

High chromium and vanadium in andalusite, phengite and retrogressive margarite in contact metamorphosed Ba-rich black slate from the Abercrombie Beds, New South Wales, Australia

VINCENT J. MORAND*

Department of Geology and Geophysics, University of Sydney, N.S.W. 2006, Australia

Abstract

Graphitic, quartz-rich black slate within the Late Ordovician Abercrombie Beds, Lachlan Fold Belt, southeast Australia, has undergone contact metamorphism adjacent to the Siluro–Devonian Wyangala Batholith. This produced porphyroblasts of andalusite and cordierite, and smaller grains of pale green phengitic mica. Later regional metamorphism caused complete retrogression of cordierite and partial retrogression of andalusite, with margarite replacing some andalusite.

The aluminous minerals andalusite, margarite and phengite all contain V and Cr substituting for Al. Andalusite has up to 1.39% V_2O_3 and 1.09% Cr_2O_3 , margarite has up to 1.07% V_2O_3 and 0.37% Cr_2O_3 , and phengitic mica has up to 6.93% V_2O_3 and 1.52% Cr_2O_3 . This mica also has BaO contents of up to 1.96%.

Chemical analyses reveal very high SiO_2 contents for these rocks (about 89%), carbon contents of about 2%, and extremely low CaO, FeO, MgO and Na_2O . Although V and Cr are prominent in aluminous minerals, their concentrations in the rock are only about average for black shales. However, Ba values range from 2000 to 6000 p.p.m., well above average for black shales. It is suggested that V and Cr probably precipitated from sea water, but Ba may have been concentrated by planktonic organisms such as radiolaria.

KEYWORDS: black slate, andalusite, mica, barium, vanadium.

Introduction

BLACK shales, deposited in anoxic conditions in mainly marine environments, are known to be enriched in a number of elements, mainly metallic, including Ba, V and Cr (Vine and Tourtelot, 1970). These elements may also be concentrated in certain porphyroblasts when black shales are metamorphosed. In particular, various metallic elements may substitute for Al in minerals such as andalusite and potassic white mica (Deer *et al.*, 1982; Guidotti, 1984; Carlson and Rossman, 1988). This study looks at both aspects of a sequence of black slates in which the aluminous minerals andalusite and margarite have high V and Cr, and potassic white mica is enriched in V, Cr and Ba.

Geological setting

Black, carbonaceous shale and slate is widespread in the Ordovician of the Lachlan Fold Belt of southeastern Australia (Joplin, 1945). It commonly contains graptolites and radiolaria. The black slate described here occurs as layers within a sequence of metapsammite, slate, quartzite and chert, known as the Abercrombie Beds, in eastern New South Wales (Fig. 1). This sequence was deposited as turbidites and pelagic sediments, probably at the base of the continental slope (Morand, 1984). It has been complexly deformed and metamorphosed to greenschist facies (Morand, 1987, 1988a). Graptolites in the black slate indicate a Late Ordovician age (Morand, 1984).

Ordovician rocks similar to the Abercrombie Beds crop out over a large area of the Lachlan Fold Belt (Packham, 1969). They are thought to have been deposited in a back-arc environment adjacent to a volcanic arc of basaltic to andesitic

* Present address: Department of Geology, James Cook University, Townsville, Qld 4811, Australia

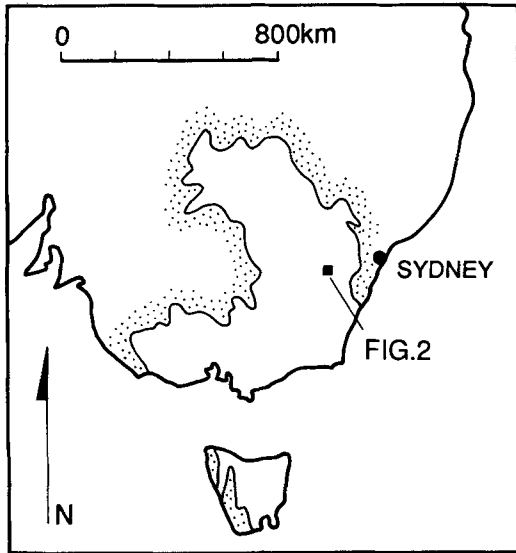


Fig. 1. Location of study area in the Lachlan Fold Belt of southeastern Australia.

character, with sediment derived from Precambrian cratonic regions to the south or west (Powell, 1983).

The Abercrombie Beds were intruded by the granitic Wyangala Batholith of Siluro-Devonian age, around which a contact aureole has been developed (Fig. 2). Intrusion was followed by folding and regional metamorphism, causing retrogression in the contact aureole (Morand, 1988a). Rocks in the contact aureole, which includes some black slate, are thus polymetamorphic.

Petrography

Black slate unaffected by contact metamorphism. Black slate in the Abercrombie Beds is carbonaceous, quartz-rich shale that has been metamorphosed to greenschist facies. It is fine-grained, commonly laminated, with layers rich in fine detrital quartz and muscovite grains alternating with hemipelagic layers consisting of quartz, metamorphic white mica, graphite and pyrite. Slaty and crenulation cleavages are ubiquitous. Chert-like layers rich in radiolarian remains (now recrystallized quartz) are common, and many black slate layers grade into chert.

Quartz is the most abundant mineral. Most is recrystallized, but small detrital grains can be recognized in many specimens, as can detrital muscovite. Accessory detrital minerals are rutile, tourmaline, epidote, apatite and monazite.

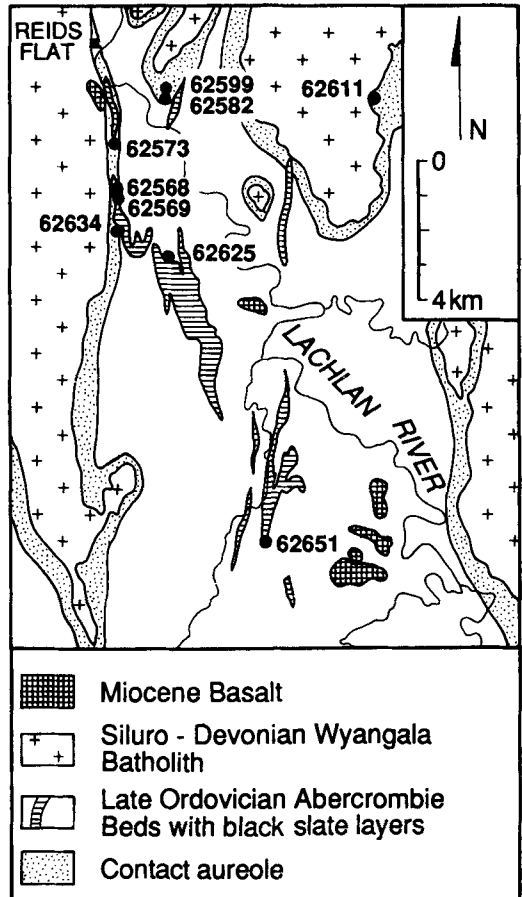


Fig. 2. Geological map of the Reids Flat area, with locations of specimens which have been analysed or have provided mineral analyses.

Chlorite and biotite zones are present in the Abercrombie Beds, but the metamorphic assemblage is the same in both zones, namely, quartz-white-mica-graphite-pyrite. Chlorite is rare, and in the biotite zone biotite is absent. This is because these rocks are poor in iron and magnesium, and most of the iron is taken up in pyrite and possibly phengitic white mica.

Contact metamorphosed black slate. The petrography of these rocks has been described by Morand (1988b). The most obvious effect of contact metamorphism is the crystallization of porphyroblasts of andalusite of the chiasstolite variety (about 0.5 to 1 mm wide and up to 8 cm long) and ellipsoidal cordierite grains (less than 1 mm across). Cordierite is completely retrogressed to micaceous aggregates, but andalusite ranges from fresh to completely altered to muscovite or mar-

garite plus muscovite. Margarite has only been found in the westernmost layer of black slate on Fig. 2.

Pale green potassic mica occurs as small porphyroblasts about 0.2 mm long. The groundmass is mainly recrystallized quartz with small flakes of white mica and granules of graphite. Other minerals observed in contact metamorphosed black slate are pyrite, tourmaline, rutile, chlorite, hematite, monazite and xenotime.

Conditions of metamorphism

Temperatures during contact metamorphism were between 500 and 550°C, with pressure probably about 3 kbar (Morand, 1984). A temperature of 450 to 530°C (at 3 kbar) has been suggested for the retrogressive metamorphism that followed (Morand, 1988b).

Mineral chemistry

The aluminous minerals andalusite, margarite and white mica (V-Cr mica) have been analysed. Analyses were performed on the electron microprobes at the University of Sydney and Monash University Department of Earth Sciences, using wavelength-dispersive techniques. Silicate standards were used for all elements except V, for which metallic V was used. Analyses of andalusite and margarite are averages of two or three spot analyses, but most analyses of white mica are single spot analyses because of the small size and chemical heterogeneity of this mineral. Specimen numbers are those of the collection at the Department of Geology and Geophysics, University of Sydney. Tables 1, 2 and 3 have only selected analyses. The complete set of analyses can be obtained from the author on request.

Andalusite. In some specimens andalusite has a pale yellow colour with the following pleochroic scheme: α = pale yellow, $\beta = \gamma$ = colourless. This is an unusual colour for andalusite, which is usually pink or green if coloured (Deer *et al.*, 1982) and is related to the high vanadium content (analyses Table 1). Values of V_2O_3 reach 1.39% and Cr_2O_3 reaches 1.09%. V and Cr replace Al, which shows an inverse relationship with V + Cr (Fig. 3a).

Reports of andalusite with significant V and Cr are rare. Chinner *et al.* (1969) reported a maximum of 0.02% V metal for andalusite, and Schreyer *et al.* (1981) reported andalusite with 2% Cr_2O_3 . The only recorded occurrence of andalusite with comparable chemistry is from a similar rock type in Texas (Carlson and Rossman, 1988). Andalusite from the Abercrombie Beds has neg-

ligible Mn and very low Fe (Table 1), so the colour cannot be attributed to these elements. Cr imparts a faint red colour to Cr-bearing andalusite from Zimbabwe (Schreyer *et al.*, 1981). Thus the yellow colour appears to be due to V. The andalusite reported by Carlson and Rossman (1988) has the same pleochroic scheme as that described herein, which they attributed to the combined effects of V and Cr.

Those grains with the strongest yellow colour have the highest V contents (e.g. specimen 62573). In specimen 62568 andalusite is colour zoned from colourless in the centre to yellow at the edges. Seven spots across one grain were analysed for Cr_2O_3 and V_2O_3 (Fig. 4). There is an increase in both Cr_2O_3 and V_2O_3 from the centre to the edges, but since Cr content is quite low, the yellow colour appears to be due to V. Only those andalusite grains with V_2O_3 greater than about 0.8% display a yellow colour.

Margarite. The chemistry of this mineral has been dealt with by Morand (1988b). In summary, margarite has significant replacement of Ca by Na, and has relatively high V and Cr, with up to 1.07% V_2O_3 and 0.37% Cr_2O_3 (Table 2). V and Cr substitute for Al^{VI} (Fig. 3b).

V-Cr mica. This is a phengitic mica with high V and Cr. Grains of this mica are not homogeneous, but are either interlayered with colourless white mica (closer to muscovite in composition) with a sharp boundary between the two phases, or else there is a continuous variation in V and Cr contents across the layers. It has a higher relief and birefringence than muscovite, and the pleochroism is: α = pale blue-green, $\beta = \gamma$ = pale green. These colours are midway between those of the Cr-mica fuchsite and the V-mica roscoelite (Deer *et al.*, 1962).

Analyses (Table 3) show that both the absolute and relative amounts of Cr and V in this mica vary for different rock specimens, with Cr_2O_3 up to 1.52% (62569) and V_2O_3 up to 6.93% (62568). However, the ratio of $V/(V+Cr)$ is similar for all parts of the one grain. As in margarite, V and Cr are assumed to be in the trivalent state, although mica with similar composition from a similar rock type reported by Snetsinger (1966) has both V^{3+} and V^{4+} .

Fig. 3c shows Al^{VI} plotted against V + Cr for V-Cr mica, and also colourless potassic mica pseudomorphing andalusite. The latter mica also contains some V and Cr. It is probably not in equilibrium with the V-Cr mica as it post-dates contact metamorphism. An inverse relationship exists between Al^{VI} and V+Cr, indicating substitution of V+Cr for octahedral Al. The amount of V+Cr in mica pseudomorphing andalusite is

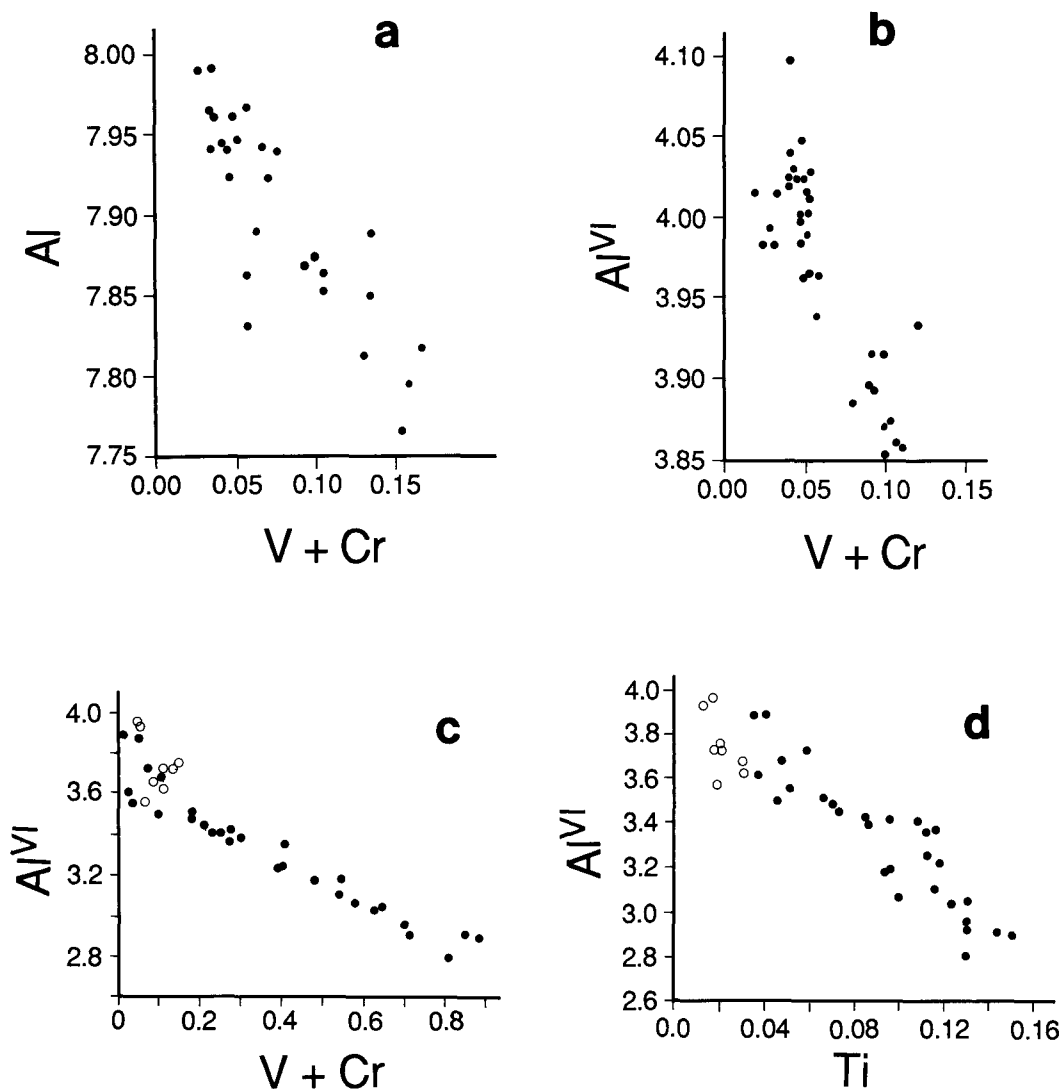


FIG. 3. (a) Cation values of Al plotted against V + Cr for andalusite. (b) Cation values of Al^{VI} against V + Cr for margarite. (c) Cation values of Al^{VI} against V + Cr for potassic micas. Open circles are micas pseudomorphing andalusite, closed circles are V-Cr micas. (d) Cation values of Al^{VI} against Ti for potassic micas. Symbols as in (c).

less than 0.15 atoms per formula unit, which is comparable to V+Cr contents in both andalusite and margarite. In the V-Cr mica, V+Cr can reach about 0.9 atoms per formula unit.

Both V-Cr mica and pseudomorphous mica are phengitic, with significant Mg and Fe contents and Si slightly high because of the celadonite substitution $(\text{Fe}^{2+}, \text{Mg}^{2+})\text{Si}^{4+} = \text{Al}^{3+} + \text{Al}^{3+}$. Titanium is also present, some grains having well over one weight percent TiO_2 . Fig. 3d shows that Ti substi-

tutes for Al^{VI} and that V-Cr mica and pseudomorphous mica form two distinct groups with a boundary at 0.03 atoms Ti. The coupled substitution $\text{Ti}^{4+} + \text{Al}^{3+} = \text{Al}^{3+} + \text{Si}^{4+}$ lowers the Si content and tends to offset the increase in Si due to the celadonite substitution.

Some micas from two rock specimens (62582 and 62568) were analysed for Ba (Table 3). There is significant Ba in both types of mica, but V-Cr mica has much less BaO (0.33 wt.%) than mica

TABLE 1 ANDALUSITE ANALYSES FROM CONTACT METAMORPHOSED BLACK SLATE, REIDS FLAT AREA, N.S.W.

	62568 AND 1	62568 AND 6	62568 AND 10	62569 AND 1	62569 AND 5	62569 AND 7	62573 AND 1	62573 AND 2	62611 AND 1	62611 AND 4
SiO ₂	37.10	36.85	36.79	36.87	36.87	36.76	37.37	37.58	36.59	37.25
TiO ₂	0.07	0.06	0.10	0.09	0.10	0.13	0.07	0.04	0.13	0.04
Al ₂ O ₃	61.49	62.39	61.34	62.18	62.49	62.82	61.59	61.35	60.07	60.57
V ₂ O ₃	1.12	0.66	1.39	0.40	0.30	0.26	0.23	0.26	0.83	1.04
Cr ₂ O ₃	0.07	0.10	0.15	0.09	0.11	0.05	0.44	0.39	1.09	0.75
Fe ₂ O ₃ *	0.06	0.01	0.03	0.09	0.04	0.03	0.07	0.12	0.07	0.07
MnO	0.00	0.00	-	0.01	0.00	0.00	0.00	0.00	0.03	0.00
MgO	0.05	0.07	0.09	0.05	0.08	0.07	0.04	0.03	0.02	0.03
Total	99.96	100.14	99.89	99.78	99.97	100.12	99.81	99.77	99.52	99.75
No. of cations/20(O)										
Si	4.019	3.980	3.994	3.997	3.985	3.968	4.047	4.071	3.994	4.051
Al	7.853	7.944	7.850	7.944	7.963	7.991	7.863	7.831	7.818	7.766
Ti	0.006	0.005	0.008	0.006	0.009	0.011	0.006	0.003	0.011	0.003
V	0.098	0.057	0.121	0.035	0.025	0.023	0.019	0.023	0.072	0.090
Cr	0.007	0.009	0.013	0.008	0.009	0.004	0.038	0.034	0.094	0.064
Fe ³⁺	0.005	0.001	0.003	0.006	0.004	0.003	0.005	0.009	0.005	0.005
Mg	0.008	0.010	0.014	0.007	0.010	0.011	0.007	0.005	0.003	0.005
Mn	0.000	0.000	-	0.001	0.000	0.000	0.000	0.000	0.003	0.000
Total	12.00	12.01	12.00	12.06	12.01	12.01	11.99	11.98	11.90	11.98
V/(V + Cr)	0.93	0.86	0.90	0.81	0.74	0.85	0.33	0.40	0.43	0.58

*All iron treated as Fe³⁺

replacing andalusite (up to about 2%). Micas in other specimens probably also have Ba substituting for K, which may account for the low *X* totals. Na is present in both mica types, usually in amounts of about 0.5% Na₂O.

In summary, the micas show substitutions in the interlayer sites and coupled substitutions in the octahedral and tetrahedral sites. Interlayer cations have paragonite (Na) and oellacherite (Ba) substitution for muscovite, and the octahedral cations show phengite (Mg,Fe), roscoelite (V) and fuchsite (Cr) substitutions, as well as Ti^{vi}Al^{iv} substitution. Micas replacing andalusite are closer to pure muscovite in composition.

Geochemistry of black slate

Six specimens of black slate were analysed by X-ray fluorescence at the Department of Geology and Geophysics, University of Sydney, for major elements and selected minor elements (Table 4). Four of the rocks are from within the contact aureole and two (62625 and 62651) come from outside the contact zone (Fig. 2). Analyses were carried out on approximately 100gm samples of clean rock chips. They were ground in a Tema tungsten carbide vessel for 90 seconds. Major element analyses were performed on fused discs. Trace elements (Mn, Cr, Ce, Nd, Sm, Ba, La

and V) were analysed on pressed powder pellets. Both sets of analyses were done on a Philips PW1450 X-ray spectrometer. Iron was oxidized to Fe₂O₃ and results were corrected for loss on ignition. Four specimens (62568, 62634, 62611, 62625) were analysed for H₂O and carbon. Carbon was analysed by LECO induction furnace combustion method, followed by gravimetric finish (Nesbitt bulb absorption tubes filled with Ascortite CO₂ absorbent). Water was analysed using the rapid water method with LECO induction furnace, followed by gravimetric finish.

With the exception of 62611, carbon plus water values are very similar to loss on ignition values, and it is assumed that L.O.I. in 62582 and 62651 is also composed almost entirely of water and carbon. A small amount of sulphur must be present since the rocks contain pyrite, and this, along with possible Cl and F, would constitute a small fraction of L.O.I. Carbon is assumed to be elemental C (graphite) and no CO₂ was indicated by qualitative tests. Iron contents are so low that oxidation to Fe₂O₃ makes a negligible contribution to L.O.I. Totals in Table 4 are low because of the high content of trace elements, especially Ba.

All the analyses have extremely high SiO₂, and thus other major elements are correspondingly low. The only oxides constituting more than 1% are SiO₂, Al₂O₃ and K₂O. Despite the extreme

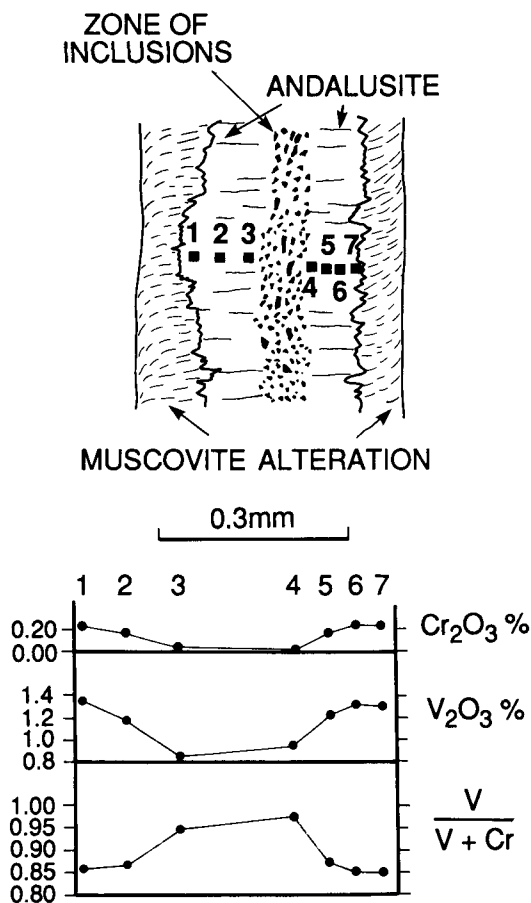


FIG. 4. Drawing of a zoned andalusite grain, with values of V₂O₃ and Cr₂O₃ for each analysed point, and ratio of V/(V + Cr) in cations. The centre of the grain is colourless, the margins are yellow.

blackness of some analysed samples, carbon contents are only about 2%.

Specimen 62625, from outside the contact aureole, differs from contact metamorphosed specimens in having lower SiO₂ and C, and higher TiO₂, Al₂O₃, MgO, Na₂O, K₂O and H₂O. Unlike the other samples analysed, this specimen has a well developed crenulation cleavage, the formation of which involves significant solution transfer of material along the cleavage seams (Gray, 1979). Thus most of the chemical differences in specimen 62625 can be ascribed to preferential dissolution and removal of quartz, with concomitant concentration of mica and therefore Al₂O₃, K₂O, Na₂O, H₂O and MgO (assuming a phengitic composition). Silica appears to have been redeposited in the abundant quartz veins that occur

in outcrops of black slate. The low C content is difficult to rationalize, as graphite should be concentrated in cleavage seams along with mica. It may simply be a primary feature of the rock.

The other specimen from outside the contact aureole (62651) has major element contents similar to those of the contact metamorphosed rocks, except that FeO and MgO are higher in this specimen. This raises the possibility of metasomatism during granite intrusion, but the data are too few to give a clear picture. Metasomatism is considered unlikely, as pelites do not normally undergo metasomatism during contact metamorphism.

Trace element contents of the contact metamorphosed rocks are quite variable, particularly Ba, V and Cr. The two specimens from outside the aureole have trace element contents within the range shown by those within the aureole, except that V in 62625 is low. As the V content in the other specimen from outside the contact aureole is relatively high, no significance in terms of metasomatism during intrusion can be attached to this value. Ba in 62625 is high, but within the range shown by contact metamorphosed rocks. Thus, black slate from the contact aureole and from outside it show non-systematic variations in some major and trace elements, but the data do not support metasomatism due to granite intrusion.

Some of the few analyses of black slates from the Lachlan Fold Belt available for comparison with the data presented here are those of Joplin (1945). Compared with black slate from the Abercrombie Beds, her analyses, which are from various Late Ordovician localities in New South Wales, have less SiO₂ and more Al₂O₃ and K₂O, but all have similar Al₂O₃/K₂O ratios of about 5. Thus black slate from the Abercrombie Beds had lower initial clay contents than those from elsewhere in the Lachlan Fold Belt, but the clay was probably the same composition in all of them. Analyses from Table 4 and from Joplin (1945) are shown on an A'KF diagram (Winkler, 1979) in Fig. 5. They mostly lie in the field andalusite-cordierite-muscovite. On Fig. 5, the analyses from the Abercrombie Beds lie within the range of compositions of Joplin (1945), and are thus considered to be typical of Ordovician black slate in New South Wales.

Although 62568 contains margarite, a calcium-bearing mica, it has less than measurable CaO (Table 4). However, the small amount of margarite present (<1% modal) would account for no more than 0.05% of CaO. All samples have CaO at or below the detection limit.

Of the trace elements determined, Ba is the

TABLE 2 MARGARITE ANALYSES FROM BLACK SLATE, REIDS FLAT DISTRICT, N.S.W.

	62568 MAGG2	62568 MAGG5	62568 MAGG7	62568 MAGG9	62568 MAGG2	62568 MAGG5	62568 MAGG7	62568 MAGG2	62568 MAGG7	62568 MAGG10
SiO ₂	31.40	30.73	31.72	31.10	31.77	31.19	30.46	30.78	30.46	30.69
TiO ₂	0.04	0.06	0.08	0.04	0.05	0.05	0.07	0.05	0.05	0.07
Al ₂ O ₃	49.36	49.85	48.96	49.52	50.18	50.31	50.76	50.16	50.63	50.57
V ₂ O ₃	0.90	0.83	0.69	1.07	0.36	0.19	0.43	0.15	0.20	0.16
Cr ₂ O ₃	0.02	0.09	0.06	0.06	0.07	0.05	0.05	0.37	0.28	0.31
FeO*	0.21	0.15	0.14	0.16	0.17	0.11	0.16	0.20	0.32	0.26
MnO	0.01	-	-	-	0.06	-	-	0.02	-	-
MgO	0.64	0.70	0.70	0.76	0.48	0.44	0.60	0.42	0.52	0.50
CaO	10.57	11.52	10.66	10.33	10.87	11.46	10.72	11.09	10.64	11.06
Na ₂ O	1.73	1.62	1.73	1.47	1.35	1.16	1.49	1.73	1.39	1.43
K ₂ O	0.02	0.02	0.37	0.03	0.02	0.03	0.03	0.02	0.05	0.04
Total	94.90	95.67	95.11	94.54	95.38	94.99	94.77	94.99	94.54	95.09
No. of cations /22(O)										
Si	4.176	4.074	4.216	4.147	4.193	4.138	4.055	4.097	4.064	4.075
Al ^{IV}	3.824	3.926	3.784	3.853	3.807	3.862	3.945	3.903	3.936	3.925
Al ^{VI}	3.916	3.861	3.885	3.933	3.999	3.993	4.017	3.964	4.028	3.990
Ti	0.004	0.006	0.009	0.004	0.005	0.006	0.007	0.005	0.005	0.008
V	0.096	0.098	0.073	0.115	0.039	0.020	0.046	0.016	0.023	0.017
Cr	0.002	0.009	0.007	0.007	0.007	0.006	0.005	0.040	0.029	0.032
Fe	0.023	0.017	0.015	0.018	0.019	0.013	0.018	0.022	0.034	0.028
Mn	0.001	-	-	-	0.007	-	-	0.003	-	-
Mg	0.127	0.138	0.140	0.151	0.094	0.088	0.117	0.083	0.103	0.099
Ca	1.507	1.635	1.518	1.476	1.547	1.630	1.530	1.580	1.502	1.573
Na	0.446	0.416	0.446	0.382	0.346	0.298	0.385	0.447	0.359	0.280
K	0.003	0.003	0.063	0.005	0.003	0.005	0.006	0.003	0.008	0.004
X	1.96	2.05	2.03	1.86	1.89	1.93	1.92	2.03	1.89	1.86
Y	4.17	4.13	4.13	4.23	4.17	4.13	4.20	4.13	4.22	4.17
V/(V+Cr)	0.98	0.92	0.91	0.94	0.85	0.77	0.90	0.29	0.44	0.35

*All iron treated as Fe²⁺

TABLE 3: ANALYSES OF POTASSIC WHITE MICA FROM BLACK SLATE

	62568 MUSC 1-1	62568 MUSC 1-3	62568 MUSC 4-2	62569 MUSC 1	62569 MUSC 2-4	62569 MUSC 4	62569 MUSC 1-1	62569 MUSC 2	62568 MUSC 2-2	62568 MUSC 3-2	62611 MUSC 2-1	62611 MUSC 3-1	62673 MUSC 1
SiO ₂	45.76	45.97	45.32	44.44	45.41	46.54	46.13	45.73	46.90	46.31	46.24	46.87	45.08
TiO ₂	1.41	1.27	0.18	1.39	1.20	0.13	1.15	0.92	1.16	0.31	0.85	0.86	0.18
Al ₂ O ₃	29.53	28.59	35.67	30.88	30.27	37.78	33.02	31.35	31.00	34.38	33.41	33.07	35.32
Cr ₂ O ₃	0.44	0.51	0.13	1.52	1.07	0.07	0.03	0.29	0.14	0.37	0.41	0.31	0.40
V ₂ O ₃	6.08	6.93	1.20	6.50	4.66	0.40	2.50	4.18	3.49	0.62	2.11	2.53	0.21
FeO*	0.24	0.24	0.13	0.64	0.43	0.19	0.37	0.54	0.35	0.32	0.59	0.48	1.25
MnO	0.02	0.06	-	0.00	0.04	0.00	0.01	0.01	-	-	0.00	0.02	0.05
MgO	1.18	1.26	0.61	1.13	1.33	0.42	1.32	1.18	1.14	1.15	1.18	1.21	1.97
CaO	0.00	0.00	-	0.00	0.00	0.01	0.09	0.01	-	-	0.00	0.00	0.01
Na ₂ O	0.40	0.39	0.49	0.27	0.34	0.61	0.45	0.27	0.35	0.39	0.40	0.39	0.54
K ₂ O	9.95	10.00	9.25	8.39	9.27	9.33	10.15	10.40	9.67	9.84	10.06	9.87	10.49
BaO	-	-	1.96	-	-	-	-	-	0.33	1.69	-	-	-
Total	95.01	95.23	94.94	95.16	94.02	95.48	95.13	94.88	94.73	95.38	95.24	95.61	95.45
No. of ions/22(O)													
Si	6.198	6.233	6.089	5.999	6.181	6.096	6.167	6.181	6.308	6.200	6.168	6.218	6.012
Al ^{IV}	1.802	1.767	1.911	2.001	1.819	1.904	1.833	1.819	1.692	1.800	1.832	1.782	1.988
Al ^{VI}	2.914	2.804	3.738	2.913	3.038	3.928	3.368	3.176	3.224	3.623	3.422	3.390	3.572
Ti	0.143	0.130	0.019	0.141	0.123	0.013	0.116	0.093	0.117	0.031	0.085	0.086	0.018
Cr	0.047	0.055	0.015	0.162	0.115	0.007	0.003	0.031	0.015	0.040	0.043	0.032	0.042
V	0.661	0.753	0.129	0.704	0.509	0.042	0.268	0.453	0.377	0.066	0.226	0.269	0.022
Fe	0.027	0.027	0.015	0.072	0.049	0.021	0.041	0.061	0.040	0.036	0.066	0.053	0.140
Mg	0.239	0.255	0.122	0.227	0.270	0.082	0.263	0.238	0.229	0.230	0.235	0.239	0.392
Mn	0.002	0.007	-	0.000	0.005	0.000	0.001	0.001	-	-	0.000	0.002	0.006
Ca	0.000	0.000	-	0.000	0.000	0.002	0.000	0.002	-	-	0.000	0.000	0.002
Na	0.016	0.103	0.128	0.069	0.116	0.153	0.116	0.071	0.144	0.100	0.104	0.100	0.140
K	1.719	1.713	1.585	1.445	1.729	1.559	1.729	1.793	1.680	1.680	1.712	1.871	1.787
Ba	-	-	0.103	-	-	-	-	-	0.017	0.089	-	-	-
X	1.74	1.83	1.82	1.51	1.70	1.71	1.85	1.87	1.82	1.87	1.82	1.77	1.93
Y	4.03	4.03	4.04	4.22	4.11	4.09	4.06	4.05	4.00	4.03	4.08	4.07	4.19
V/(V+Cr)	0.93	0.93	0.90	0.81	0.82	0.87	0.99	0.94	0.96	0.82	0.84	0.89	0.34

*All iron treated as Fe²⁺

62568 MUSC 4-2, 62569 MUSC 4, 62582 MUSC 3-2 and 62573 MUSC 1 are micas pseudomorphing andalusite; other analyses are of V-Cr mica.

TABLE 4 WHOLE ROCK ANALYSES OF BLACK SLATE FROM THE ABERCROMBIE BEDS

	62568	62582	62634	62611	62625	62651
SiO ₂	87.99	88.43	89.08	89.48	84.92	89.67
TiO ₂	0.23	0.26	0.20	0.18	0.39	0.18
Al ₂ O ₃	5.83	5.49	5.16	4.08	7.77	5.32
FeO*	0.17	0.13	0.18	0.32	0.29	0.46
MgO	0.21	0.20	0.21	0.23	0.69	0.40
CaO	<0.05	0.06	<0.05	<0.05	<0.05	<0.05
Na ₂ O	0.36	<0.10	0.24	<0.10	0.54	<0.10
K ₂ O	1.28	1.36	1.43	0.86	1.97	1.25
P ₂ O ₅	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
H ₂ O ⁺	0.82	-	0.60	0.57	1.20	-
H ₂ O ⁻	0.12	-	<0.01	0.21	0.07	-
C**	2.41	-	2.35	2.27	1.14	-
Total	99.42	95.93	99.45	98.20	98.98	97.28
L.O.I.	3.35	3.06	2.98	3.41	2.57	1.88

Trace Elements in p.p.m.

Mn	<20	154	23	22	35	23
Ba	2210	1670	2060	6260	5540	2550
V	785	582	609	212	97	663
Cr	62	85	126	89	82	77
La	17	21	18	45	22	15
Ce	29	34	23	47	46	40
Nd	15	20	13	24	12	16
Sm	3	<3	<3	<3	<3	4

* All iron treated as FeO. Separate FeO and Fe₂O₃ values not determined.

** All carbon treated as elemental carbon. No CO₂ was detected.

L.O.I. = loss on ignition.

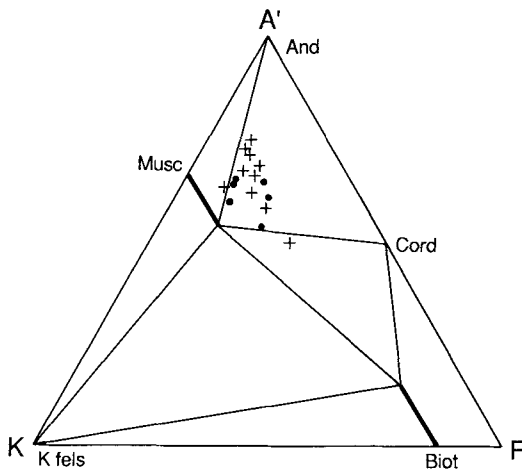


FIG. 5. A'KF diagram with black slate compositions from the Reids Flat area (dots) and from Joplin (1945) for various localities in New South Wales (crosses). Mineral assemblages shown are those of medium grade contact metamorphism (Winkler, 1979).

most abundant, ranging up to more than 6000 p.p.m. or about 0.7% BaO. The only mineral in these rocks that can accommodate a large cation such as Ba is potassic mica. Micas in two specimens, 62582 and 62568, have significant Ba substitution in the interlayer sites (Table 3). No distinct Ba phase, such as baryte, has been observed.

In order to determine if these black slates have unusual chemistry, given their distinctive mineral compositions, it is instructive to compare them to 'average' black shale or slate. The only comprehensive data set on black shale compositions is that of Vine and Tourtelot (1970), who studied the geochemistry of black shales from the U.S.A. and Canada, with major and trace elements determined for 20 sets of black shales. These sets were drawn from various ages and environments. Of the 12 elements Al, Fe, Mg, Mn, Ca, Na, K, Ti, Ba, Cr, V and La, only Ba and V average values from this study are in quantities greater than the average for American black shales (Table 5). The major elements Al, Fe, Mg, Mn, Ca, Na and K are present in significantly lower concentrations than in the American shales. Although several minerals in the black slate from the Abercrombie

TABLE 5 AVERAGE ELEMENTAL ABUNDANCES IN PERCENT OF BLACK SHALES

	Average American Black Shale*	Average from this Study
Al	7.0	3.0
Fe	2.0	0.2
Mg	0.7	0.2
Ca	1.5	<0.04
Na	0.7	0.14
K	2.0	1.1
Ti	0.2	0.17
Mn	0.015	0.004
Ba	0.03	0.34
Cr	0.01	0.01
La	0.003	0.002
V	0.015	0.05

* From Vine & Tourtelot (1970).

TABLE 6

MINIMUM ENRICHMENT VALUE FOR ELEMENTS IN BLACK SHALES FROM VINE & TOURTELOT (1970), COMPARED TO THIS STUDY. VALUES IN PERCENT.

	American Black Shale	Maximum Value from this Study
Ti	0.7	0.27
Mn	0.1	0.02
Ba	0.1	0.63
Cr	0.07	0.01
La	0.007	0.005
V	0.1	0.08

Beds have significant V and Cr, whole-rock Cr is equal to the average value for American black shale and V is not greatly higher than the American average.

Of the averages of trace elements for the black slates, only Ba has a value greater than Vine and Tourtelot's minimum enrichment value, that is, the amount of an element above which the rock is considered to be enriched in that element (Table 6). When the individual analyses of Table 4 are considered, no samples have any elements in abundances exceeding their minimum enrichment value except Ba, which is above this value in all samples.

Thus black slate from the Abercrombie Beds is not enriched in any metallic element except Ba, and has significantly different major element chemistry compared to average American black shale. Although minerals such as andalusite and mica have unusually high V and Cr contents in these rocks, the whole-rock V and Cr are not much higher than average. It is therefore likely that minerals in black slate or its higher grade

equivalents from other parts of the world also have significant V and Cr, as is the case for the occurrence described by Carlson and Rossman (1988).

When mineral analyses are compared with the whole-rock compositions, it appears that the relative amounts of V and Cr in the various minerals are determined largely by their relative amounts in the rock. The ratio $V/(V+Cr)$ is similar in most mineral analyses for each specimen (Fig. 6), and for the whole-rock specimens which were analysed (62568, 62582, 62611) this ratio is similar for the whole rock and mineral analyses, although in 62611 the mica is more V-rich than the andalusite.

Discussion

Provenance of the black slate. The high SiO_2 content and fine grain-size of Ordovician black shales in the Lachlan Fold Belt led Joplin (1945) to postulate that they were derived from silicic volcanic activity. However, silicic volcanics are virtually absent from the Ordovician of the Lachlan Fold Belt (Cas, 1983). The absence in these rocks of detrital feldspar or altered relics thereof also mitigates against such an origin.

Features such as the high quartz content and detrital minerals such as muscovite, tourmaline, rutile, monazite, apatite, epidote and xenotime, indicate that these rocks are derived from source rocks similar to those of the quartz-rich turbidites of the Abercrombie Beds, namely, Precambrian or Cambrian rocks from the nearby Gondwana craton (Powell, 1983). Silica precipitated from sea water also contributed to the high quartz contents, especially in the more chert-like layers. The black slates were deposited as the finest fraction carried by turbidity currents or bottom currents, mixed with pelagic material such as organic remains and very fine quartz detritus which settled out of the water column.

Origin of vanadium, chromium and barium. In the rocks of this study, the analysed trace elements which occur in greatest quantity are Ba, V and Cr. Holland (1979) and Berry *et al.* (1986) found that metal enrichment in organic-rich sediments can probably be achieved by chemical precipitation from sea water and reactions with dead organic remains. As V and Cr are not present in excessive amounts in the Abercrombie Beds, there is no need to invoke concentration by organisms (cf. Goldberg, 1957).

Ba in these rocks is in much higher concentrations than average, and is also much more abundant than any other trace element analysed. BaO is generally higher than TiO_2 , FeO, CaO,

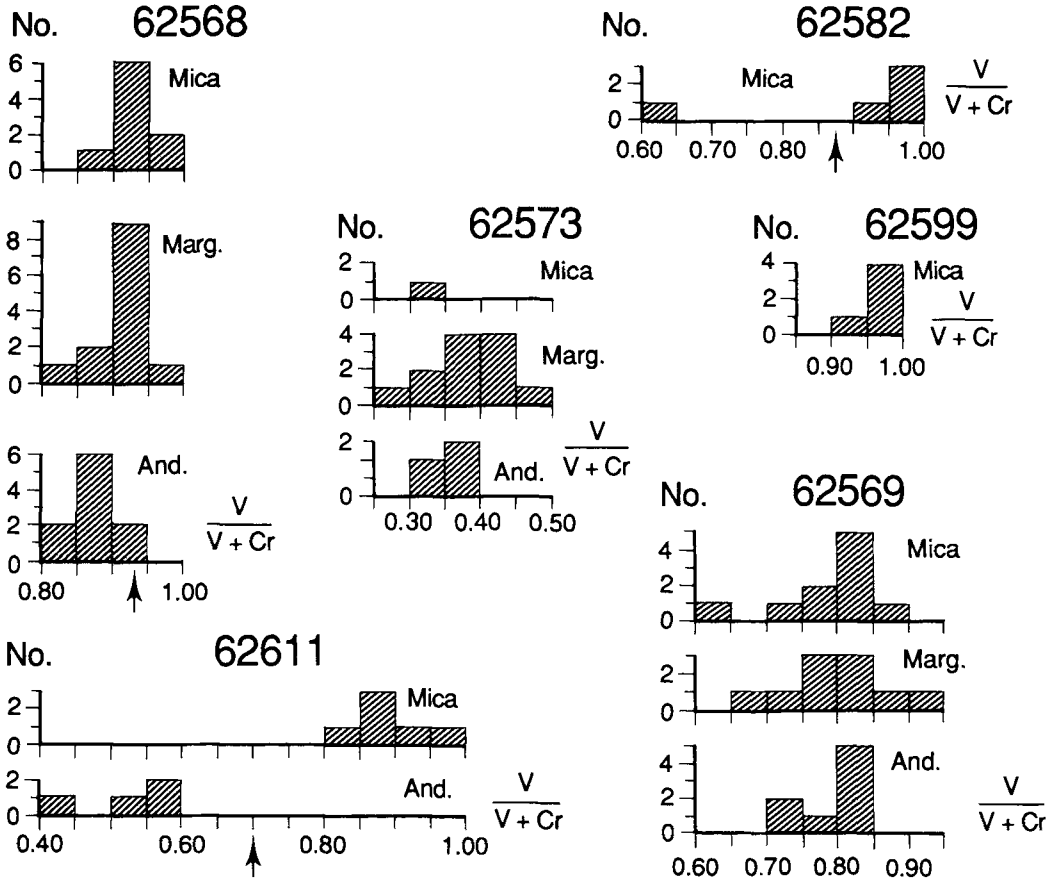


FIG. 6. $V/(V + Cr)$ ratios plotted against number of analyses for mica, margarite and andalusite in six specimens of black slate, and whole rock value (indicated by arrow) for specimens 62568, 62611 and 62582.

Na_2O and P_2O_5 , and is about equal to MgO in concentration (Table 4).

Organic activity may be responsible for concentrating Ba in these rocks. Certain organisms in the Black Sea are known to concentrate Ba (Vinogradova and Koval'skiy, 1962), including zooplankton whose ash contains up to 2000 p.p.m. Ba, and some phytoplankton which can have up to 30,000 p.p.m. Ba. Ordovician black slate in the Abercrombie Beds contains radiolarian remains, and it is possible that these planktonic organisms were able to concentrate Ba and hence lead to high Ba values in the black shale.

Conclusions

Late Ordovician black slate in the Abercrombie Beds, Lachlan Fold Belt, New South Wales, was derived from hemipelagic sediments deposited

within a turbidite sequence. Detrital material in the black slate suggests the same provenance as the turbidites, namely the Gondwana craton to the south or west.

Contact metamorphism against the Siluro-Devonian Wyangala Batholith produced andalusite, cordierite and a phengitic mica containing V and Cr. Margarite replaces andalusite in some rocks. It grew during retrogressive regional metamorphism. Both andalusite and margarite contain V and Cr. In all these aluminous minerals V and Cr substitute for Al, with the ratio of V to Cr similar for all minerals in the one rock. Ba is present in the phengitic mica.

The rocks have very high silica (about 89%) and high Ba (2000 to 6000 p.p.m.). V and Cr occur in about average amounts for black shale, whereas all other major elements, and those trace elements determined, are well below average. V

and Cr were probably precipitated from sea water, but Ba may have been concentrated by planktonic organisms such as radiolaria.

Acknowledgements

This work was part of a Ph.D. project at the University of Sydney which was funded by a Commonwealth Post-graduate Research Award. Diana Benson and Alf Hohmann assisted with electron microprobe analyses. Rolf Beck greatly assisted in the whole-rock analysis. Mike Rubenach provided critical discussion of the manuscript.

References

- Berry, W. B. N., Wilde, P., Quinby-Hunt, M. S. and Orth, C. J. (1986) *Norsk Geol. Tidss.* **66**, 45–51.
- Carlson, W. D. and Rossman, G. R. (1988) *Am. Mineral.* **73**, 1366–9.
- Cas, R. A. F. (1983) *A review of the palaeogeographic and tectonic development of the Palaeozoic Lachlan Fold Belt of south eastern Australia*. Geol. Soc. Austral. Spec. Publ. No. 10.
- Chinner, G. A., Smith, J. V. and Knowles, C. R. (1969) *Am. J. Sci.* **267A**, 96–113.
- Deer, W. A., Howie, R. A. and Zussman, J. (1962) *Rock-forming Minerals, Vol. 3, Sheet Silicates*, John Wiley, New York.
- (1982) *Rock-forming Minerals, Vol. 1A, Orthosilicates*. 2nd ed. Longman, London.
- Goldberg, E. D. (1957) In *Ecology* (Hedgpeth, J. W., ed.) *Geol. Soc. Am. Mem.* **67**, 1: 345–57.
- Gray, D. R. (1979) *Am. J. Sci.* **279**, 97–128.
- Guidotti, C. V. (1984) In *Micas. Reviews in Mineralogy, Vol. 13* (Bailey, S. W., ed.) *Mineral. Soc. Am.*, 357–467.
- Holland, H. D. (1979) *Econ. Geol.* **74**, 1676–80.
- Joplin, G. A. (1945) *Proc. Linn. Soc. N.S.W.* **70**, 158–72.
- Morand, V. J. (1984) Ph.D. thesis, University of Sydney.
- (1987) *Austral. J. Earth Sci.* **34**, 119–33.
- (1988a) *Ibid.* **35**, 339–53.
- (1988b) *Mineral. Mag.* **52**, 341–5.
- Packham, G. H. (1969) In *Geology of New South Wales* (Packham, G. H., ed.) *J. Geol. Soc. Austral.* **16**, 76–103.
- Powell, C. McA. (1983) *Ibid.* **30**, 353–74.
- Schreyer, W., Werding, G. and Abraham, K. (1981) *J. Petrol.* **22**, 191–231.
- Snetsinger, K. G. (1966) *Am. Mineral.* **51**, 1623–39.
- Vine, J. D. and Tourtelot, E. B. (1970) *Econ. Geol.* **65**, 253–72.
- Vinogradova, Z. A. and Koval'skiy, V. V. (1962) *Dokl. Acad. Nauk S.S.S.R.* **147**, 1458.
- Winkler, H. G. F. (1979) *Petrogenesis of Metamorphic Rocks*, 5th ed. Springer-Verlag, New York.

[Manuscript received 17 July 1989; revised 5 November 1989]