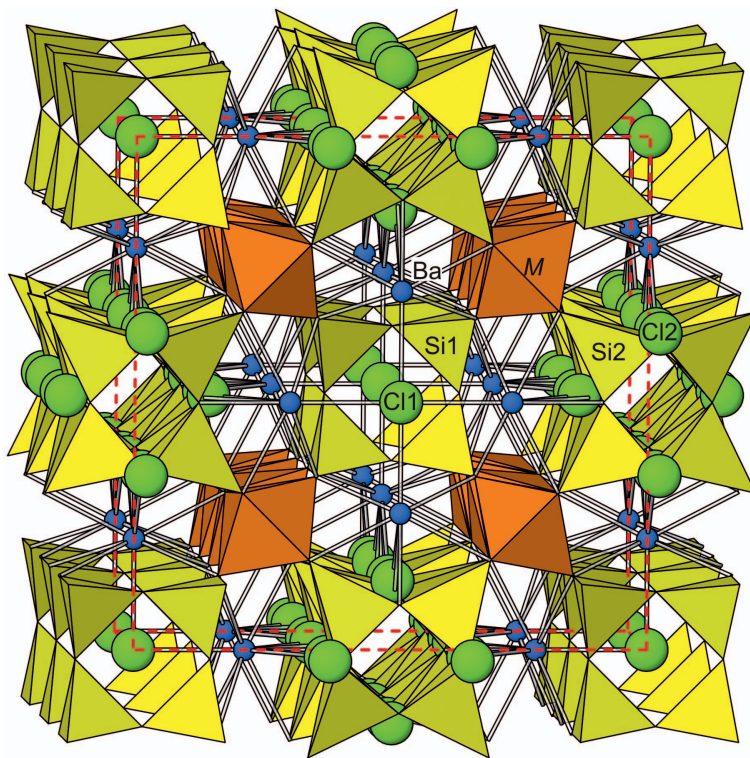


FIG. 5. Structure of cerchiarite (Esq8) viewed slightly canted down [001].

TABLE 7. Bond-valence analysis for cerchiarait-(Fe). Values are expressed in valence units.

	O1	O2	O3	O4	O5	Cl1	Cl2	Sum
Ba	$0.19 \times 2 \downarrow \times 4 \rightarrow$	$0.21 \times 2 \rightarrow$		$0.49 \times 0.24 \rightarrow$	$0.26 \times 1.04 \rightarrow$	$0.32 \times 4 \downarrow$	$0.33 \times 0.21 \rightarrow$	2.05
M	$0.52 \times 2 \rightarrow$	$0.45 \times 2 \downarrow \times 4 \rightarrow$						2.84
Si1	$1.03 \times 2 \rightarrow$		$0.99 \times 2 \downarrow \rightarrow$					4.06
Si2		0.14		$0.94 \times 2 \downarrow$	$0.47 \times 2 \downarrow$			2.45
Sum	1.93	1.25	1.98	2.37	0.94	1.28	0.33	

Multiplicity is indicated by $\times \rightarrow \downarrow$; Ba²⁺-O and Fe³⁺-O bond strengths from Brown and Altermatt (1985); Al³⁺-O and Si⁴⁺-O bond strengths from Brese and O'Keefe (1991). The bond strengths for the M site are based upon the refined Fe/Al occupancy. Multiplicities for O4, O5 and Cl2 are also based upon occupancies.

proportion of the Fe being Fe²⁺. For calculation of the empirical formulae for the Esq1, Esq7 and Esq8 samples (Table 1), these considerations led us to an approximate Fe allocation of 90% Fe³⁺ and 10% Fe²⁺.

Some comments on the highly unusual acid disilicate group, Si₂O₃(OH)₄, are warranted. This group was reported in the structure of cerchiarait by Basso *et al.* (2000) and we noted the same group with a more distorted geometry in our refinement of the cerchiarait-(Fe) structure. The OH groups were regarded by Basso *et al.* (2000) as being necessary from a bond-valence perspective. They dismissed the possibility of two insular silicate groups, SiO(OH)₃, on opposite sides of the channel rather than the disilicate group because that required too high a water content, and too high an occupancy for the O4 site. The statistical occupancy and disorder within the channel leaves some doubt about the nature of the silicate group. The distorted geometry of the Si2 tetrahedron and particularly its very long Si-O bond lengths (which provide a very low bond-valence sum for Si2) are probably an artefact of the positional disorder.

It is worth noting that the disorder within the channel suggests that other constituents, such as H₂O, SO₄ or CO₃, could be accommodated, as in the closely related structures of bobmeyerite, Pb₄(Al₃Cu)(Si₄O₁₂)(S_{0.5}Si_{0.5}O₄)(OH)₇Cl(H₂O)₃ (Kampf *et al.*, 2013) and ashburtonite, Pb₄Cu₄(Si₄O₁₂)(OH)₄Cl(HCO₃)₄ (Grice *et al.*, 1991).

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