## Interlayered biotite-kaolin and other altered biotites, and their relevance to the biotite isograd in eastern Otago, New Zealand

D. CRAW, D. S. COOMBS, AND Y. KAWACHI

Geology Department, University of Otago, Dunedin, New Zealand

ABSTRACT. Green biotite-like material occurring in Haast Schist at Brighton, eastern Otago, consists of biotite and a kaolin-group mineral interlayered on a 1  $\mu m$  scale. Electron probe analyses of composite grains show K<sub>2</sub>O contents of 4.4 to 8.5 wt. %, in part reflecting the kaolin content, and in part, leaching of K<sup>+</sup> ions. Phengitic muscovite shows similar but less extreme effects. Kaolin, siderite, calcite, and titanium oxides have formed in the rock during hydrothermal alteration of epidote, sphene, and biotite by carbonated waters. Potassium leaching due to surficial weathering processes appears to be widespread in biotites from the schists of eastern Otago, and biotites (hydrobiotites?) with K<sub>2</sub>O as low as 4 wt. % are reported. Similar material with 0.8 to 2.4% K<sub>2</sub>O and with Na<sub>2</sub>O about 1% is thought to be more highly degraded biotite. Microprobe analyses of kaolin and chlorites from associated rocks are given in addition to those of 'biotite' and phengitic muscovite. Analyses of sheet biotite and sheet muscovite from the Mataketake Range pegmatites in the highest grade parts of the Haast Schist terrane are presented for comparison. The study shows that biotite is more widespread in eastern Otago than was previously thought, and that almandine-rich garnet is not confirmed down-grade of the first appearance of biotite in eastern Otago.

THE Otago schists, which form part of the New Zealand Haast Schist terrane, have been commonly regarded as forming an unusually large tract within the chlorite zone of the greenschist facies. Nevertheless Turner and Hutton (1941) noted greenishbrown biotite and small garnets in porphyroblastic albite schists from the South Branch of the Waikouaiti River (fig. 1), and Hutton (1940) described biotite in schists from western Otago. Following Tilley (1925) sporadic occurrences of green or greenish-brown biotite, particularly in greenschists, have commonly been disregarded in mapping a biotite isograd, but more recently authors such as Mather (1970) and Brown (1971, 1975) place such assemblages within the lowergrade part of the biotite zone. Brown distinguishes a 'lower biotite zone' in which the assemblages muscovite-stilpnomelane and muscovite-actinolite

© Copyright the Mineralogical Society

are stable, from an 'upper biotite zone' in which these are effectively excluded as a result of continuous reactions which extend the Mg-Fe composition range of biotite.

Robinson (1958) and McNamara (1960) reported further occurrences of green and greenish-brown biotite from eastern Otago. Brown (1967) mapped a biotite isograd but suggested that his predecessors had misidentified altered chlorite ('chloritevermiculite') as biotite. Robinson's and McNamara's localities were excluded from Brown's isograd, which he placed 25 km northeastwards up-grade from that of McNamara.



FIG. 1. Sketch geologic map of the Brighton-Middlemarch area, eastern Otago, showing some biotite localities (black circles). M = Maungatua (OU 42209); H =Mt. Hyde; W = South Waikouaiti (Turner and Hutton, 1941). Brown's (1967) biotite isograd is shown as a dashed line (up-grade to the north-east), and the Textural Zone 4 isotect (Robinson, 1958; Brown, 1967; Bishop, 1972) is shown as a dotted line, with Textural Zone 4 on the north-east side. Pu = last appearance of pumpellyite in coastal section; pumpellyite actinolite facies occurs south-

west of this. Cover rocks are stippled.

Brown (1967, 1969) found that garnet containing subequal amounts of almandine, spessartine, and grossular components appears in small amounts in quartzo-feldspathic (semi-pelitic) schists in eastern Otago at about the position of the biotite isograd as he mapped it. He also recorded two occurrences of garnets, richer in spessartine and poorer in almandine, from below his biotite isograd. This early appearance of almandine-bearing garnet relative to biotite, if confirmed, would contrast with observations in the Alpine sector of the Haast Schist (Cooper, 1972). This might suggest an analogy with the Sanbagawa high-pressure facies series of Japan, where garnet appears before biotite (Banno, 1964) rather than with metamorphism of Barrovian type. Refinement of the position of the biotite isograd in eastern Otago is therefore a matter of some interest.

The seemingly simple task of identifying biotite in the Otago schist has been complicated by three factors: (a) fine grain size, the micas commonly occurring in flakes less than 0.1 mm long; (b) intimate association of muscovite, chlorite, biotite, and often stilpnomelane, making mechanical separation of phyllosilicates for X-ray study difficult; and (c) a tendency to pervasive alteration, in part resulting from deep weathering during Cretaceous and early Tertiary peneplanation, and in part from weathering during and after the partial removal of a veneer of later Tertiary sediments and volcanics. Localized hydrothermal alteration is shown below to be a further problem.

Many biotite-like materials are shown by the electron microprobe to be low in  $K_2O$  and they may show other peculiarities (e.g. Tenney, 1977). Craw (1981) has shown that the lowest grade biotite in very recently deglaciated regions of mountainous western Otago is olive-green to grass-green in colour but that this commonly changes to brown during post-glacial weathering. The colour change is accompanied by loss of  $K_2O$  to values as low as 3%. In some cases there is little change in other components, though there may be a loss of SiO<sub>2</sub> and, or, changes in the ratio Fe:Mg:Al as well as a presumed increase in oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>.

Certain biotite-like materials from eastern Otago have been reinvestigated. Electron probe analyses were obtained with a JEOL JXA-5A microprobe analyser, accelerating voltage 15 kV, specimen current  $0.02 \,\mu$ A on MgO, using standards and data reduction as described by Nakamura and Coombs (1973) with procedures modified for semiautomated operation (Kawachi and Okumura, 1978). Numbered samples are in the collection of the Geology Department, University of Otago. Grid references are for the NZ National Yard Grid, on NZMS 1 series (1:63360) maps. Green biotite schist, Brighton. A zone 100 m wide, of conspicuously greenish micaceous quartzofeldspathic schist, occurs at Brighton domain, grid reference S163/012622, some 16 km south of Dunedin. The locality contains the most southerly, down-grade, biotite recognized by Robinson (1958). Bleached, clay-rich patches are present. Rock a few metres to the west of the green-coloured schist contains the mineral assemblages quartz-albitemuscovite-epidote-actinolite-chlorite-sphene (OU 34962).

The green-coloured schists are moderately well foliated and contain quartz-albite segregation veins about 1.5 mm wide, several mm apart. Typical grains of quartz and albite range from 0.05 to 0.15 mm in diameter, and reach 0.3 mm in segregation lamellae, whereas muscovite and biotite form flakes up to 0.1 mm in length.

The analysed sample, OU 37658, collected by P. Robinson, shows no trace of weathering oxidation, even siderite being unstained. Minerals include quartz, albite  $(Ab_{99.5}An_{0.3}Or_{0.2}$  by microprobe analysis), phengitic muscovite, 'green biotite', clinozoisitic epidote, sphene, apatite, and tourmaline, together with calcite, siderite, a kaolin-group mineral, and titanium oxide minerals. Specimen OU 42208 from a small headland on the east side of the conspicuously green schist is very similar to OU 37658 but is greyish in colour and contains chlorite, dispersed graphitic material, and pyrrhotine, as well as minerals present in OU 37658.

In OU 37658 calcite occurs as a pervasive fine mesh along grain boundaries and as larger pools. Siderite is observed as small pools, streaks, and occasional rhombs. Both carbonates have in places penetrated along biotite cleavages. The Fe component of the siderite ranges in cationic percentages from 67 to 81, Mn 0 to 2, Mg 6 to 20, Ca 8 to 15, the average composition being  $Fe_{75}Mn_1Mg_{12}Ca_{12}$ . The calcites contain 2% siderite component, 0-2% magnesite, and negligible Mn.

Epidote and sphene, normally ubiquitous minerals in Otago schists, are found only as small inclusions within albite and in the case of epidote as corroded remnants in pools of carbonate. Titanium minerals in the rock occur principally as aggregates of  $TiO_2$  crystallites embedded in carbonate. Their crystal habits suggest the presence of anatase and rutile.

Late metamorphic crenulations in both rocks are cross-cut by veinlets and films of calcite and minor siderite 0.02–0.1 mm in thickness. These films are particularly noticeable where they cross quartzose laminae, in which they often contain stubby prisms of rutile,  $2-5 \mu m \log n$ . In OU 37658 the kaolin-group mineral is visible as sparse colourless foliae showing first-order grey interference tints, interleaved with muscovite.

Specimen OU 42208 is more obviously altered. There is less secondary carbonate but the 'green biotite' is largely replaced by pale-green optically negative chlorite and by colourless booklets of length-slow kaolin. This material is also interlayered with the white mica, and is particularly noticeable where the cross-cutting calcite veinlets intersect phyllosilicate laminae.

Textural evidence indicates that epidote, sphene, and in some places biotite have been largely destroyed, and calcite, siderite, kaolin, and secondary titanium oxides have been introduced in an event that post-dates the metamorphic peak, but



FIG. 2. X-ray diffractogram of OU 37658 whole rock powder. (a) Untreated; (b) heated 600 °C, one hour; (c) unheated, treated with potassium acetate and left overnight; (d) material from (c) washed with 10M NH<sub>4</sub>NO<sub>3</sub> in centrifuge five times, dried at 100 °C; (e) material from (d) washed with H<sub>2</sub>O. Scanning speed 1°/minute, rate meter = 4. Cu-K $\alpha$  radiation.

precedes oxidative weathering. Minor smectite referred to below may have been produced either during the same event or during weathering.

Biotite and muscovite interlayered with a kaolin mineral. Optical properties of the green biotite-like material in OU 37658, are as follows:  $\beta = \gamma = .1.616-1.620 \pm 0.002$ ,  $\gamma - \alpha \simeq 0.04$ ; pleochroism X = pale-straw colour, Y = Z = emerald green. The birefringence is noticeably higher than that of the co-existing white mica.

A pure hand-picked concentrate was X-rayed in a powder camera, the following lines being measured (spacing in Å units) 10.03 m, 7.20 w, 3.53 w, 3.33 s, 3.13 w, 2.973 m, 2.612 s, 2.518 w, 2.449 m, 2.154 m, 1.978 m, 1.762 w, 1.675 m, 1.537 m, All but the 7 Å and 3.5 Å lines can be ascribed to biotite, and the 7 Å and 3.5 Å lines suggest an interlayered kaolin-group phase. These lines are also present in X-ray powder diffraction photographs of white mica separated from the same rock, and in whole-rock diffractograms. Further studies were made on whole-rock powders. A treatment sequence involving potassium acetate and ammonium nitrate as outlined by Andrew et al. (1960) was followed. The results of this, and a heating test (fig. 2) confirm that the 7 Å and 3.5 Å peaks are due to the presence of a kaolin-group mineral.

Electron microprobe scanning traverses were made across biotite and muscovite grains in OU 37658 using the narrowest beam available (1.5  $\mu$ m diameter on periclase). The profiles (fig. 3a, b) confirm the presence of a phase with higher Al and Si, but lower K, Fe, Mg than biotite, and higher Al but lower Si and K than muscovite. This is compatible with a kaolin-group mineral but is incompatible with chlorite or vermiculite. Since the potassium profiles in fig. 3a, b are always above zero, the beam cannot have been confined to kaolin at any time. Kaolin interlayers on a scale of up to 1  $\mu$ m thickness can be inferred.

For quantitative analysis of the biotite and muscovite interlayered minerals (Table I, anal. 3-7; fig. 4), a broad beam (10-15  $\mu$ m diameter) was used to minimize migration and loss of potassium (Craw, 1981). Interlayering on the scale indicated by the scanning profiles makes it inevitable that the resulting analyses will be composites of the interlayered phases. Extreme values of 8.48% and 4.38%  $K_2O$  were recorded in 32 analyses of 'biotites' in OU 37658. The sum (K + Na + Ca) has been plotted against Al (fig. 4). The green 'biotites' of OU 37658 show a considerable scatter. This may be attributed to a combination of at least two effects. First, it will be noted that the field extends from points near EB, eastern Otagio biotite analyses of Brown (1967), towards kaolin, and so can in part be explained by interlayering of biotite



FIG. 3. Semiquantitative microprobe scans across phyllosilicates in OU 37658. (a) Biotite-kaolin interlayered structure; (b) muscovite-kaolin interlayered structure. Count rate scale is relative only, and scale is different for each element. Scanning speed 10  $\mu$ m/minute, beam diameter 1-1.5  $\mu$ m on periclase.

with up to about 35% kaolin. Secondly, a large number of analyses show less K than can be explained in this way. These imply the loss of K as described by Craw (1981) during incipient oxidation of green biotites in western Otago. Charge balance without major changes in other metallic cations could be maintained in such cases by oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  and, or, by replacement of K<sup>+</sup> by H<sup>+</sup> ions, while Fe:Mg ratios became somewhat variable.

The muscovites in OU 37658, like others from eastern Otago, prove to be phengites with 6.5 to over 7 Si per 22 oxygen atoms, and with significant Mg,Fe in octahedral sites. In 17 analyses  $K_2O$ varies from 10.0 to 6.97 wt. % and  $\Sigma K$ ,Na,Ca from 1.77 to 1.15 per 22 oxygen atoms. Data points plotted on fig. 4 show a spread from Brown's (1967) eastern Otago phengites (EP) towards kaolin. There is also a tendency towards depressed K contents, which may result from loss of K to give illite or hydromica.

Kaolin in OU 42208 (Table I, anal. 8 and 9) contains about 2-4.5% FeO and 0.6-1% MgO. The Fe: Mg ratio is not readily compatible with interlayered biotite or chlorite, and electron microprobe scanning profiles failed to show inhomogeneity in the grains analysed. Chlorite in OU 42208 (Table I, anal. 10) is typical for Otago schists and shows MnO values higher than those of the co-existing biotite or phengite, and negligible Ti and alkalis.

A clay fraction was concentrated from OU 42208 by gentle grinding, washing, then allowing the coarser material to settle. This fraction consisted predominantly of kaolin and muscovite with minor quartz, albite, and a 14 Å mineral. The 14 Å peak is displaced to 18 Å with glycerol and ethylene glycol, and to about 19 Å with water. It almost disappears on heating at 300 °C for one hour, and totally disappears on heating at 500 °C for one hour. These responses indicate the presence of smectite (Walker, 1961; Carroll, 1970).

Schist from Brighton with greenish-brown 'biotite'. Specimen OU 13206 (grid reference S163/014626 0.5 km north-east of the green biotite locality), contains an abundant greenish-brown mineral of biotite-like aspect, with birefringence 0.035-0.04, noticeably higher than co-existing phengitic muscovite. Optically negative chlorite is also present in small amounts. Texturally as well as in general appearance of the micas, the rock is very similar to the previous rocks but it contains plentiful epidote and no carbonates or recognizable kaolin. Microprobe analyses (Table I, anal. 11 and 12; fig. 4) show that 14 grains of the biotite-like phase contain 0.75 to 2.35% K<sub>2</sub>O and 0.67 to 1.31 % Na<sub>2</sub>O, the latter being markedly higher than in less altered biotites of eastern Otago, or in co-existing phengite. In contrast the chlorite (Table I, anal. 15) is normal and contains negligible alkalis, and the phengitic muscovites (Table I, anal. 13 and 14) are also unremarkable. Data points for the biotite-like mineral on the plot of (K + Na + Ca)vs. Al (fig. 4) fall on a trend between chlorite and biotite. Microprobe scanning traverses reveal no inhomogeneity on the  $< 2 \mu m$  scale in individual grains, using beam diameter 1–2  $\mu$ m on periclase.

Clay-fraction diffractograms on this rock are

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	Pegmatite biotite OU 15127 Moeraki River	Pegmatite muscovite OU 14742 Moeraki River	Green "biotite" OU 37658 Brighton			Phengite OU 37658 Brighton		Kandite OU 42208 Brighton		Chlorite OU 42208 Brighton	Greenish-brown "biotite" OU 13206 Brighton		Phengite OU 13206 Brighton		Chlorite OU 13206 Brighton	Biotite OU 42209 Maungatua
•i0,	35.4	46.2	38.9	40.7	42.1	50.4	47.4	44.3	45.3	25.2	30.0	31.9	49.4	48.5	25.7	36,6
Al,0	20.0	34.7	16.3	17.7	21.6	26.9	29.7	36.9	37.4	20.6	20.2	21.7	30.6	30.5	22.4	21.6
TiO	1.72	0.37	0.02	0.05	0.01	0.11	0.05	b.d.	b.đ.	0.01	0.03	0,06	0,11	0.12	0.04	0.02
Fe0*	21.0	1.77	18.1	16.1	14.8	4.42	3.54	2.38	4.55	28.3	22.7	22.5	3,15	3.23	28.4	13.8
MnO	0.43	0.01	0.20	0.20	0.14	0.08	0.02	0.07	0.02	0.46	0.29	0.31	0.01	0.02	0.42	0.26
Mg0	7.30	1.06	11.2	9.3	7.32	3.34	2.24	0.61	1.05	12.4	10.6	10,5	2.46	2.42	12.2	8.15
Ca0	b.d.	b.d.	0.08	0.08	0.05	0.01	0.04	0.03	0.04	0.01	0.06	0.10	0.07	b.d.	0.01	0.52
Na <sub>2</sub> 0	0.22	0.59	.0.14	0.19	0.14	0.21	0.19	0.11	0.08	0.07	0.67	1.07	0.31	0,23	0.06	0.23
к <sub>2</sub> 0	9.22	10.7	8.48	6.71	4.92	10.0	7.11	0.07	0.06	0.02	2.28	1.38	10.36	8.03	0.04	4.08
Cr203	b.d.	b.d.	-	b.d.	b.d.	b.d.	b.d.	-	-	0.02	0.04	0.01	b.d.	0.05	b.d.	b.d.
Total	95.29	95,40	93,42	91.03	91.08	95.47	90.29	84.47	88.50	87.09	86.87	89.53	96.47	93,10	89,27	85.26
		Cation	, on ba	usis of	22 oxy	en aton	ns for n	nicas, a	nd 28 o	xygen atom	s for ch	lorites	and kar	udites.		
Si	5.42	6.18	5,93	6.19	6.20	6.76	6.58	7.90	7.82	5.45	4.96	5.05	6.54	6,55	5.39	5,80
Al	2.58	1.82	2.07	1.81	1.80	1.24	1.42	0.10	0.18	2.55	3.04	2.95	1.46	1.45	2.61	2.20
Total Z	8.00	8.00	8,00	8.00	8.00	8.00	8.00	8.00	8,00	8.00	8.00	8.00	8.00	8,00	8,.00	8.00
Al	1.08	3.64	0.85	1.36	1.96	3.02	3.44	7.76	7.43	2.71	0.91	1.09	3.31	3.41	2.93	1.84
Ti	0.20	0.03	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0,01	0.01	0.01	0.01	0.00
Fe	2.69	0,20	2.31	2.04	1.83	0.50	0.41	0,36	0.66	5.11	3.14	2.98	0,35	0.37	4.98	1.83
Min	0.06	0.00	0.03	0.03	0.02	0.01	0.00	0.00	0.00	0.08	0.04	0.04	0.00	0.00	0.07	0.04
Mg	1.67	0.21	2.55	2,10	1.61	0.67	0.47	0.16	0.27	3.99	2.61	2.48	0.48	0.49	3.82	1.93
Total Y	5.70	4.08	5.77	5.54	5.42	4.21	4.33	8,28	8.36	11.89	6.67	6.60	4.15	4.28	11.81	5.64
Ca	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.02	0.00	0.00	0.00	0.09
Na	0.07	0.15	0.04	0.06	0.04	0.06	0.05	0.04	0.03	0.03	0.22	0.33	0.08	0.06	0.02	0.07
к	1.80	1.82	1.65	1.30	0,93	1.71	1.26	0.02	0,01	0.01	0.48	0.28	1.75	1.39	0.01	0.83
Total X	1.87	1.97	1.70	1.37	0.98	1.77	1.31	(0.07)	(0.05)	(0.04)	0.71	0.63	1.83	1.45	(0.03)	0,99

TABLE I. Representative electron microprobe analyses of phyllosilicates from lower biotite zone, eastern Otago. FeC\*: all Fe as FeO.



FIG. 4. Plot of X-site occupancy versus total aluminium for Brighton phyllosilicates: ● = biotite, ■ = phengite from OU 37658; ○ = 'biotite', □ = phengite from OU 13206; ● = chlorite from OU 42208 and OU 13206; ● = Maungatua 'biotite' OU 42209. Data from presumably fresh eastern Otago biotite (= ○, EB) and phengite (= ,EP)(Brown, 1967), and from pegmatitic biotite (= ▲, MB) and muscovite (= △, MM) from Mataketake Range are plotted for comparison. Solid arrows show expected trend in analyses due to kaolin interlayering. Hatched field (from Craw, 1981) shows trend due to leaching of K from biotite, and dashed arrow shows trend due to K-leaching, or illite formation, from phengite. Cations were all calculated on the basis of 22 oxygens.

complicated by the known presence of phengite and chlorite as well as the biotite-like mineral. There is a rather weak non-swelling 14 Å peak which is enhanced and becomes sharper on heating to 400 °C for one hour, and is therefore attributed to chlorite. No stepwise movement of any peak from 14 Å to 10 Å on heating was detected and it is believed that if vermiculite or smectite is present, it is minor. A substantial excess of octahedral cations compared with trioctahedral mica requirements (Table I, anal. 11 and 12; contrast anal. 1 and 3) indicates that the probed material must either contain some of these cations in interlayer positions, or consist of a sub-micron interlayering of hydrobiotite with chlorite. Submicroscopic goethite may be another possibility. On the basis of the data presented as well as analogy with the nearby biotite rock we believe, however, that the material is degraded biotite trending towards a chloritic composition rather than oxychlorite or chlorite-vermiculite.

Biotite-bearing schist, Maungatua, Specimen OU 42209 has been recollected from one of McNamara's localities, at grid reference S163/ 093744. It is a quartz-albite-muscovite-biotiteepidote-actinolite schist, the biotite showing straw to chestnut pleochroism, and forming plates and booklets to 0.1 mm diameter. Its birefringence is 0.045, noticeably higher than co-existing muscovite. Microprobe analyses of the 'biotite' (Table I, anal. 16; fig. 4) show about  $4\% K_2O$  and significantly higher CaO and Na<sub>2</sub>O than in fresh biotite, as well as relatively low SiO<sub>2</sub> and high Al<sub>2</sub>O<sub>3</sub>. Scanning profiles reveal no inhomogeneity and the X-ray pattern shows no 14 or 7 Å peaks, indicating that chlorite, kaolin, vermiculite, and smectite are not present in detected amounts. We regard the material as biotite chemically modified and hydrated without major change of structure.

Kaolin-bearing schist, South Waikouaiti River. Turner and Hutton (1941) describe porphyroblastic albite schists from the South Waikouaiti River containing 'colourless chlorite' with positive elongation. Re-examination of their samples OU 6245 and OU 6247 show that this colourless mineral is a kaolin-group mineral as found in the Brighton rocks. Sample OU 6247 is cross-cut by veinlets of siderite and calcite, and the kaolin is commonly interleaved with muscovite. The alteration of this rock thus has similarities to that described above for OU 37658.

Mica pegmatite, near Moeraki River, Mataketake Range, South Westland. Microprobe analyses of biotite and muscovite sheet mica from a mica pegmatite in the highest grade portion of the Haast Schist terrane are presented (Table I, anal. 1 and 2; fig. 4 MB, MM) for comparison with the low-grade and degraded micas described above. The region is upgrade of a staurolite locality and is probably of kyanite or perhaps sillimanite grade (Wallace, 1974; Cooper, 1980, p. 159).

## Discussions and conclusions

Alteration of biotite. The alteration of the Brighton green biotite rock can be attributed to invasion of the rocks concerned by hydrothermal fluids having sufficiently high  $\mu_{CO_2}$  to destroy both epidote and sphene with the production of calcite, kaolin, and secondary titanium oxides. The fluids also caused the partial alteration of phengite and biotite to kaolin, with precipitation of siderite and removal of  $K^+$  and  $Mg^{2+}$  ions. According to Hemley (1959), at 200 °C the muscovite-kaolinite reaction takes place at KCl/HCl ratios of 10<sup>3</sup>, the equilibrium ratio increasing with decreasing temperature and vice-versa. Zoisite is destroyed to yield calcite plus anorthite at values of  $X_{CO}$ , from 0.02 to 0.06 for pressures 2 to 5 kbar (Storre and Nitsch, 1972), and will yield kaolinite plus calcite at somewhat higher values of  $X_{CO_2}$ . Sphene yields anatase or rutile, quartz and calcite at quite low values of  $\mu_{CO_2}$  (Hunt and Kerrick, 1977). We conclude that carbonated waters have locally affected biotite-bearing schists in eastern Otago both at Brighton and in the South Branch of the Waikouaiti River.

More widespread, we believe, is alteration of green biotite to greenish-brown hydrobiotite,  $K_2O$  content falling to values as low as 1% by weight. This has taken place during deep weathering and can lead to complete destruction of the biotite.

Composition of very low-grade biotite and phengite. Ti contents of some of the lowest grade biotites in the schists of eastern Otago (but not those of Brown, 1967) are extremely low and sometimes below detection limits. Al contents of these and other greenschist-facies biotites, and phengites are lower than those of biotites and muscovites of high-grade schists and pegmatites in the Haast Schist terrane.

Biotite and garnet isograds. The data above support Robinson's (1958) identification of biotite at Brighton, a very short distance up-grade of the Textural Zone 4 isotect, and 9 km north-east of the last appearance of pumpellyite. The occurrence of biotite in the Maungatua area, also far downgrade from the biotite isograd shown by Brown (1967), is similarly confirmed. Significantly the composition of the green biotite co-existing with phengite in the Brighton rock is in the restricted Mg-Fe composition field shown by Brown (1971, fig. 9) for biotite from his 'lower biotite zone'. We believe that the spasmodic presence of biotite below Brown's isograd is due in part to this compositional restriction and in part to destruction by secondary alteration. There is no good evidence at present that almandine-bearing garnet appears before biotite in the schists of eastern Otago, though we do not preclude the possibility that further discoveries will be made.

Acknowledgements. The authors acknowledge research funds from the New Zealand University Grants Committee, and the University of Otago Research Committee. They are grateful for discussion and critical comments from Professors P. Robinson, G. W. Brindley, and E. H. Brown, and Drs A. F. Cooper and R. J. Norris. Valuable technical assistance has been provided by Messrs J. M. Pillidge, E. I. McKenzie, and A. S. Cosgrove.

## REFERENCES

- Andrew, R. W., Jackson, M. L., and Wada, K. (1960) Soil Sci. Soc. Am. Proc. 24, 422-4.
- Banno, S. (1964) J. Fac. Sci. Univ. of Tokyo, Section II, 15, 203-319.
- Bishop, D. G. (1972) Geol. Soc. Am. Bull. 83, 3177-98.
- Brown, E. H. (1967) Contrib. Mineral. Petrol. 14, 259-92. ----(1969) Am. Mineral. 54, 1662-7.
- -----(1971) Contrib. Mineral. Petrol. 31, 275-99.
- -----(1975) J. Petrol. 16, 258-71.
- Carroll, D. (1970) Geol. Soc. Am. Spec. Paper, 126.

- Cooper, A. F. (1972) J. Petrol. 13, 457-92.
- -----(1980) Contrib. Mineral. Petrol. 75, 153-64.
- Craw, D. (1981) Lithos, 14, 49-57.
- Hemley, J. J. (1959) Am. J. Sci. 257, 241-70.
- Hunt, J. A., and Kerrick, D. M. (1977) Geochim. Cosmochim. Acta, 41, 279-88.
- Hutton, C. O. (1940) New Zealand Dept. Sci. Ind. Res. Geol. Mem. 5.
- Kawachi, Y., and Okumura, K. (1978) Bull. Geol. Survey Japan, 29, 593-609.
- McNamara, M. J. (1960) Geology of Maungatua. M.Sc. thesis, Univ. of Otago.
- Mather, J. D. (1970) J. Petrol. 11, 253-75.
- Nakamura, Y., and Coombs, D. S. (1973) Contrib. Mineral. Petrol. 42, 213–28.
- Robinson, P. (1958) Structural and metamorphic geology of the Brighton-Taieri Mouth area, East Otago, New Zealand. M.Sc. thesis, Univ. of Otago.
- Storre, B., and Nitsch, K.-H. (1972) Contrib. Mineral. Petrol. 35, 1-10.
- Tenney, S. M. (1977) The geology of the Flat Hill area, Otago, New Zealand. M.Sc. thesis, Univ. of Otago.
- Tilley, C. E. (1925) Q. J. Geol. Soc. 81, 100-12.
- Turner, F. J., and Hutton, C. O. (1941) Trans. R. Soc. New Zealand, 71, 223-40.
- Walker, G. F. (1961) In X-ray identification and crystal structures of clay minerals (G. Brown, ed.), Mineralogical Society, London.
- Wallace, R. C. (1974) J. R. Soc. New Zealand, 4, 253-66.