

Cerchiaraitite and Ca-bearing noélbensonite from Woods mine, New South Wales, Australia

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Abstract: Cerchiaraitite occurs as tiny blocky crystals and sheafs of irresolvable fibres in the Woods mine in northern New South Wales, Australia. It forms veinlets from <10 to ~90 µm wide in fractures cutting serandite-quartz-namansilite-ungarettiite assemblages. It also replaces these minerals in the rock matrix. It is accompanied by and locally replaces noélbensonite, but in much smaller amount. These two Ba-bearing minerals are among the latest Mn³⁺-rich phases that locally replace Mn²⁺-rich assemblages in the quarry. EMP analyses supported by ion-probe conform with end-member composition Ba₄Mn³⁺₄O₃(OH)₃(Si₄O₁₂)(Si₂O₃)(OH)₄Cl with some substitution of (Ca,Sr,Mn²⁺,Na) for Ba, Al for Mn³⁺, and (OH) for Cl. It contains about 1000 ± 500 ppm F. The mineral is tetragonal or, as suggested by optical observation, pseudotetragonal. A tetragonal *I4/mmm* unit cell and X-ray powder diffraction data give: *a* = 14.219(8) Å, *c* = 6.118(5) Å, *V* = 1237.0(1.7) Å³; *Z* = 2.

EMP analyses of noélbensonite of both blocky and radial fibrolamellar habit coexisting with the cerchiaraitite show a range of Ca : Ba from Ca below detection limit to 0.52 : 0.48. This suggests the possibility of a Ca-dominant species amongst the Mn³⁺ analogues of lawsonite. It is not known whether the observed limit of approximately 50% Ca for Ba substitution results from limited available Ca or structural features. Ion probe data show about 18 ppm Cl in the noélbensonite. Late-stage hydrothermal alteration at the Woods Mine was effected by complex interactions with solutions of changing composition.

Key-words: cerchiaraitite, noélbensonite, lawsonite group, manganese minerals, Woods mine.

Introduction

The Woods mine in northern New South Wales, Australia, is worked for pink rhodonite ornamental stone (Goodwin, 1998). Other assemblages at the same locality contain rare manganese silicate minerals (Kawachi, 1987; Kawachi & Coombs, 1993; Kawachi *et al.*, 1994; Kawachi *et al.*, 1996; Kawachi *et al.*, 2002). The BaMn³⁺-mixed-anion-cyclosilicate cerchiaraitite, with a structure containing [Si₄O₁₂] rings, separate [Si₂O₇] dimers, (OH), and essential Cl (Basso *et al.*, 2000), is now added to that list. This is its second reported occurrence, the first being in the Cerchiarait mine, north Apennines (Basso *et al.*, 2000). Its mode of occurrence, properties, and composition are discussed. New analytical data for co-existing calcian noélbensonite show substantial substitution of Ca for Ba and low but variable contents of Sr.

Occurrence

The Woods mine (UTM Grid Reference LL 099906), 35 km NNE of Tamworth in the New England Fold Belt of northern New South Wales, exposes manganese-rich pods in a Paleozoic subduction complex. The area experienced re-

gional prehnite-pumpellyite to pumpellyite-actinolite facies metamorphism followed by a hornblende-hornfels overprint in the contact zone of a Permian adamellite intrusion (Kawachi, 1987; Brown *et al.*, 1992). Pink rhodonite rock is exploited by the quarrying operations, but dark-coloured rocks of more complex chemistry are also exposed. These contain pale pink and darker-stained serandite coexisting with quartz and localized occurrences of other manganese minerals of low oxidation state including johannsenite, tephroite, sugilite, members of the nambulite group, and rhodochrosite, as well as minor amounts of barite, carbonate-fluorapatite, Ba-bearing K-feldspar, and albite.

The serandite and other Mn²⁺ minerals are locally replaced by the more highly oxidized Mn³⁺ minerals braunite, ungarettiite, and namansilite. Minor fractures cutting both quartz-serandite and oxidized assemblages are occupied by paper-thin late-stage veinlets (Fig. 1) typically as little as 10 µm thick, but sometimes reaching 90 µm in thickness. These veinlets often contain noélbensonite (the BaMn³⁺ analogue of lawsonite), and less commonly they contain cerchiaraitite. Noélbensonite (Kawachi *et al.*, 1996) and cerchiaraitite also occur as scattered grains and segregations in the surrounding rock. The cerchiaraitite appears in places to have co-precipitated with noélbensonite, but in places it mantles and re-

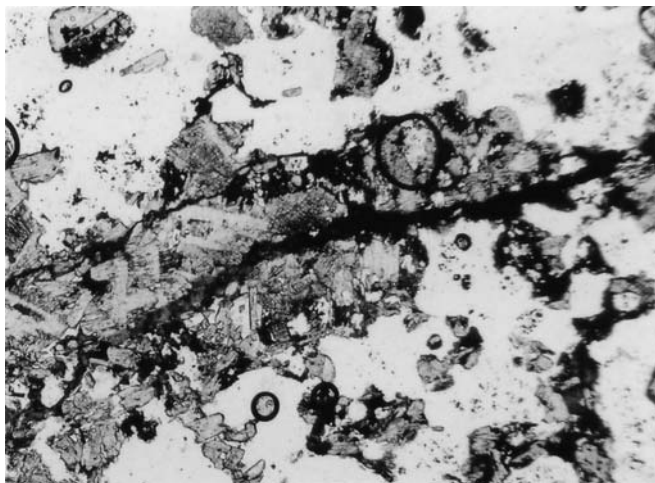


Fig. 1. Fracture-filling noélbenzonite-cerchiaraites (dark) cutting a serandite aggregate (medium grey) in quartz-serandite rock (OU 68677), Woods mine, New South Wales. Field of view: 3 x 2 mm.

places it. Some occupies discrete lengths of the same veinlets as noélbenzonite. In both the veinlets and surrounding rock, cerchiaraites may appear as blocky crystals rarely exceeding 30 μm in size (Fig. 2), as very fine-grained aggregates, and as sheafs of irresolvable fibres up to 100 μm in length. Cerchiaraites mantles and replaces namansilite, serandite, and ungarettiite. A 1-mm patchwork of aggregates of cerchiaraites and noélbenzonite (Fig. 3) is interpreted as replacing serandite and namansilite. Overall, cerchiaraites occurs in much smaller amount than noélbenzonite.

Optical and other physical properties of Woods mine cerchiaraites

Aggregates observed on broken surfaces in reflected light under a binocular microscope are dark greenish grey in colour with a bright vitreous lustre, streak pale greenish grey. Refractive indices exceed 1.70, with $\gamma - \alpha = 0.14$, estimated by comparison with quartz in thin section. Interference figures have been observed ranging from uniaxial to slightly biaxial positive, $2V_z$ (estimated) $\leq 20^\circ$ with distinct dispersion $v > r$. Pleochroism is strong, ϵ = deep green, ω = yellowish brown; absorption $\epsilon > \omega$. Where fibrous, the mineral is length slow, elongated along the c axis. Blocky crystals are approximately equidimensional. Mohs hardness is about 5.5.

Chemical composition

Electron microprobe (EMP) analyses were carried out with a JEOL JXA 8600 instrument using beam diameters of less than 5 μm , excitation voltage 15 kV, 20 nA probe current, and standard ZAF correction. Standards were natural albite and adularia, barite, hematite, synthetic SrTiO_3 , scapolite



Fig. 2. Veinlet of cerchiaraites cutting a serandite-quartz aggregate in OU 68677. Replacement of serandite (light grey with cleavages) by cerchiaraites (dark) spreads from the veinlet into the upper part of the field (quartz clear). Plane-polarized light; darkest areas in the vein result from deep-green absorption tints for the e -ray; medium-dark areas result from yellow-brown colour for the o -ray. Field of view: 450 x 300 μm .

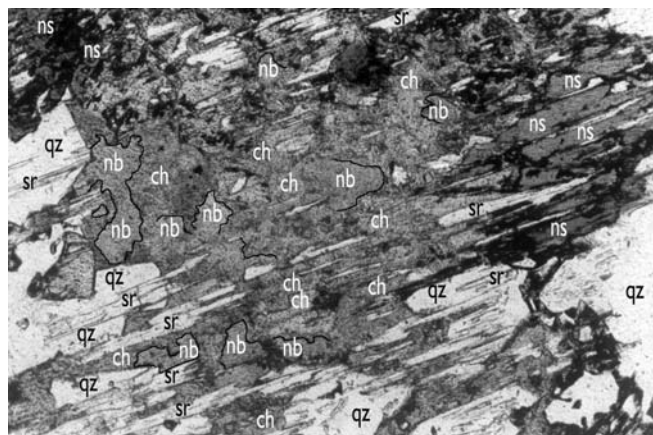


Fig. 3. Aggregate in OU 68686 of cerchiaraites (ch) and noélbenzonite (nb) interpreted as replacing remnants of a single crystal of serandite (sr) intergrown with quartz (qz) and itself partly replaced by namansilite (ns) which is also being replaced by cerchiaraites and Ca-rich noélbenzonite. The patches of cerchiaraites are aggregates of granules about 5–20 μm diameter, and those of noélbenzonite are fan-shaped sheafs of platelets up to 100 μm long. Length of field of view: 1.3 mm.

for Cl, topaz for F, synthetic wollastonite for Ca, and synthetic oxides for other elements. Averages for a batch of 16 EMP spot analyses of Woods mine cerchiaraites of blocky habit and for 5 spot analyses made on sheafs of irresolvable fibrous habit are presented in Table 1. Total Mn is reported as Mn^{3+} . Many other spot analyses were made on grains of varying habit, grain size, and juxtaposition with other minerals. Except where possibilities of contamination could not be precluded, for example in some fibrolamellar aggregates with substantial Fe and Ti, no substantial variations in composition were observed in spite of the very different crystal habits represented.

Tab. 1. Averages of EMP analyses and atomic proportions of cerchiaraita from Cerchiar mine, Italy (Basso *et al.*, 2000), and Woods mine, New South Wales, OU 68686.

	Cerchiar mine (mean of 42 EMP analyses)	Woods mine blocky habit (average of 15 EMP analyses)	Woods mine fibrous sheaves (average of 5 EMP analyses)		
	wt.%	wt.%	st.dev.	wt.%	st.dev.
SiO ₂	26.18	26.45	0.62	25.37	0.25
Al ₂ O ₃	1.02	1.08	0.17	0.56	0.03
TiO ₂		0.05	0.03	bdl	
Fe ₂ O ₃	2.09	0.01	0.02	0.02	0.05
Mn ₂ O ₃	19.57	22.43	0.59	21.88	0.29
CaO		0.72	0.52	0.19	0.04
Na ₂ O		0.08	0.03	0.09	0.04
BaO	43.29	41.20	1.57	41.43	0.34
SrO		0.34	0.19	0.37	0.08
Cl	3.93	2.01	0.12	2.07	0.06
less O for Cl	-0.89	-0.45		-0.47	
H ₂ O (by ion probe)		6.09			
Total	95.19	100.01		91.52	
atoms per 14 cations					
Si	6.03	5.96		5.97	
Al	0.28	0.29		0.16	
Ti	0.00	0.01		0.00	
Fe	0.36	0.00		0.00	
Mn	3.43	3.85		3.92	
Ca	0.00	0.17		0.05	
Na	0.00	0.03		0.04	
Ba	3.91	3.64		3.82	
Sr	0.00	0.04		0.05	
Cl	1.53	0.77		0.83	

Total Fe and Mn reported as Fe³⁺ and Mn³⁺; MgO, K₂O, and F below detection limit (bdl).

Ion probe analysis of Woods mine cerchiaraita by Dr R.W. Hinton (personal communication, see Kawachi *et al.*, 2002, for methods) using the associated noélsenite, BaMn³⁺₂[Si₂O₇](OH)₂·H₂O, as a standard, indicates that if the noélsenite has its calculated 7.87% H₂O, the cerchiaraita has 6.09%. The ion probe analysis indicated 0.37% SrO in the cerchiaraita in good agreement with the EMP analyses. The cerchiaraita has approximately 1000 ± 500 ppm F.

Atomic proportions for cerchiaraita are here calculated on the basis of 14 cations pfu with total Mn as Mn³⁺. The Woods mine analyses closely resemble those from the Cerchiar mine (Table 1). Differences include negligible Fe at Woods, significant but variable Ca (0.04–0.45 atoms pfu, corresponding to 1–12% substitution of Ca for Ba) and Sr (0.01–0.1 atoms pfu), and lower Cl, mostly about 2% by weight (0.8 atoms pfu). One spot analysis, not included in the data set for the averages in Table 1, showed 2.4% Cl (1.0 atoms pfu). With substitution of (Ca,Sr,Mn²⁺,Na) for Ba, Al for Mn³⁺, and (OH) and trace F for Cl, the analyses conform well with the end-member formula Ba₄Mn³⁺₄O₃(OH)₃(Si₄O₁₂)(Si₂O₃)(OH)₄Cl proposed for cerchiaraita by Basso

et al. (2000). A slight deficiency for the large Ba sites and excess for the octahedral sites suggests that minor Mn may be present as Mn²⁺ in the larger sites. The ion-probe determination of water gives H + Cl = 9.98 atoms pfu as against the theoretical 8.00.

XRD study and space group

A powder concentrate of the mineral was hand-picked under the binocular microscope and mounted on a glass fibre. It was not possible to completely exclude contamination by other phases, especially serandite. Powder diffraction patterns were obtained with the sample set on the Micro area X-ray diffractometer MAC Science MDS-3, using Cu-K α radiation, 40 kV, and current 250 mA, X-ray beam diameter 0.1 mm, exposure time 120 minutes. The position-sensitive proportional counter was calibrated by Si standard. The sample was rotated on the χ axis (120–210°) and ϕ axis (-360 + 360°) to reduce any orientation effect. Most of the diffraction peaks listed by Basso *et al.* (2000) were recorded. Adopting the tetragonal *I4/mmm* cell of Basso *et al.* (2000), the unit cell parameters are $a = 14.219(8)$, $c = 6.118(5)$ Å, $V = 1237.0(1.7)$ Å³. However, distinctly biaxial interference figures with distinct dispersion were observed in thin sections of the Woods mine cerchiaraita, in addition to strictly uniaxial figures. This suggests that the true symmetry, in part or in whole, is pseudotetragonal rather than tetragonal.

Chemical substitutions in noélsenite

As described above, noélsenite was used as a standard for ion-probe data for co-existing cerchiaraita. Conversely, using the cerchiaraita as a standard with 2% Cl as determined by EMPA, the noélsenite has only about 18 ppm Cl.

Analytical data reported in the original description of noélsenite (Kawachi *et al.*, 1996) included CaO contents of up to about 1.0%, corresponding to 9% occupancy of the large-cation sites. Lucchetti *et al.* (1988) reported an unidentified mineral from the Cerchiar mine, north Apennines, which has subsequently been shown to be noélsenite (Kawachi *et al.*, 1996). A representative EMP spot analysis given by Lucchetti *et al.* (1988) gave 2.68% CaO with Ca : Ba : Sr : = 0.197 : 0.628 : 0.179. The compositions of individual clusters of crystals and submicroscopic crystal aggregates in the Woods mine specimens vary significantly in different specimens and in different parts of the same thin section. In a 1-mm area of thin section OU 68686 (Fig. 3), fan- and bow-tie-shaped sprays of platy noélsenite, 50–100 μ m long, are interspersed with aggregates of blocky 5–20 μ m granules of cerchiaraita, the two minerals jointly replacing namansilite and serandite. EMP spot analyses in the noélsenite sprays showed unusually high Ca content reaching a maximum of 7.0% CaO by weight corresponding to Ca : Ba = 0.52 : 0.48. Analyses of extremely fine-grained noélsenite aggregates replacing namansilite crystals in part of another thin section (Table 2, column B) show that in this

Tab. 2. EMP analyses and atomic proportions for noélsenite from Woods mine, New South Wales. C: very fine grained in 12- μ m veinlet;

	A Kawachi <i>et al.</i> (1996)	B ultra fine, replacing namansilite OU 68687B	C moderate Ca. very fine in 12- μ m veinlet OU 68686D	D med.- high Ca, fibrola- mellar, OU 68687	E high Ca, large crystal. OU 68686
	average of 23	average of 7	average of 2	average of 3	
wt.% oxides					
SiO ₂	26.02	25.64	26.81	27.08	28.77
Al ₂ O ₃	0.17	0.03	0.17	0.16	0.26
TiO ₂	0.01	0.11	bdl	bdl	bdl
Fe ₂ O ₃	0.19	0.20	0.09	bdl	bdl
Mn ₂ O ₃	34.76	34.25	35.08	33.53	36.28
CaO	0.31	1.38	2.23	4.70	6.35
Na ₂ O	0.14	0.07	0.08	0.07	0.06
BaO	29.08	29.08	25.15	21.12	18.52
SrO	1.51	bdl	2.72	2.55	1.79
H ₂ O (calc)	7.87				
Total	100.06	90.76	92.33	89.22	92.03
cations, O = 8					
Si	1.98	1.98	1.99	2.01	2.01
Al	0.01	0.00	0.01	0.01	0.02
Ti	0.00	0.01			
Fe	0.01	0.01	0.01		
Mn	2.02	2.01	1.98	1.90	1.93
Ca	0.03	0.11	0.18	0.37	0.48
Na	0.02	0.01	0.01	0.01	0.01
Ba	0.87	0.88	0.73	0.62	0.51
Sr	0.07		0.12	0.11	0.07
Total cations	5.01	5.01	5.03	5.03	5.03
Total Fe and Mn reported as Fe ³⁺ and Mn ³⁺ ; bdl = below detection limit.					

cluster, not only has virtually all Na of the host been lost, H₂O and Ca introduced, and atomic proportions of Si, Mn and Ba modified, but Sr, present in significant amounts in most Woods noélsenite, was below detection limits.

Spot analyses of noélsenite in rock specimens OU 68686 and 68687 reveal CaO from below detection limits to 7 wt%. Representative groups of analyses are given in Table 2 and data from 91 spot EMP analyses are shown on the Ca-BaSr triangle, Fig. 4. High-Ca grains at Woods mine include both tightly appressed fibrolamellar aggregates (Table 2, column D) and crystals of normal blocky habit (Table 2, column E).

The observations indicate solid solution in noélsenite half way towards a hypothetical Ca end-member. They also suggest that late-stage alteration responsible for forming noélsenite and cerchiarite in the Woods mine occurrence involved solutions of locally variable composition, implying a correspondingly complex history.

Noélsenite is the Ba,Mn³⁺ analogue of lawsonite. Hennomartinite (Armbruster *et al.*, 1993) is the Sr,Mn³⁺ an-

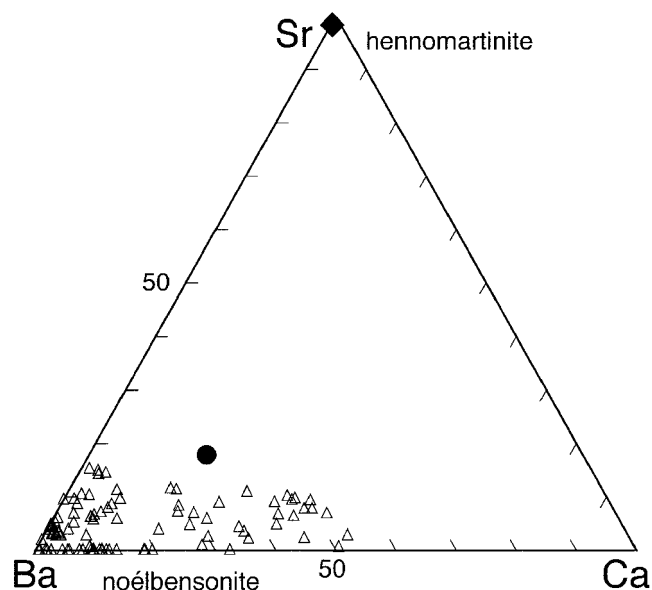


Fig. 4. Ca,Ba,Sr atomic proportions in noélsenite from Woods mine (open triangles, 91 EMP spot analyses) and Cerchiarite mine (filled circle, Lucchetti *et al.*, 1988); also hennomartinite (filled square, Armbruster *et al.*, 1993).

alogue. In lawsonite and hennomartinite Ca and Sr are contained in irregular 8-cornered O polyhedra with six relatively short cation to O distances and two more distant linkages (Baur, 1978; Armbruster *et al.*, 1992). The same presumably applies in noélsenite although its structure has not been refined. The difference between ionic radii of Ca²⁺ (about 1.2 Å) and Ba²⁺ (about 1.5 Å) in 8-fold co-ordination is even larger than that between Ca²⁺ and Sr²⁺ (about 1.33 Å) and would be expected to severely limit mutual substitution between Ca and Ba. Nevertheless, the data in Table 2 and Fig. 4 show no miscibility gap in noélsenite from the Ca-free end member to midway to a hypothetical Ca-end member of composition CaMn³⁺₂[Si₂O₇](OH)₂H₂O. Among various possibilities that are at present untested, the apparent cut-off at about 50% may simply reflect limited available Ca, or it might result from two distinct sites for large cations in noélsenite, one accommodating Ca and Ba in variable proportions, the other Ba only. This could be accompanied by a doubling of the unit cell.

Conclusions

The occurrences of Mn³⁺-rich silicates ungarettiite, namansilite, sugilite, and braunite at the Woods mine result from an event involving oxidation of Mn²⁺ minerals. With declining temperature, fine fractures allowed passage of Ba-rich and still later Ba,Cl-rich fluids resulting in the crystallization of noélsenite followed by cerchiarite.

Optical observations suggest that the Woods mine cerchiarite may be in part or in whole pseudotetragonal rather than strictly tetragonal as described from the type locality (Basso *et al.*, 2000).

New data show up to about 50% substitution of Ca for Ba in noélbensonite.

Textures and mineral parageneses in the Woods Mine require a complex history of recrystallizations. The late-stage hydrothermal alteration that was responsible for the formation of noélbensonite and cerchiaraita itself requires complex interactions with solutions of changing compositions.

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