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Cookeite and diaspore in the Back Creek pyrophyllite deposit near Pambula, New South Wales

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SUMMARY. The occurrence of cookeite, a di/trioctahedral chlorite of composition $(Al_{3\cdot95}Fe_{0\cdot02}Mg_{0\cdot01}Li_{0\cdot81})(Al_{0\cdot74}Si_{3\cdot26})O_{10}(OH)_8$, in the Back Creek pyrophyllite deposit near Pambula is described. The mineral is restricted to a relatively narrow zone near the centre of the deposit and although diaspore is also present in this zone the two have not been found in intimate association. It is concluded that the introduction of lithium has been the principal factor controlling development of the cookeite.

THERE are three known deposits of pyrophyllite in New South Wales (Loughnan, 1960) of which that at Back Creek near Pambula on the far south coast appears the most extensive. But, although the material has been worked intermittently for many years, until recently little in the way of subsurface exploration had been carried out, and hence specific information on the mineral composition and origin of the deposit was lacking. However, renewed interest in the use of pyrophyllite, particularly for the making of refractory ladle bricks, has resulted in a reappraisal of the deposit by the Pyrophyllite Corporation with a series of diamond and percussion drillholes and an extensive open cut in the southern part of the outcrop.

Geological setting. The deposit is situated 10·5 km south-west of Pambula and occurs within the Eden Rhyolite, which according to Hall (1957) is of Middle Devonian age and comprises mainly rhyolite with interbeds of ignimbrite, tuff, agglomerate, felsite, and conglomerate; the estimated maximum thickness is 275 m. These rocks, which in places are extensively faulted and sheared, immediately overlie an eroded surface of folded Ordovician metasediments and in turn are succeeded uncomformably by redbeds and volcanics of the Upper Devonian Locheil Formation. Steiner (1962) recognized three distinct flows with accompanying ignimbrites and pyroclastics within the unit and concluded that the bulk of the sequence was extruded as 'two nuées ardentes of decreasing volatile content'. In the vicinity of Back Creek, however, rhyolite conglomerate appears the dominant rock type, although pyroclastics and silicified lavas in varying stages of decomposition are abundant in places. The lavas not infrequently have a fluidal fabric and generally are porphyritic, the phenocrysts being quartz, plagioclase, and K-feldspar, whereas the groundmass is commonly devitrified glass. Chemical analyses of a sample of rhyolite conglomerate (PA163) and one of altered rhyolite (PA164) are given in Table I.

The pyrophyllite is associated with a series of minor shear fractures that strike approximately 320° and dip at angles little removed from the vertical. The pyrophyllitized zone can be traced for 400 m along the strike of the shears and varies in width up to 120 m. However, the walls are poorly defined, with pyrophyllite grading almost imperceptibly into the country rock. Apparently there was little discrimination by the alteration processes since clastic volcanic rocks as well as lavas were converted with seemingly equal facility to pyrophyllite thus giving credence to the concept that the alteration postdated consolidation of the parent rocks.

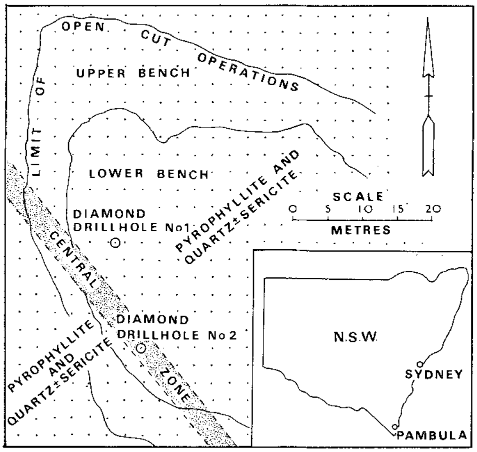


FIG. 1. Plan of the open cut at Back Creek showing locations of the central zone and two of the diamond drillholes.

X-ray, chemical, and petrographic examination of a wide array of samples obtained from percussion and diamond drillholes as well as from the walls of the open cut has revealed that the bulk of the deposit comprises mainly microcrystalline pyrophyllite with variable amounts of chalcedony and sericite. Toward the centre of the deposit, however, is a zone several metres wide (fig. 1) in which silica and potash are relatively deficient and, hence, quartz and sericite are virtually absent. Instead, appreciable quantities of chlorite, and to a less extent diaspore, are associated with the pyrophyllite. Since the chlorite has a dioctahedral X-ray diffraction pattern and is characterized by abundant aluminium and a small but nevertheless significant lithium content, it corresponds to the mineral cookeite. As far as can be determined this is the first recorded occurrence of cookeite associated with abundant pyrophyllite.

Cookeite is a relatively rare member of the chlorite group that has been found mostly as an alteration product of lithium-rich minerals in pegmatites. Nevertheless, Brammall *et al.* (1937) described an occurrence in Carmarthenshire, Wales, where the mineral forms a minor constituent of auriferous quartz veins. According to these authors, cookeite from this locality comprises a dioctahedral 2:1 layer of composition $[Al_2(AlSi_3)O_{10}(OH)_2]^{-1}$ and a trioctahedral interlayered hydroxide sheet consisting of $[LiAl_2(OH)_6]^{+1}$. But, from examination of a wide array of cookeites from various parts of the world, Černý (1970) concluded that the composition of both segments of the mineral structure is somewhat variable with the silicon content ranging from 2·93 to 3·17 and the octahedral-site occupancy from 4·90 to 5·35. Nevertheless, the X-ray diffraction pattern appears unaffected by these compositional variations. Moreover, despite the presence of a trioctahedral sheet, the 060 spacing for the mineral is at

1·49 Å, which is characteristic of dioctahedral layer silicates generally and contrasts with values of 1·53 Å to 1·56 Å obtained for trioctahedral chlorites.

In the Back Creek deposit cookeite has been found only within the relatively narrow central zone, where it occurs as felted aggregates of microcrystalline flakes in association with pyrophyllite. Of the samples obtained from this zone approximately half the number were found to contain cookeite, the content of the mineral varying up to 90 % of the total constituents. Identification of cookeite was made by petrographic, chemical, X-ray diffraction, infra-red absorption, and differential thermal techniques.

TABLE I. *Chemical analyses*

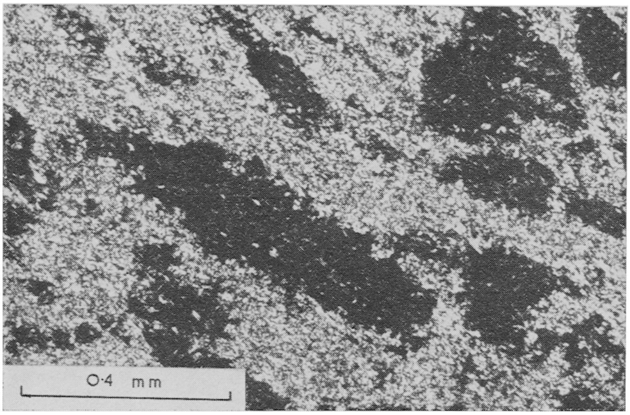
	Cookeite*	PA8	PA21	PA43	PA46	PA53	PA163	PA164
SiO_2	37·58	65·7	37·7	34·2	48·4	55·4	83·2	76·3
Al_2O_3	45·87	27·8	43·7	53·8	36·7	35·0	9·3	12·2
Fe_2O_3†	0·35	0·40	0·67	0·31	0·82	0·21	1·4	1·8
TiO_2	—	0·20	0·09	0·26	0·35	0·25	0·4	0·2
CaO	0·04	<0·01	0·07	0·03	0·05	<0·01	0·04	0·04
MgO	0·08	0·01	0·08	<0·01	0·06	0·19	0·06	0·01
Na_2O	0·02	—	—	—	—	—	0·22	0·72
K_2O	0·16	0·16	0·37	0·01	0·73	0·24	3·13	5·81
Li_2O	—	0·03	1·86	0·01	1·02	0·73	0·01	0·03
MnO	—	<0·01	<0·01	<0·01	<0·01	<0·01	—	—
Ign. loss	—	5·2	15·7	11·3	11·0	8·6	1·9	2·4
Total	—	99·5	100·3	99·9	99·1	100·6	99·6	99·5

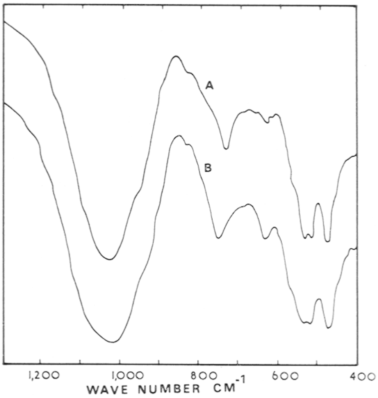
* Mean of 8 electron microprobe analyses by Dr. K. Norrish.
† Total iron as Fe_2O_3.
PA8, pyrophyllite.
PA21 to PA53, cookeite concentrates: PA21 contains about 85 % cookeite, PA43 about 45 % diaspore, PA46 about 50 %, and PA53 about 30 %, all with pyrophyllite.
PA163, rhyolite conglomerate.
PA164, altered rhyolite.

In thin section the mineral is colourless and, since the relief is almost identical with that of the associated pyrophyllite, considerable difficulty is experienced in differentiating the two minerals in plane polarized light. Under crossed polars, however, the contrast is apparent (fig. 2), pyrophyllite yielding bright second- and third-order interference colours whereas cookeite polarizes in greys of the first order and indeed bears a close resemblance to the serpentine mineral antigorite.

Since samples of cookeite free from contamination by pyrophyllite were unobtainable, the chemical composition was determined in part by electron microprobe through the courtesy of Dr. Keith Norrish and the results representing the mean of eight points are given in Table I. Lithium, however, cannot be evaluated by this method and consequently a number of samples of differing cookeite content were analysed for Li_2O by standard wet means. The values obtained were plotted against the calculated amount of cookeite in each sample and from the results it is apparent that the mineral contains between 2·2 and 2·4 % Li_2O. According to Černý (1970) considerable replacement of silicon by beryllium or boron is possible in the cookeite structure but emission spectrographic examination of several cookeite-rich samples from Back Creek revealed concentrations of less than 500 ppm beryllium and 200 ppm boron. On this basis therefore the composition of the mineral approximates

$$[(Al_{1\cdot95}Fe_{0\cdot02}Mg_{0\cdot01}Li_{0\cdot81})(OH)_6]^{+0\cdot74}[Al_2(Al_{0\cdot74}Si_{3\cdot26})O_{10}(OH)_2]^{-0\cdot74}.$$





FIGS. 2 and 3: FIG. 2 (left). Photomicrograph of cookeite aggregates (low birefringence) in pyrophyllite from Back Creek. Crossed polars. FIG. 3 (right). Infra-red absorption spectra of cookeite from Back Creek (A) and from Auburn, Maine (B).

Comparing this formula with the compositional variations cited by Černý (1970) it is apparent that the Back Creek cookeite has a relatively high silicon content and a low octahedral-site occupancy. Analyses of some of the samples used for the calculation of the Li_2O content of the mineral are given in Table I. Sample PA21 contains about 85 % cookeite, PA46 about 50 %, and PA53 about 30 %, whereas sample PA8 is of relatively pure pyrophyllite.

X-ray diffraction data for cookeite from Back Creek and from Londonderry, Western Australia, are given in Table II and it is apparent that despite some differences in intensities there is very close agreement in the positions of the reflections including the 060 spacing. Glycol saturation of the Back Creek cookeite failed to produce detectable change to the diffractogram, thus establishing the absence of expandable layers, whereas after heating at 600 °C for 1 hour a marked intensification of the 001 reflection resulted and the higher orders of the basal spacing were destroyed. This behaviour is characteristic of orthochlorites (Grim, 1968).

In fig. 3 the infra-red absorption spectra obtained for the Back Creek material are compared with those of cookeite from Auburn, Maine, and it will be observed that the two curves are almost identical. In fact, neither differs appreciably from that recorded by Hayashi and Oinuma (1965) for high-aluminium chlorite.

Differential thermal analyses of several cookeite-rich samples from Back Creek carried out at a heating rate of 15 °C/minute revealed a strong endothermic reaction centred about 545 °C and a smaller exotherm at 900 °C. It should be noted however, that these results are somewhat at variance with those obtained by Brown and Henley (1972) for the Londonderry cookeite.

Diaspore. From the work of Iwao (1953), Broadhurst and Councill (1953), Swindale and Hughes (1968), and Fujii *et al.* (1971) it is apparent that diaspore is rather common as a minor constituent of pyrophyllite deposits. In the Back Creek deposit however, diaspore appears restricted to the central zone, where less than 20 % of the samples contain the mineral, the content ranging up to 45 %. It is present as colourless, bladed crystals approximately 0·5 mm in length (fig. 4), mainly within small, dark-coloured veins (fig. 5) and much less frequently in patchy disseminations. It is generally, but not invariably, accompanied by minor amounts of kaolinite in addition to abundant pyrophyllite but at no point has it been found in intimate association with cookeite. The crystals are length-fast, have a high relief, and polarize in interference colours of the third order.

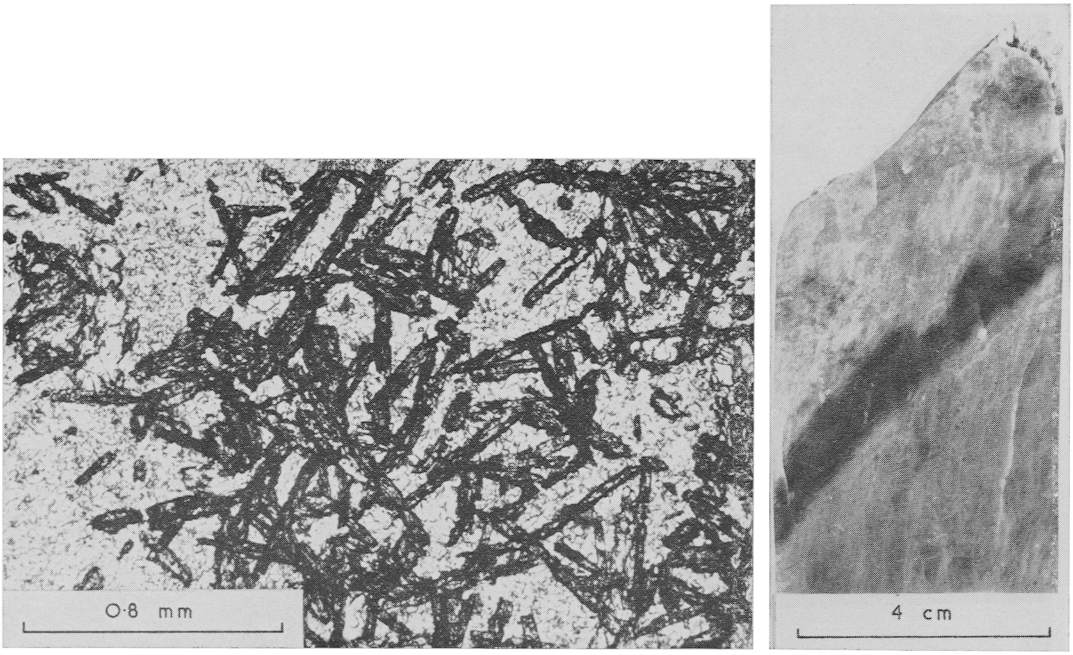
TABLE II. *X-ray diffraction data for cookeite from Londonderry, Western Australia and from Back Creek near Pambula, N.S.W.*

Londonderry*			Back Creek†		Londonderry*			Back Creek†	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*
14·1Å	80	001	14·2Å	100	—	—	—	2·31	45
7·05	70	002	7·10	50	2.205Å	10	$20\bar{4}$	—	—
4·70	90	003	4·74	100	2·14	5	203	—	—
4·47	40	02; 11	4·47	75	2·015	30	205, 007	2·02	10
3·52	90	004	3·55	50	1·96	50	204	1·97	25
2·815	30	005	2·84	20	1·845	5	$20\bar{6}$	—	—
2·56	40	200	2·56	70	1·76	10	008	—	—
2·505	70	$20\bar{2}$	2·51	65	1·685	30	15; 24; 31	1·68	10
2·465	5	201	—	—	1·635	45	206	1·65	20
2·37	5	$20\bar{3}$	—	—	1·54	25	208	—	—
2·35	5	006	—	—	1·489	70	060	1·49	55
2·315	100	202	2·33	60					

* After Bailey and Brown (1962).
† Pyrophyllite lines omitted.

Diaspore is readily detectable by X-ray diffraction even where present in small amounts but very fine grinding is necessary to obviate preferred orientation and anomalous intensification of the 020 reflection. Differential thermal analyses of samples containing a high proportion of diaspore indicate a single, rather intense endotherm at about 560 °C attributable to the loss of combined water. A chemical analysis of one of these diaspore-rich samples (PA43) is given in Table I.

Origin of cookeite and diaspore. In discussing the origin of the Pambula deposits, Hall (1957) concluded that the pyrophyllite resulted from the metasomatic alteration of host rocks by ascending hydrothermal solutions along shear zones, a concept rather similar to that proposed previously by Stuckey (1928) to account for the development of the widespread deposits in North Carolina and also to that invoked by Iwao (1953) to explain the zonal distribution of minerals in many of the Japanese occurrences. According to Iwao, the vertical succession of diaspore–pyrophyllite–kaolinite–alunite–silica was achieved through the alteration of lavas and pyroclastic rocks at shallow depth by ascending acid solutions of volcanic or subvolcanic derivation. During the ascent the temperature decreased from approximately 600 °C to between 150 and 200 °C and the solutions became progressively more acidic, selectively mobilizing the alkalies, which migrated laterally giving rise to zones enriched in sericite and montmorillonite. Simultaneously the residue, mainly alumina and silica, reacted with components of the solutions. Iwao's concept is shown diagrammatically in fig. 6 and it will be observed that if at a later date erosion extended to a depth indicated by the line A—A, horizontal zonation only would be in evidence.



FIGS. 4 and 5: FIG. 4 (left). Photomicrograph of diaspore crystals in microcrystalline pyrophyllite in the central zone at Back Creek. FIG. 5 (right). Diaspore-rich vein (dark coloured) in pyrophyllite from the central zone at Back Creek.

Possibly the pyrophyllite and associated minerals at Back Creek originated by this means although mineral segregation in this deposit is nowhere as complete as Iwao has indicated for the Japanese occurrences. Moreover, since at Back Creek the central zone has apparently been depleted of much of the original silica and concomitantly enriched in lithium as well as aluminium, it is difficult to understand how the alteration could have been effected by solutions of low pH.

Zen (1961) has offered an alternative explanation to account for the zonal segregation of minerals in pyrophyllite deposits. In a re-examination of the North Carolina occurrences he concluded that the mineral assemblages are inconsistent with derivation through the action of ascending hydrothermal solutions. He suggested instead that the deposits formed from a saprolite of highly weathered volcanic material that was subsequently buried and ultimately subjected to relatively low-grade metamorphism. Variations in the mineral composition of the deposit were attributed to differences in the relative amounts of silica, alumina, and water in the parent saprolite.

Such a mechanism could have given rise to the zonal distribution of minerals at Back Creek since the Eden Rhyolite was emplaced in a subaerial environment (Steiner, 1972) and there is a strong possibility that the rocks were subjected in part to deep weathering. Nevertheless, the concept fails to account for the relative abundance of lithium in the central zone.

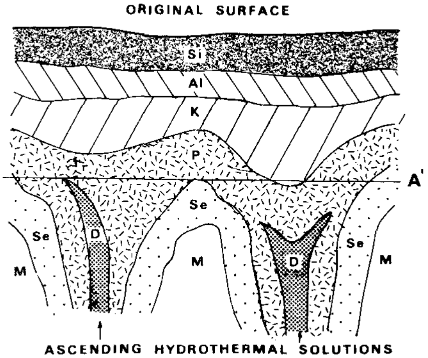


FIG. 6. Diagrammatic representation of Iwao's concept of mineral segregation within hydrothermal deposits in Japan. (Modified from Iwao, 1953.) D = diaspore, P = pyrophyllite, K = kaolinite, Al = alunite, Si = silica, Se = sericite and M = montmorillonite.

Irrespective of the mechanism by which aluminium was concentrated in the central zone and potassium and silicon translocated to other parts of the deposit, there can be little doubt that the development of cookeite at Back Creek is directly attributable to the introduction of lithium from an external source. But, since diaspore is also present in the same zone, presumably the concentration of lithium was insufficient to fix all excess aluminium in the cookeite structure. Kaolinite, also present in this zone, probably developed during a retrogressive stage, possibly by silicification of diaspore but more likely from cookeite through the loss of lithium.

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