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THE FORMATION OF HYDROTHERMAL COOKEITE IN THE BRECCIA PIPES OF THE ARDLETHAN TIN FIELD, NEW SOUTH WALES, AUSTRALIA

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ABSTRACT

Cookeite, a di/trioctahedral chlorite, occurs in the breccia pipes of the Ardlethan tin field, New South Wales, Australia. Cookeite formed as a late-stage, low-temperature (150 to 190°C) hydrothermal product in pore spaces in breccias which host disseminated cassiterite and sulfide mineralization. The coupled substitution Al + Li = Si + □ results in high Si and low Li and Al contents which consequently results in a low occupancy of octahedral positions. Refined cell parameters are *a* 5.158(1), *b* 8.929(1), *c* 14.232(2) Å, *β* 96.91(1)°.

Keywords: high-Si cookeite, Ardlethan tin field, breccia pipes, hydrothermal, late-stage, New South Wales, Australia.

SOMMAIRE

Nous avons trouvé un exemple de cookeite, chlorite di/trioctaédrique, dans les conduits bréchifiées du camp stannifère de Ardlethan (New South Wales, Australie). Elle a été formée à un stade tardif, à basse température (entre 150 et 190°C), dans un milieu hydrothermal; elle occupe les cavités des brèches qui renferment la cassitérite et les sulfures. La substitution du coupe Al + Li pour Si + □ explique la teneur élevée en Si et la déficience en Li et en Al, ainsi que les lacunes dans les sites octaédriques. Un affinement des paramètres réticulaires donne: *a* 5.158(1), *b* 8.929(1), *c* 14.232(2) Å, *β* 96.91(1)°.

(Traduit par la Rédaction)

Mots-clés: cookeite siliceuse, champ stannifère de Ardlethan, conduits bréchifiés, hydrothermal, stade tardif, New South Wales, Australie.

INTRODUCTION

Though most chlorite species are trioctahedral, di/trioctahedral chlorites occur of which cookeite is the best known and characterized. Cookeite has been reported as the product of bauxite alteration (Vrublevskaja *et al.* 1975, Goffé 1977), in veins in sandstone (Miser & Milton 1964), and as replacements of spodumene, petalite and other Li-rich minerals in pegmatite (Rubai 1981, Kanaoka & Kato 1971). The cookeite studied in this report is associated with quartz and fluorite in vugs in the breccias of the Ardlethan tin field. The cookeite postdates cassiterite and sulfide formation, and probably was deposited by late-stage magmatic fluids.

GEOLOGY AND DEPOSIT GENESIS

The Ardlethan tin field (Fig. 1) is in central New South Wales about 570 km southwest of Sydney, at the western extremity of the Lachlan Fold Belt (Paterson 1976). Disseminated cassiterite and sulfides are associated with breccia pipes within a late-Silurian S-type granite (the Mine granite) which is typically coarse grained, grey- to cream-colored, weakly foliated and biotite-rich. The breccia pipes and the tin mineralization are related to a later series of well-differentiated, volatile-rich, peraluminous intrusive bodies: a garnet-bearing quartz-feldspar porphyry, the Ardlethan granite, microgranite dykes, and the Mine porphyry. It is believed that overpressure from volatiles, accumulated during differentiation of the Ardlethan granite at depth, resulted in the brecciation of the Mine granite near its contact with the Ordovician sediments. The breccia pipes focused subsequent flow of fluids and localized the cassiterite mineralization which may be subdivided on the basis of mineralogy and style of brecciation of the host pipes into the following groups of deposits: (1) Ardwest - Wildcherry - Wildcherry South - Perseverance; (2) Blackreef - Godfrey - Godfrey South - Carpathia - Stackpool; and (3) White Crystal. Each group appears to represent a phase of brecciation and mineralization: the Ardwest group of deposits apparently formed first, followed by the Blackreef-Godfrey group, followed by the White Crystal deposit.

The Ardwest group of deposits (Figs. 2, 3) formed on the margins of an intrusive breccia pipe which had an impermeable core of rock flour and granite fragments. The mineralogy in these deposits is zoned with depth. In the upper levels (Ardwest-Wildcherry-Wildcherry South) disseminated cassiterite occurs with later sulfides and chlorite. At deeper levels in the Perseverance deposit, which is an extension to the Wild Cherry South deposit, cas-

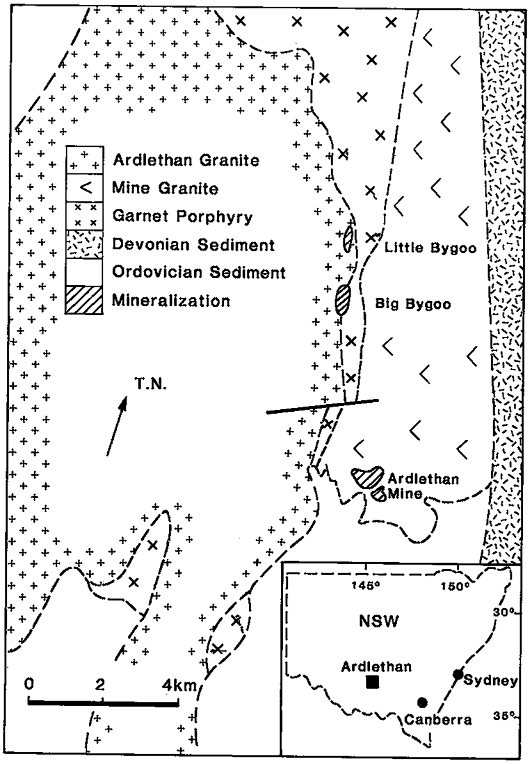

FIG. 1. Geology of the Ardlethan area.

siterite occurs with sericite, tourmaline, siderite and minor cookeite. Beneath the zone of tin mineralization secondary biotite occurs.

The Blackreef–Godfrey deposits are steeply dipping pods of high-grade cassiterite–sulfide–tourmaline mineralization spatially associated with sediment-rich breccia pipes. A sericite–siderite alteration halo around the Blackreef deposit overprints earlier assemblages. Minor cookeite also occurs in these deposits.

Cookeite is best developed in the White Crystal deposit (Figs. 2, 4) which sits within a collapse breccia pipe (Clarke *et al.* 1985). The cores of granite fragments within the breccia have been altered to topaz and quartz and are rimmed by an assemblage of quartz, tourmaline, cassiterite and wolframite. Remaining vugs are lined by quartz and sulfides and infilled by toothy quartz, fluorite and cookeite. The cookeite is white to brownish white, very fine grained and commonly infills the spaces between the toothy quartz crystals. Masses of cookeite have volumes of several cubic centimeters. This material was examined using optical microscopy, X-ray diffraction, transmission electron microscopy of a grain mount, and scanning electron microscopy; no contaminating phases were detected. Rarely, fine veinlets of galena occur in the cookeite.

The cookeite in the Perseverance, Blackreef, Godfrey and Godfrey South deposits also occurs as vug

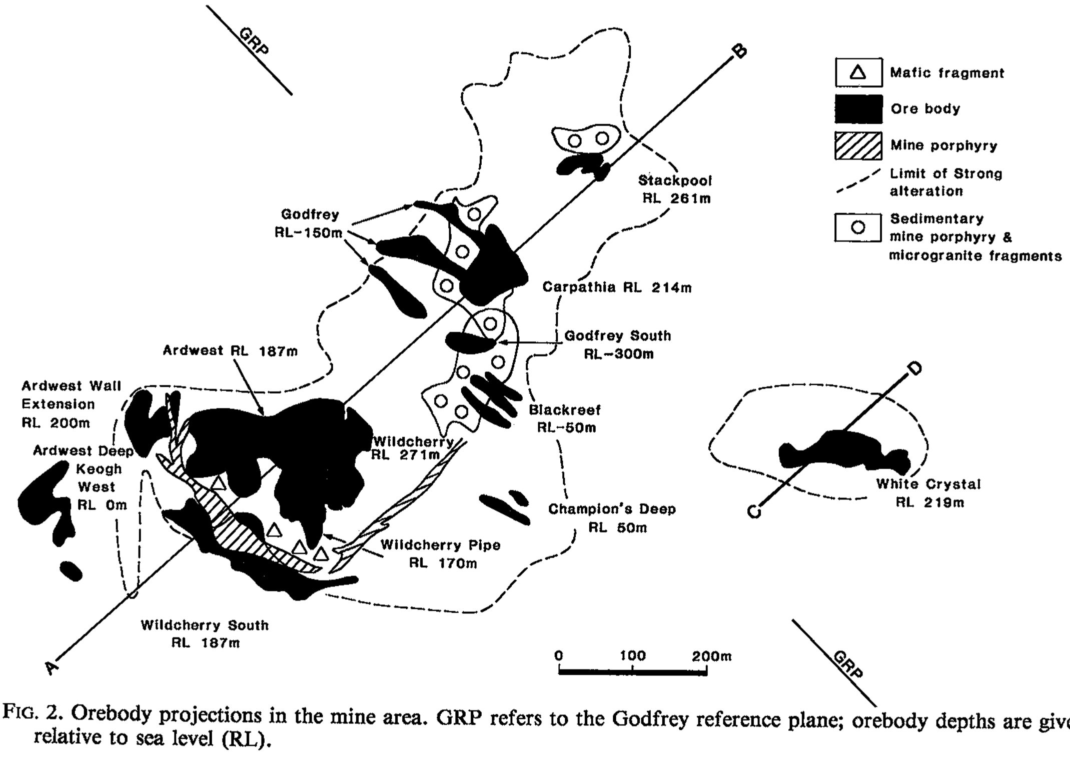

FIG. 2. Orebody projections in the mine area. GRP refers to the Godfrey reference plane; orebody depths are given relative to sea level (RL).

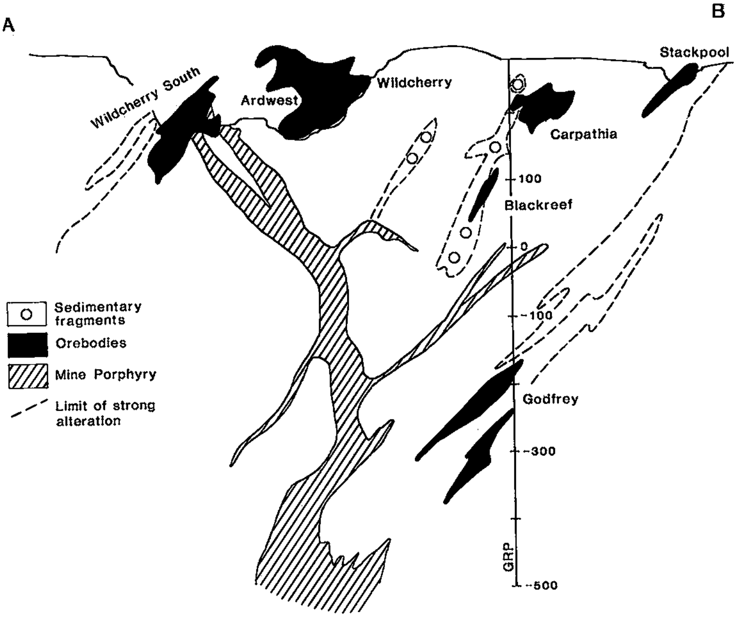

FIG. 3. Section A–B shown on Figure 2. Vertical scale in meters; V/H = 1.

infillings with toothy quartz and fluorite. Pyrite and siderite are associated with cookeite in the Blackreef deposit; rare tourmaline occurs with cookeite in drill cores of the Godfrey deposit. It is common to see volumes of cookeite up to 10 cubic centimeters in vugs in the Blackreef deposit, but the vug population is smaller than that of the White Crystal deposit.

FLUID-INCLUSION DATA

Two types of fluid inclusions occur in quartz, topaz, and fluorite from the White Crystal deposit: (1) CO_2-rich inclusions containing liquid CO_2, CO_2-rich vapor, and an aqueous phase, and (2) H_2O-rich inclusions containing vapor and aqueous phases only. Microthermometry measurements (Fig. 5) confirm that the formation of cookeite was a late-stage, low-temperature hydrothermal event of this magmatic–hydrothermal system.

Primary fluid inclusions of both types in topaz and quartz, representing the cassiterite stage of mineralization, homogenize between 320 and 350°C into an aqueous phase or vapor phase, allowing a pressure estimate of 400 to 450 bars on the assumption that primary inclusions close together were trapped simultaneously. Primary fluid inclusions in quartz associated with sulfide mineralization homogenize between 190 and 250°C, and the primary and secondary fluid inclusions in the later toothy quartz and fluorite all homogenize between 150 and 190°C (Fig. 5). CO_2-rich and H_2O-rich fluid inclusions coexist along fractures in inclusion-bearing material

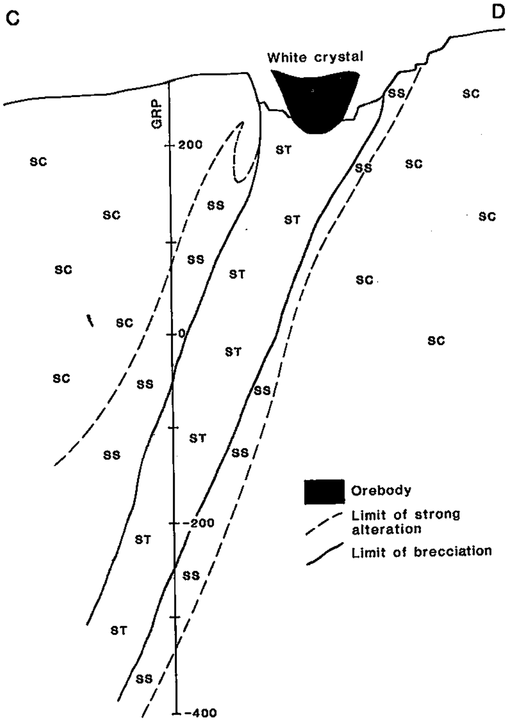

FIG. 4. Section C-D through White Crystal breccia pipe. St: strong sericite and tourmaline alteration; SS: strong sericite and siderite alteration; SC: weak sericite and chlorite alteration. Vertical scale in meters; V/H = 1.

TABLE 1. CHEMICAL ANALYSES OF COOKEITE

component	1	2	3	4	5	means
SiO2	36.09	36.94	36.12	36.13	37.12	36.48
Al2O3	45.06	45.34	45.36	44.84	44.91	45.10
FeO	<0.04	0.04	0.07	0.05	0.05	0.04
MgO	0.11	0.09	0.09	0.10	0.10	0.10
CaO	0.06	0.08	0.09	0.09	0.09	0.08
Na2O	0.03	0.05	0.06	0.03	0.05	0.04
K2O	0.14	0.13	0.19	0.16	0.14	0.15
Li2O*	1.87	1.82				1.85
Total*	83.40	84.49	83.40	83.28	84.31	83.84

unit cell based on 18 O, OH and F

Si(T)	3.241	3.267	3.288	3.249	3.294	3.256
Al(T)	0.759	0.733	0.712	0.751	0.706	0.744
Al(O)	4.010	3.993	4.005	4.002	3.991	4.000
Fe(O)	0.000	0.003	0.005	0.004	0.004	0.003
Mg(O)	0.015	0.012	0.012	0.013	0.013	0.013
Ca(O)	0.006	0.008	0.009	0.009	0.009	0.008
Na(O)	0.005	0.009	0.010	0.005	0.009	0.008
K(O)	0.016	0.015	0.022	0.018	0.016	0.017
Li(O)*	0.668	0.658	0.665	0.669	0.660	0.664
Total	8.720	8.698	8.731	8.720	8.702	8.714

* Values of analysis 3, 4 and 5 are calculated based on the average Li2O content of 1.85 wt.%.

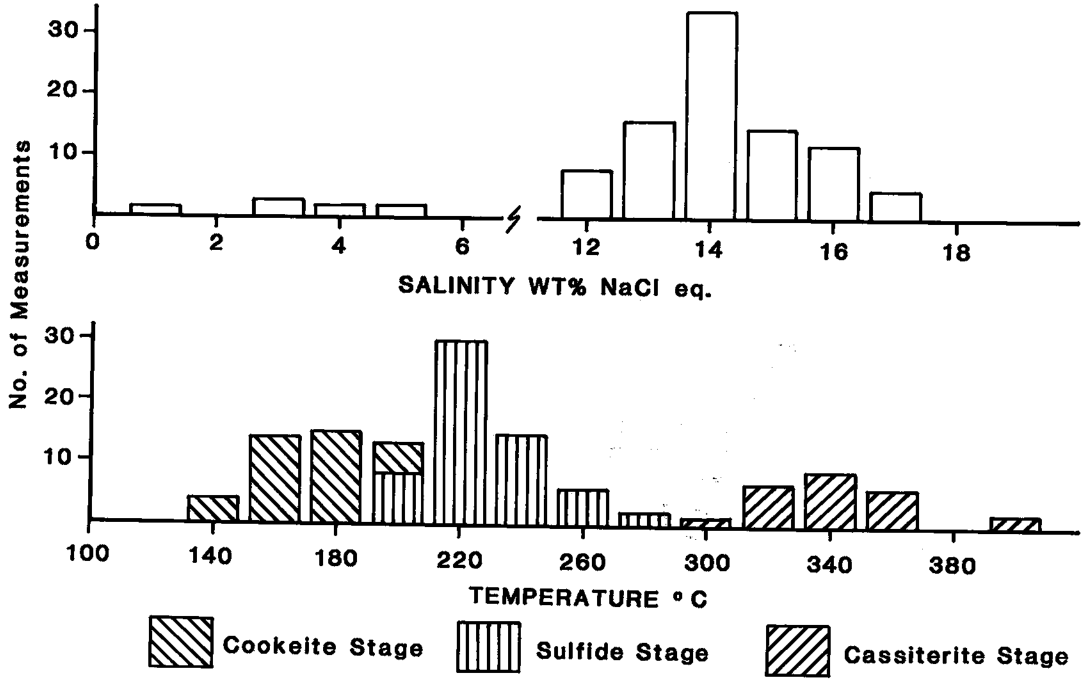

FIG. 5. Fluid-inclusion results from samples from the White Crystal deposit.

from all stages of mineralization, thus indicating that the fluids continued to boil as temperature and pressure declined sympathetically. The salinity (Fig. 5) of type 2 fluid inclusions, calculated from temperature depressions of ice melting using the method of Roedder (1984), varies between 11 and 18 wt.% NaCl equiv. and correlates poorly with filling temperatures. The salinity of type 1 fluid inclusions, calculated from temperature depressions of clathrate melting (Collins 1979) vary between 1 and 4 wt.% NaCl equiv. The temperatures of cookeite formation are taken to be the same as the filling temperatures of both the primary and secondary fluid-inclusions in the toothy quartz and fluorite, *i.e.*, between 150 and 190°C.

Fluid-inclusion filling temperatures from quartz and fluorite in the Blackreef and Godfrey deposits are slightly higher than those obtained from the White Crystal deposit. Cassiterite-stage temperatures are between 330 and 360°C, and sulfide-stage temperatures are mostly between 220 and 270°C. Primary and secondary fluid-inclusions in toothy quartz and fluorite, representing the formation of cookeite, mostly homogenize between 160 and 205°C. Fluid-inclusion filling temperatures from quartz in the Godfrey South and Perseverance deposits are not significantly different from those obtained from the Blackreef deposit and suggest that the temperatures of cookeite formation in all deposits are similar.

CHEMISTRY AND POWDER X-RAY DIFFRACTION

Five cookeite samples from the White Crystal deposit were analyzed for all elements except lithium using a CAMECA electron microprobe. Lithium was determined in two of these samples by atomic absorption spectrometry (Table 1). The cookeite was found to contain 36.5 ± 0.6 wt.% SiO_2, 45.1 ± 0.3 wt.% Al_2O_3 and 1.8 wt% Li_2O. The total amount of FeO, MgO, CaO, Na_2O and K_2O was less than 0.4 wt.%, and the levels of Ti, Mn, Ni and Cr were below detection limits.

The structural formula based on 14 oxygen atoms is $[Al_{4.02}Li_{0.66}\square_{0.287}Fe_{0.003}Mg_{0.013}K_{0.017}]\ [Si_{3.27}Al_{0.73}]\ O_{10}(OH)_8$ which gives an octahedral occupancy value of 4.71. This is significantly lower than the ideal value of 5 given by Brammall *et al.* (1937) but is close to the minimum of 4.75 given by Černý (1970) in a summary of reported values based on Miser & Milton (1964).

The low octahedral vacancy is unlikely to be the result of quartz contamination in the analyzed samples as various tests failed to detect any contaminating phases (see above). Neither could the presence of Be or B in the structure account for the difference; for example, an assumption of 3 wt.% BeO in the samples would only increase the octahedral occupancy to 4.79. Most likely the high vacancies are the result of the coupled subsitution

$$Al + Li = Si + \square$$

which leads to higher Si and lower Al and Li contents in the mineral.

The results of an X-ray diffraction study of cookeite samples from the White Crystal deposit are given in Table 2. The refined cell parameters are *a* 5.158(1), *b* 8.929(1), *c* 14.232(2) Å, *β* 96.91(1)°. These are similar to the results of Lister (1966). However, the slightly smaller values of *a* and *b* and slightly larger values of *c* may be the result of the proposed coupled subsitution.

DISCUSSION AND CONCLUSIONS

The cookeite in the breccia pipes of the Ardlethan tin field is a hydrothermal product occurring as vug infillings. The textural relationships and the freshness of the associated minerals exclude the possibility that cookeite is a product of weathering. The relatively low Li content of the Mine granite (40–70ppm, R. Paterson, pers. comm., 1985) indicates that

TABLE 2. X-RAY DIFFRACTION PATTERN OF COOKEITE

hkl	Intensity	d Å (obs)	d Å (cal)
001	100	14.10	14.128
002	30	7.058	7.064
003	80	4.708	4.709
020			4.464
110	20	4.450	4.442
111	10	4.124	4.116
004	60	3.532	3.532
113	5	3.050	3.075
005	1	2.830	2.826
200	60	2.561	2.560
$20\bar{2}$	75	2.505	2.505
202	90	2.318	2.319
220	1	2.221	2.221
221	5	2.153	2.160
$20\bar{5}$	30	2.020	2.022
007			2.018
204	30	1.964	1.964
150			1.686
240			1.682
310	10	1.685	1.676
206	20	1.638	1.638
$20\bar{8}$	5	1.543	1.543
060	70	1.488	1.488
062	1	1.455	1.456
063			1.419
$20\bar{9}$	10	1.417	1.416
064			1.371
208	5	1.376	1.378

refined cell-parameters

	Ardlethan	(Lister 1966)
a (Å)	5.158	5.162
b (Å)	8.929	8.938
c (Å)	14.232	14.162
β (°)	96.91	96.97

Diffraction pattern was obtained with Co radiation and a d=114mm camera for 24 hours. Si internal standard was used for corrections.

cookeite formation must involve hydrothermal transport of Li; the close association of cookeite and fluorite suggests that the Li was transported by late-stage, Li- and F-rich magmatic fluids, probably from the Ardlethan granite, which contains 100 to 500 ppm Li. Fluid-inclusion data confirm that the formation of cookeite was a late, low-temperature event in the hydrothermal history of the Ardlethan tin field. It is inferred that the coupled substitution Al + Li = Si + □, resulted in a high Si content, low occupancy of octahedral sites, and a departure of the cell parameters from the ideal values for cookeite. The substitution probably reflects the physicochemical conditions of formation.

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