Babingtonite, fluorapophyllite and sphene from Harcourt, Victoria, Australia

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ABSTRACT. Small crystals of babingtonite and rare sphene occur in a coarse-grained aggregate of fluorapophyllite, stilbite, and calcite, infilling a late-stage cavity in granodiorite from Harcourt, Victoria. This is the first reported occurrence of babingtonite in Victoria. The assemblage crystallized from fluids in which Ca and F were significant and under P–T conditions of the order of 0.5 kbar, 100–150 °C. Some of the fluorapophyllite has been altered to opaline silica suggesting that the residual solutions were acidic.

THE Harcourt granodiorite forms the southern 'lobe' of a large arcuate composite intrusion of Devonian age in west-central Victoria, about 90–120 km north west of Melbourne. The intrusion has not been studied in detail, but the granodiorite in the vicinity of Harcourt is light grey, even-grained and hornblende-free (Rossiter, 1973). It is marked by conspicuous biotite-rich metasedimentary xenoliths (McInerny, 1929). The Harcourt Quarries are situated on the side of Mt. Alexander and have been the most important source of 'granitic' building stone in Victoria since the 1860s. Rare druses or vugs containing stilbite and apophyllite (variety 'albin') were described from the quarries by Hall (1894).

Two specimens of the Harcourt granodiorite in the collections of the National Museum of Victoria are matching portions of a fibrous aggregate, 10 cm across, of colourless to pale pink stilbite, together with a white, platy mineral with a pearly lustre and a few crystals of a black mineral superficially resembling hornblende. The aggregate fills what was probably a late-stage gas cavity within the granodiorite (figs. 1 and 2). X-ray diffraction analysis showed the white mineral to belong to the apophyllite group and the black mineral to be babingtonite, the first record of the latter mineral in Victoria.

Mineralogy of the aggregate

Babingtonite. The babingtonite occurs as an elongated black crystalline aggregate, 2 cm by 3 mm in cross-section, enclosed partly by stilbite
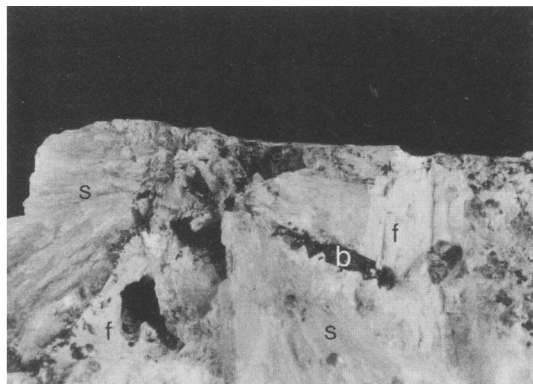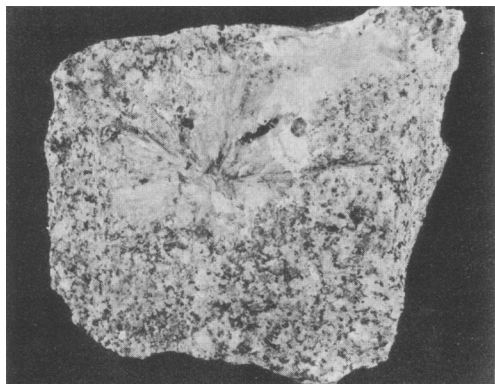
FIGS. 1 and 2. FIG. 1 (*left*). The granodiorite specimen (NMV No. M1570) containing the stilbite-fluorapophyllite-babingtonite aggregate. The upper edge measures 16 cm. FIG. 2 (*right*). Part of the second specimen (M2703) of the same aggregate showing stilbite (s), fluorapophyllite (f), babingtonite (b). The babingtonite crystal is 2 cm long. The dark areas to the left of the babingtonite are an irregular cavity in which smaller babingtonite crystals occur.

and partly by apophyllite (fig. 2). In addition, many small single crystals, up to 5 mm long, are enclosed in stilbite or apophyllite, or project into a small irregular cavity which has been etched from the apophyllite (fig. 2). The babingtonite crystals are glossy black, crushing to a dark greyish green. They tend to be slightly tabular and may show coffin-shaped longitudinal sections. Faces in the plane of flattening may be striated. No goniometric work was carried out, but the crystals appear to consist of up to 6 or 7 forms (fig. 3). In thin section, the babingtonite shows its characteristic strong pleochroism in green, brown, and lilac (Franzini et al., 1978).
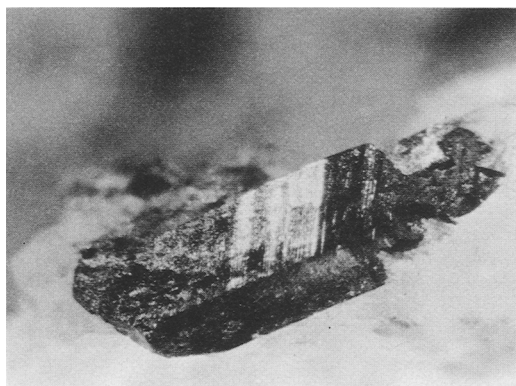

FIG. 3. Tabular crystal of babingtonite 4 mm long.

X-ray powder diffraction analyses were carried out on the Harcourt babingtonite, using a Philips PW 1130 diffractometer and Ni-filtered Cu-$K\alpha$ radiation. The diffraction pattern shows general agreement with that of the Figline babingtonite studied by Franzini et al. (1978), who pointed out the discrepancies between this and the JCPDS standard (No. 14-321). Apart from intensity variations and the absence of some minor reflections, the major difference in the patterns are two prominent reflections for the Harcourt mineral at d spacings of 3.01 Å and 2.90 Å, whereas the Figline mineral has a single strong reflection at $d = 2.95$ Å. Examination of babingtonite specimens from other localities showed this 'doublet' to be present in all.

A number of crystals were analysed by electron microprobe (Table I). Fe^{2+} and Fe^{3+} were allocated by assuming stoichiometry, with a structural formula based on 9 cations, 15 oxygens, and 1 hydroxyl. The analyses show slightly variable Mg and Mn contents and Fe^{3+}/Fe^{2+} ratios, probably due to zonation, with Mn increasing and Fe^{3+}/Fe^{2+} and Mg decreasing towards the crystal margins. Trace amounts of fluorine were detected.

Natural babingtonite has a very restricted composition range (e.g. Palache and Gonyer, 1932), with the major substitution being Mn^{2+} for Fe^{2+}, leading to the species manganbabingtonite (Vinogradova et al., 1967). Mg and Al are very minor substituting elements and no Mg or Al analogues of babingtonite are known. The chemistry of the Harcourt babingtonite conforms to these observed characteristics.

Sphene. A number of small groups of elongated, wedge-shaped sphene crystals, up to about 1 mm long, occur intimately associated with the babingtonite. They are transparent and pleochroic from nearly colourless to pale brown.

Electron microprobe analysis showed that the ratio of the atomic proportion of Si to that of the octahedral cations $(Al + Fe^{3+} + Ti)$ is close to unity, in agreement with most natural sphene compositions (Higgins and Ribbe, 1976). Up to 25% of Ti in the octahedral sites was replaced by Al and Fe^{3+}. The Harcourt sphene also contained up to 2% F. Th, U and rare earth elements were not determined.

Although sphenes rich in F and Al have a tendency to be metamict (Cerny and Povondra, 1972), the optical properties of the Harcourt sphene indicate it is non metamict. Using an empirical formula developed by Higgins and Ribbe (1976), the Harcourt mineral has an effective octahedral cation radius (EOCR) of 0.596 Å and lattice parameters, which vary directly with EOCR, of $a = 7.052$ Å, $b = 8.684$ Å, and $c = 6.540$ Å (from Higgins and Ribbe, Fig. 3).

Fluorapophyllite. The pearly, white apophyllite mineral forms irregular patches up to 2 or 3 cm across in the aggregate (fig. 2). The material bordering the etched cavity is quite pulverulent but tends to become harder at the margin of the aggregate where it is in contact with the granodiorite. In thin section, the pulverulent material is brownish and turbid. Remnant cleavage is occasionally preserved.

X-ray diffraction analysis of the pulverulent mineral showed that it consists largely of opaline silica and calcite, with only trace amounts of apophyllite. The harder, marginal material gave strong apophyllite reflections, but optical examination also revealed some incipient alteration.

Microprobe analyses from unaltered areas of apophyllite gave fluorine contents between 1.4 and 2.2% (Table II) corresponding to fluorapophyllite (Dunn et al., 1977).

Stilbite. Colourless to pale pink, translucent, bladed stilbite, without crystal terminations filled 90% of the aggregate in which the babingtonite occurs. A typical analysis is shown in Table I.

Calcite. A few irregular patches of white calcite

TABLE I. *Representative microprobe analyses of minerals from the Harcourt granodiorite*

	1	2	3	4
SiO_2	53.11	52.05	30.36	58.85
TiO_2	0.05	0.08	31.86	—
Al_2O_3	0.23	0.12	4.20	15.89
Fe_2O_3	13.01	14.56	2.60	0.10
FeO	9.87	7.68	0.05	—
MnO	1.05	2.53	0.06	—
MgO	1.23	0.85	—	—
CaO	19.61	19.88	29.04	8.01
Ma_2O	—	—	—	0.34
K_2O	—	—	—	0.09
F	—	0.05	2.00	0.11
H_2O(cal)	1.59	1.55	0.21	—
$-O = F$	—	-0.02	-0.84	-0.04
Total	99.75	99.33	99.54	83.35

	Structural formulae based on 9 cations, 15 oxygens, and 1 (OH,F)		Structural formula based on 12 cations, 20 oxygens, and 1 (OH,F)	Structural formula based on 72 oxygens
Si	5.021 ⎫ 5.047	4.965 ⎫ 4.979	3.941	27.357 ⎫
Al	0.026 ⎭	0.014 ⎭	0.643	8.708 ⎬ 36.100
Fe^{3+}	0.925	1.045	0.254	0.035 ⎭
Fe^{2+}	0.780 ⎫	0.613 ⎫	0.005	
Ti	0.004 ⎪	0.204 ⎪	3.119	
Mg	0.174 ⎬ 1.042	0.121 ⎬ 0.944	—	Na 0.307
Mn	0.084 ⎭	0.006 ⎭	0.006 ⎫ 4.045	K 0.056
Ca	1.986	2.032	4.039 ⎭	Ca 3.989
F	— ⎫ 1.000	0.015 ⎫ 1.000	0.821 ⎫ 1.000	
OH	1.000 ⎭	0.985 ⎭	0.179 ⎭	

1, 2, Babingtonite; 3, Sphene; 4, Stilbite.

Analyst: W. Birch

occur in the aggregate, as well as within the altered apophyllite.

Discussion

Babingtonite is a rare mineral, with a single-chain pyroxenoid structure similar to rhodonite. It occurs in a range of rock types including granite pegmatites and gneisses (Palache and Gonyer, 1932; Richmond 1937a, b) altered basic igneous rocks ('diabase') (e.g. Franzini et al., 1978) and less commonly in skarns (Verkaeren, 1974). It is generally associated with such minerals as zeolites, prehnite, quartz, calcite, epidote, and albite, and its stability field, although not well defined, is similar to that of zeolites (Burt, 1971).

Sphene occurs in an equally wide variety of lithologies as babingtonite, but is much more common and probably has a less restricted stability field. Coexisting babingtonite and sphene have apparently not been reported previously.

From the composition of the two phases in the Harcourt assemblage, almost all Ti and Al entered sphene, with Mn, Mg, and Fe incorporated nearly exclusively in babingtonite. The mineral chemistry also indicates that the late-stage fluids from which the Harcourt phases crystallized were rich in Ca, depleted in K and almost devoid of Na.

The existence of babingtonite rather than the closely related mineral ilvaite is indicative of relatively lower temperature, more-oxidizing conditions in which CO_2 is depleted and H_2O enriched (Burt, 1971). It may therefore be assumed that the major volatile elements present in the cavity were water and fluorine (which is present in all the silicate phases) with CO_2 of lesser significance. The residual solutions attacked the fluorapophyllite, etching the margins of the cavity (fig. 2) and converting the surrounding mineral to an opaline silica-calcite mixture. Bailey (1941) described a similar alteration, involving the leaching and 'skeletonization' of apophyllite and its replacement by

TABLE II. *Microprobe analysis of Harcourt fluorapophyllite*

	wt. %	Structural formula based on 13 cations, 21 oxygens, and 1 OH group		
SiO_2	49.73			
TiO_2	0.04	Si	7.911	7.932
Al_2O_3	0.11	Al	0.021	
CaO	24.29	Ti	0.005	
Na_2O	0.10	Ca	4.140	
K_2O	4.76	Na	0.031	0.997
F	1.87	K	0.966	
H_2O^*	0.05	F	0.941	0.998
$-O = F$	0.79	OH^*	0.057	
Sub-total	80.16	calc.		

* H_2O calculated only to fill (OH,F) position.

Analyst: W. Birch

hydrous silica. It therefore appears that these residual solutions were weakly acidic, as the effects of acids in breaking down apophyllite is well documented (e.g. Bailey, 1941). The absence of any dissolution features on the enclosed babingtonite indicate that hydrofluoric acid was not involved. Hydrochloric acid also appears unlikely from the lack of attack on the stilbite and the presence of calcite. It is possible that a carbonic acid solution was the agent, as this would be in keeping with the suggested fluid components.

Field relations suggest that the Harcourt granodiorite intruded to within about 2 km of the surface, in which case the assemblages may have crystallized under lithostatic pressures as low as 0.5 kbar. The upper stability limit of stilbite at this pressure would be between 100 °C and 150 °C, assuming that the fluid (i.e. water) pressure was equal to total pressure (Liou, 1971). If, however, $P_{H_2O} < P_{Total}$, and other volatile elements were present, crystallization temperatures could have been lower.

The babingtonite-bearing cavity appears closed and therefore represents isolated, late-stage volatile entrapment, rather than alteration by fluids migrating along veins and fractures when the granodiorite was substantially cooled.

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