Coulsellite, a new mineral from the Cleveland mine, Luina, Tasmania

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ABSTRACT

Coulsellite, ideally $CaNa_3AlMg_3F_{14}$, is a new mineral from the Cleveland tin mine, Luina, Tasmania, Australia (41°28'57"S, 145°23'7"E). Coulsellite forms pseudo-octahedral crystals up to 2 mm across associated with quartz, fluorite, morinite, gearksutite, orthoclase (adularia), siderite, pyrite and vivianite. Crystals are colourless to white with a white streak, and are transparent to translucent with a vitreous lustre. The Mohs hardness is 4.5, fracture conchoidal and no cleavage is present. Twinning is not observed optically but can be detected in diffraction patterns; crystals are multiply twinned about the pseudocubic 3-fold axes. Coulsellite is rhombohedral R-3m, with a = 7.1756(1) Å, α = 59.867(1)°, V = 260.560(7) Å^3 and Z = 1. Calculated density is 2.994 g cm^{-3}, compared to a measured density of 2.99(1) g cm^{-3}. Coulsellite crystals are optically isotropic, with mean refractive index 1.40 (at 589 nm). Microprobe analysis led to an empirical formula (based on 14 anions) of $Ca_{0.98}Na_{2.88}Al_{1.03}Mg_{2.86}P_{0.07}F_{13.47}(OH)_{0.53}$. The simplified formula $CaNa_3AlMg_3F_{14}$ requires Al 5.67, Ca 8.43, Mg 15.4, Na 14.5 and F 56.0, total 100.00 wt %. The five strongest powder diffraction lines [d in Å, (I/I_0), (hkl)] are 2.926, (100), (006, 202); 1.791, (66), (208, 220); 2.325, (33), (107, 205, 211); 1.528, (20), (0210, 226, 042); 1.949, (19), (009, 125, 303). Coulsellite has pyrochlore stoichiometry, but its crystal structure is based on a modified pyrochlore framework that is possibly unique amongst published structures of pyrochlore-like minerals in having 1:3 ordering of Ca and Na in the A site and Al and Mg in the B site.

INTRODUCTION

Well-formed crystals of a Ca-bearing ralstonite-like mineral (UM1990-21-F:AlCaHMgNa; Smith and Nickel, 2007) from the Cleveland mine, Luina, Tasmania, were investigated by Birch and Pring (1990). Aspects of the chemistry indicated that the mineral was probably a new species, but the difficulty of determining its crystal structure prevented full characterisation at the time. Recent studies have resolved this problem and the mineral has been formally approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (2009-070). With a chemical formula $CaNa_3AlMg_3F_{14}$, the new mineral has been named coulsellite in recognition of Ruth Elise Coulsell (1912–2000). Ruth was a foundation and honorary life member of the Mineralogical Society of Victoria, an enthusiastic collector, generous benefactor and dedicated educator (Hall *et al.*, 2000) (Figure 1). A full description of the crystal structure of coulsellite has been published by Mumme *et al.* (2010).

The type locality for coulsellite, the Cleveland tin mine, is situated 14 km south-west of Waratah, in western Tasmania (41°28'57"S, 145°23'7"E) (Figure 2) The deposit was discovered in 1898, but its main period of operation was between 1968 and 1986. Collecting during mining resulted in some fine crystals of quartz and fluorite being preserved, as well as a suite of samples containing coulsellite and other gangue minerals (Hall, 1990), including another new species (IMA 2009–046). The type specimen of coulsellite was donated to Museum Victoria by Peter Hall in 1986 and is registered M41450 in the mineral collection.

Figure 1: Ruth E. Coulsell

OCCURRENCE AND GEOLOGICAL SETTING

The Cleveland tin–copper deposit consists of several lenses of pyrrhotite–cassiterite–stannite–chalcopyrite mineralisation within a complex Early Cambrian sequence of altered mafic volcanic rocks and sediments, including chert and limestone (Cox and Glasson, 1971; Ransom and Hunt, 1975; Collins, 1981). The Late Devonian Meredith Granite underlies the deposit. Mineralisation proceeded in several stages via fluids derived from the granite late in its intrusion. An early stockwork system of quartz–fluorite–

wolframite–molybdenite veins was followed by emplacement of sulfide mineralisation (with quartz, tourmaline and fluorite) during dissolution and replacement of limestone beds. Veins and vughs filled with quartz, fluorite and carbonate formed last. Studies of fluid inclusions and stable isotopes indicate a temperature interval between 500 and 250°C for the mineralisation, involving fluids with low to moderate salinity and variable CO_2 contents (Collins, 1981).

The new mineral occurs on specimens consisting of quartz and fluorite overlain by whitish crusts made up of unusual fluoride minerals including gearksutite and morinite, together with orthoclase ('adularia'), bertrandite, siderite, pyrite and vivianite (Birch and Pring, 1990; Hall, 1990). The assemblage shows exceptionally developed crystals. Coulsellite tends to occur early in the fluoride sequence, growing directly on quartz crystals (Figures 2 and 3), followed by morinite (Figure 4) and gearksutite (Figure 5), suggesting crystallisation from Na–Ca–Mg-bearing solutions derived by reaction between F-bearing magmatic brines and the enclosing carbonate beds. The fluoride minerals are likely to represent a low-temperature assemblage characteristic of late-stage veins and vughs, although where in the mine these samples were collected is not known precisely. However, it is reported that they were found in "fault zones between levels 11 and 15 during the 1970s" (Michael Newnham, personal communication). Another occurrence of coulsellite may be in greisenised dykes at the Mt Bischoff tin mine, Tasmania, where Wright (1985) recorded a variety of ralstonite in which Ca replaced part of the Na.

APPEARANCE AND PROPERTIES

Coulsellite crystals are very well-formed pseudo-octahedra up to 2 mm across, usually intergrown to form crusts (Figures 2 and 3). They have a vitreous lustre and are transparent to translucent with a white streak. The estimated Mohs hardness is 4.5; tenacity is brittle, fracture conchoidal, and neither cleavage nor parting is observed. The crystals do not fluoresce under UV light. The density measured by the sink–float method in diiodomethane/chloroform is 2.99(1) g cm^{-3}; the calculated density is 2.994 g cm^{-3}. Coulsellite crystals are essentially optically isotropic, with the mean refractive index being 1.40 (at 589 nm). The only form observed is pseudo-octahedral '{111}' (probably {00.1} and {12.1} for rhombohedral symmetry); twinning is not observed optically but is observable in diffraction patterns. The *a*:*c* ratio is 2.457 (hexagonal setting).

Table 1: Electron microprobe data for coulsellite

Element	Average	Range	Birch & Pring (1990) M38127	Calculated for $CaNa_3AlMg_3F_{14}$
Al	5.93	5.76–6.04	6.21	5.67
Ca	8.41	8.30–8.49	8.71	8.43
Mg	14.9	14.8–15.1	15.09	15.4
Na	14.2	14.0–14.3	14.1	14.5
F	54.8	54.1–55.5	49.2	56.0
O	1.81	1.39–2.23	5.25	
P	0.49	0.28–0.65	0.53	
Total	100.54		99.25	

CHEMICAL COMPOSITION

Chemical analyses (12) were conducted on crystals from Museum Victoria sample M41459 using a JEOL 8500 Hyperprobe operated at an accelerating voltage of 15 kV, a beam current of 10 nA and in WDS mode for all elements other than O. The beam was defocussed to 20 µm and the sample stage was moved during analyses to minimise beam damage and ion migration. Standards used were cryolite (Na_3AlF_6) for Na, Al and F, $CaSiO_3$ for Ca, fluorapatite for P, and $MgAl_2O_4$ for Mg and O. Overestimation of the O content due to an overlapping second-order Na peak was corrected by using a quantitative energy dispersive method. Small amounts of P were detected in all analyses. It is possible that this is due to a fine-scale intergrowth of crandallite, $CaAl_3H(PO_4)_2(OH)_6$. The analytical data are shown in Table 1, along with an analysis of 'calcian ralstonite' from Birch and Pring (1990) and the calculated ideal composition of $CaNa_3AlMg_3F_{14}$. The empirical formula (based on 14 anions) is $Ca_{0.98}Na_{2.88}Al_{1.03}Mg_{2.86}P_{0.07}F_{13.47}(OH)_{0.53}$. This compares with the formula obtained from the analysis of Birch and Pring (1990) on crystals from a different sample (M38127) of $Ca_{1.04}Na_{2.94}Al_{1.10}Mg_{2.98}P_{0.08}F_{12.42}(OH)_{0.90}O_{0.68}$. The simplified formula is $CaNa_3AlMg_3F_{14}$.

CRYSTALLOGRAPHY

X-ray powder diffraction data for coulsellite were collected using a Philips diffractometer, equipped with a graphite monochromator and using Cu$K\alpha$ radiation (Table 2). Unit cell parameters were refined by the Rietveld method, using the hexagonal setting for *R*-3*m*. Coulsellite is rhombohedral, space group *R*-3*m*, with *a* 7.1756(1) Å, α 59.867(1)° (*a* 7.1620(1) Å, *c* 17.5972(3) Å (in the hexagonal setting), 260.560(7) Å^3 and $Z = 1$.

Fragments taken from crushed coulsellite crystals and examined by oscillation, precession and Weissenberg methods all gave photographs showing the presence of multiply split spots at high angles, indicating twinning and symmetry lower than cubic. One of these fragments was chosen for intensity data collection using a Bruker Apex II CCD diffractometer. Indexing of all reflections led initially to a triclinic cell, but through continued attempts to improve the refinement on the basis of the pseudocubic parent pyrochlore cell, and by taking the observed twinning into account, this cell was successfully transformed into one with rhombohedral symmetry (Mumme *et al.*, 2010). Such a cell is consistent with the 1:3 ordering of both

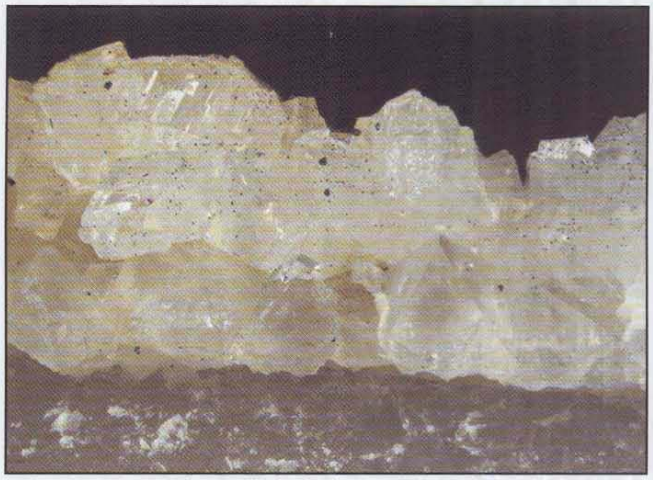

Figure 2: Coulsellite crystals (colourless octahedra) growing on quartz and encrusted with morinite crystals. Museum Victoria specimen M41450; field of view is 7 mm across. Photograph by Bill Birch and Sarah McCaffrey.

Figure 3: (top right) Coulsellite crystals (colourless octahedra) on quartz. Museum Victoria specimen M41450; field of view is 8 mm across. Photograph by Bill Birch and Sarah McCaffrey.

Ca:Na and Al:Mg at the *A* and *B* sites, respectively, of the pyrochlore cell. It is this ordering which makes the structure of coulsellite possibly unique amongst pyrochlore minerals. The structure itself consists of a pyrochlore-like framework of corner-connected octahedra with composition $AlMg_3F_{12}$ (Figure 6). The Al and Mg ions are ordered into alternate layers along [111] of the rhombohedral cell. The Mg-centred octahedra form hexagonal tungsten bronze (HTB)-type layers parallel to (111), with the Ca ions located in the centres of the hexagonal rings in the HTB layers. These HTB layers alternate with layers containing the AlF_6 octahedra, and Na atoms with pyrochlore-type distorted cubic coordination.

While coulsellite has the stoichiometry of ralstonite-type minerals, most of which have the cubic pyrochlore ($A_2B_2X_6Y$) structure of the prototype mineral $(Na,Ca)_2Nb_2O_6(OH,F)$ (Pabst, 1939; Pauly, 1965; Effenberger and Kluger, 1984), the rhombohedral structural modification it displays is unusual. A recent example of a rhombohedral pyrochlore confirmed by a full crystal structure refinement is parabariomicrolite, $BaTa_4O_{10}(OH)_2{\cdot}2H_2O$ (Ercit *et al.*, 1986).

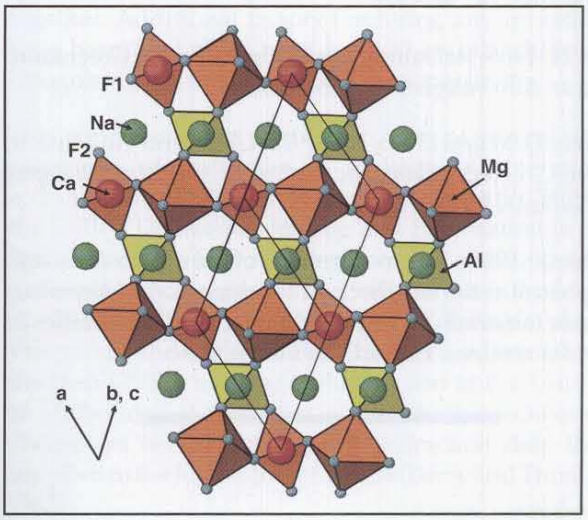

Figure 4: Clusters of morinite crystals. Museum Victoria specimen M41450; field of view is 17 mm across. Photograph by Bill Birch and Sarah McCaffrey.

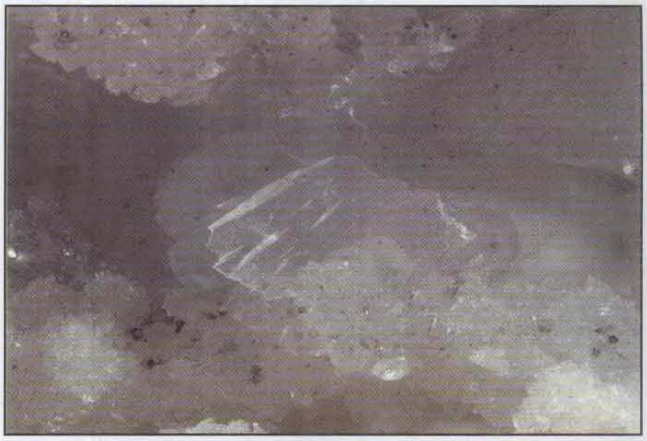

Figure 5: Gearksutite crystal 1.3 mm across with morinite. Museum Victoria specimen M38124. Photograph by Bill Birch and Sarah McCaffrey.

Figure 6: (left) View of the structure for coulsellite along $[01\text{-}1]_{rh}$. Atom labels and unit cell axes are shown.

Table 2: X-ray powder diffraction data for coulsellite

I	d_{meas}	d_{calc}	hkl
12	5.86	5.87	003
		5.89	101
5	5.07	5.07	012
3	3.584	3.589	104
		3.581	110
8	3.054	3.061	015
		3.056	113
		3.054	021
100	2.926	2.932	006
		2.925	202
33	2.325	2.330	107
		2.327	205
		2.324	211
8	2.067	2.073	018
		2.069	214
		2.067	030
19	1.949	1.955	009
		1,951	125
		1.950	303
66	1.791	1.794	208
		1.790	220
1	1.712	1.712	223
		1.712	131
4	1.603	1.604	128
		1.602	134
2	1.545	1.546	315
		1.545	401
20	1.528	1.530	0210
		1.528	226
		1.527	042
3	1.463	1.462	404
3	1.420	1.422	2011
		1.421	309
		1.418	321
3	1.320	1.321	1211
		1.320	229
		1.319	235
		1.319	143
5	1.267	1.267	048
3	1.238	1.238	327
		1.237	051
1	1.196	1.196	0312
3	1.194	1.195	238
		1.194	054
		1.194	330
1	1.165	1.165	2014
7	1.162	1.163	4010
		1.162	2014
		1.162	422
2	1.135	1.135	2212
2	1.133	1.133	244
1	1.037	1.037	0216
3	1.034	1.034	428
		1.034	060

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REFERENCES

Birch, W. D. and Pring, A. 1990: A calcian ralstonite-like mineral from the Cleveland Mine, Tasmania, Australia. *Mineralogical Magazine*, 54, 599–602.

Collins, P. L. F. 1981: The geology and genesis of the Cleveland tin deposit, western Tasmania: fluid inclusion and stable isotope studies. *Economic Geology*, 76, 365–392.

Cox, R. and Glasson, K. R. 1971: Economic geology of the Cleveland mine, Tasmania. Economic Geology, 66, 861–878.

Effenberger, V.H. and Kluger, F. 1984: Ralstonit: ein beitrag zur kenntnis von zusammensetzung und kristallstruktur. *Neues Jahrbuch fur Mineralogie Monatshefte*, 97–108.

Ercit, T.S., Hawthorne, F.C. and Cerny, P. 1986: Parabariomicrolite, a new species and its structural relationship to the pyrochlore group. *Canadian Mineralogist*, 24, 655–663.

Hall, P. 1990: Minerals of the Mt Cleveland mine, Luina, Tasmania. *Australian Mineralogist*, 5, 82–92.

Hall, P., Pring, A. and Vince D. 2000: Obituary for Ruth Elise Coulsell. *Australian Journal of Mineralogy*, 6, 129–130.

Mumme, W. G., Grey, I. E., Birch, W. D., Pring, A., Bougerol, C. and Wilson, N. C. 2010: A rhombohedral pyrochlore with 1:3 ordering in both A and B sites in $CaNa_3AlMg_3F_{14}$, a ralstonite-like mineral from the Cleveland Mine, Tasmania, Australia. *American Mineralogist*, in press.

Pabst, A. 1939: Formula and structure of ralstonite. *American Mineralogist*, 24, 566–576.

Pauly, H. 1965: Ralstonite from Ivigtut, South Greenland. *American Mineralogist*, 50, 1851–1864.

Ransom, D. M and Hunt, F. L. 1975: Cleveland Tin Mine: in Knight, C. L. (ed.), *Economic Geology of Australia and Papua New Guinea. I Metals*, 584–591.

Wright, J. 1985: The occurrence of rare fluorides and phosphates at the Mt Bischoff tin deposit. In *Minerals of Tasmania* (abstracts). Combined mineralogical societies of Australia seminar, Hobart, Tasmania, June.