

Vanadium-bearing margarite from the Lachlan Fold Belt, New South Wales, Australia

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Abstract

Margarite occurs in Ordovician black slate within the contact aureole of the Wyangala Batholith, in the Lachlan Fold Belt in New South Wales. This occurrence is the first described from New South Wales. It is a regional metamorphic mineral replacing chialstolitic andalusite, and contains up to 1.07% V_2O_3 and up to 0.37% Cr_2O_3 . Vanadium and chromium here substitute for octahedral aluminium. Margarite is produced by a local reaction in which Ca and H_2O are introduced into andalusite grains. There is a significant paragonite component in the margarite but negligible muscovite solid solution.

Introduction

AN important mode of occurrence of margarite is as a replacement of aluminium silicates, this being a reflection of its high aluminium content. Margarite replacing andalusite has been reported from Brittany, France (Velde, 1970), Maine, U.S.A. (Guidotti and Cheney, 1976), California, U.S.A. (Guidotti *et al.*, 1979), and South Australia (Teale, 1979), while margarite replacing kyanite has been reported from Scotland (Chinner, 1974; Baltatzis and Katagas, 1981), Fiordland, New Zealand (Gibson, 1979), and the Southern Alps of New Zealand (Cooper, 1980). This paper reports an occurrence from New South Wales, Australia, of margarite, containing both vanadium and chromium, which is a replacement product of andalusite.

Geological setting

The rocks in which vanadium-bearing margarite occurs are carbonaceous black slates belonging to the Abercrombie Beds within the Lachlan Fold Belt of eastern Australia (Fig. 1). The Abercrombie Beds are a sequence of quartz-rich deep-water meta-sedimentary rocks of Late Ordovician age which have been regionally metamorphosed to greenschist facies and are complexly deformed (Hobbs, 1965; Morand, 1987). Distinctive layers of carbonaceous, siliceous black slate occur within this sequence. Margarite occurrences are close to the

village of Reids Flat (Fig. 1), approximately 200 km WSW of Sydney, situated in the northern part of the Goulburn 1:250 000 Geological Sheet (Brunker and Offenber, 1970).

For several kilometres south of Reids Flat a layer of black slate lies within the contact aureole of the Siluro-Devonian Wyangala Batholith (Fig. 1). This layer was deformed prior to granite intrusion, producing a slaty cleavage, and then thermally metamorphosed by the Wyangala Batholith to hornblende hornfels facies, producing assemblages bearing cordierite and andalusite. Subsequent deformation and regional metamorphism (the second deformation in the area, D2) led to the breakdown of cordierite to micaceous aggregates, still recognizable as white spots in hand specimen, and breakdown of andalusite to aggregates of potassic white mica and margarite (Morand, 1984). Margarite is thus a regional metamorphic mineral growing at the expense of a contact metamorphic mineral.

Petrography

The specimens in which margarite occurs are typical of contact-metamorphosed Ordovician black slates from the Lachlan Fold Belt. Porphyroblasts of cordierite and andalusite occur within a groundmass of fine-grained quartz, graphite, and white mica. Bedding lamination, defined by alternating quartz-rich layers and darker layers rich in opaque minerals and mica, is evident in some specimens. Slaty cleavage formed during the first deformation was largely obliterated by contact

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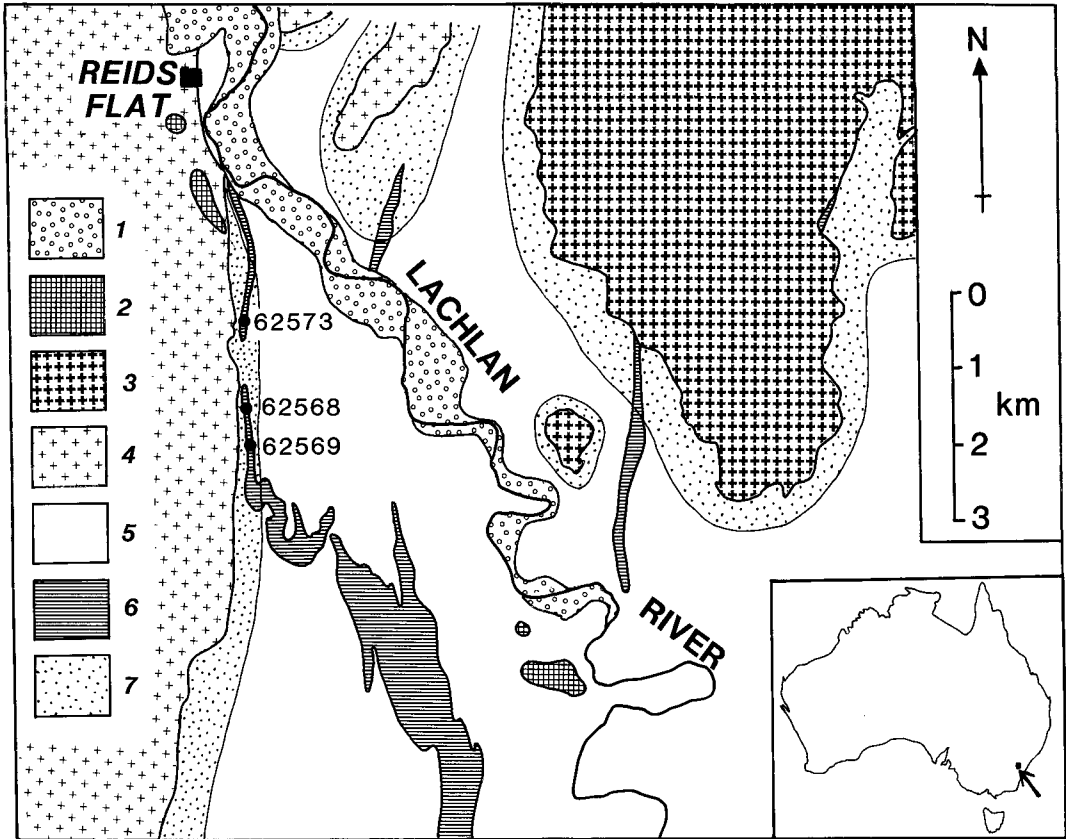


Fig. 1. Geological map of the area south of Reids Flat, with locations of margarite-bearing samples indicated. 1. Alluvium. 2. Miocene basalt. 3. Massive granite of the Wyangala Batholith (Siluro-Devonian). 4. Foliated granite of the Wyangala Batholith. 5. Abercrombie Beds (Ordovician). 6. Black slate layers within the Abercrombie Beds. 7. Contact aureole.

metamorphism (Morand, 1984). Another slaty cleavage was formed during D2, and cordierite and andalusite porphyroblasts were deformed and rotated toward this cleavage.

Cordierite in all specimens is completely replaced by micaceous aggregates, but the elliptical outlines of the original porphyroblasts (usually less than 1 mm across) are maintained. Andalusite, of the chiastolite variety, occurs as prisms about 1 mm wide and up to 8 cm long. It ranges from completely fresh in some specimens to completely altered to white mica and margarite in others. Andalusite is commonly boudinaged as a result of extension along its length.

Scattered grains of a pale green potassic mica, distinct from the white mica replacing andalusite and containing vanadium and chromium, are present in most specimens. They are much larger than the groundmass mica although still quite small

(about 0.2 mm long) and they constitute a contact metamorphic phase since they are found only in the contact aureole. Other minerals observed in these black slates are orange-brown tourmaline, rutile, pyrite, hematite, and rare chlorite, monazite, xenotime, and gahnite. The last three minerals were identified by electron microprobe. These accessory minerals are all fine grained. No paragonite has been identified.

Margarite occurs between boudins of deformed andalusite (Fig. 2) and in cross-cutting veinlets within andalusite grains. Its occurrence between boudins of andalusite suggests that it grew syntectonically. Andalusite is never completely pseudomorphed by margarite: most of the alteration products are white mica aggregates, with margarite occurring in localized patches. This white mica is a phengitic potassic mica with small but significant amounts of chromium and

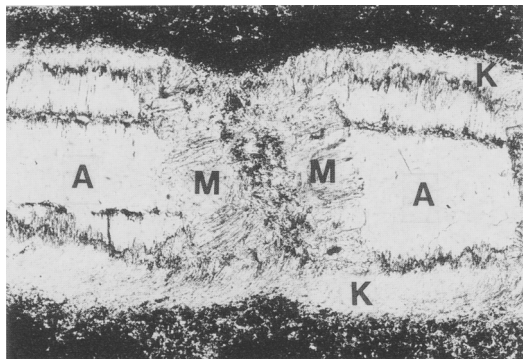


FIG. 2. Occurrence of margarite (M) between boudins of andalusite (A). The outer parts of the andalusite are replaced by potassic white mica (K) which forms fine-grained aggregates with a sigmoidal pattern. Plane polarized light. Width of photograph = 1 mm.

vanadium. Margarite forms coarse, colourless plates, whereas phengite replacing andalusite is fine grained and commonly forms a sigmoidal pattern resulting from syntectonic crystallization as andalusite grains rotated relative to the matrix (Fig. 2). Within cross-cutting veinlets margarite plates are typically oriented perpendicular to the length of the veinlets; this is similar to margarite replacing

andalusite in the Georgetown area, California (Guidotti *et al.*, 1979).

In all specimens examined margarite has not been observed to be in contact with quartz, but only occurs in contact with potassic white mica and (metastable) andalusite. Margarite is restricted to altered chiasolite grains and does not occur in the groundmass.

Mineral chemistry

Analyses of margarite from three specimens are presented in Table 1. These analyses were performed on the electron microprobes at the University of Sydney and at Monash University, using wavelength-dispersive spectrometers, following the method of Bence and Albee (1968). Metallic V was used as a standard for V, and silicate standards were used for all other elements. Values of Cr_2O_3 were corrected for the overlap of the V-K β peak with the Cr-K α peak.

Na values are about 0.4, which is typical for margarite from other localities (Frey *et al.*, 1982; Teale, 1979; Guidotti *et al.*, 1979). Si values are also high because of the paragonite substitution $\text{Na}^+\text{Si}^{4+} = \text{Ca}^{2+}\text{Al}^{3+}$ which is the most important substitution in natural margarite (Frey *et al.*, 1982).

Another important substitution in the margarite of these rocks is $(\text{V}^{3+}, \text{Cr}^{3+}) = \text{Al}^{3+}$. Vanadium

Table 1 Selected analyses of margarite from black slate south of Reids Flat, New South Wales

Analysis	1	2	3	4	5	6	7
SiO ₂	31.40	31.10	31.72	30.46	31.77	31.25	30.78
TiO ₂	0.04	0.04	0.08	0.07	0.05	0.03	0.05
Al ₂ O ₃	49.36	49.52	48.96	50.76	50.18	50.20	50.16
V ₂ O ₅	0.90	1.07	0.69	0.43	0.36	0.17	0.15
Cr ₂ O ₃	0.02	0.06	0.06	0.05	0.07	0.31	0.37
FeO*	0.21	0.16	0.14	0.16	0.17	0.33	0.20
MnO	0.01	-	-	-	0.06	0.03	0.02
MgO	0.64	0.76	0.70	0.60	0.48	0.41	0.42
CaO	10.57	10.33	10.66	10.72	10.87	10.46	11.09
Na ₂ O	1.73	1.47	1.73	1.49	1.35	1.61	1.73
K ₂ O	0.02	0.03	0.37	0.03	0.02	0.05	0.02
Total	94.90	94.54	95.11	94.77	95.38	94.85	94.99
Number of cations on the basis of 22 oxygens							
Si _{iv}	4.176	4.147	4.216	4.055	4.193	4.152	4.097
Al _{vi}	3.824	3.853	3.784	3.945	3.807	3.848	3.903
Al _{iii}	3.916	3.933	3.885	4.017	3.999	4.015	3.964
Ti	0.004	0.004	0.009	0.007	0.005	0.004	0.005
V	0.096	0.115	0.073	0.046	0.039	0.018	0.016
Cr	0.002	0.007	0.007	0.005	0.007	0.033	0.040
Fe	0.023	0.018	0.015	0.018	0.019	0.036	0.022
Mn	0.001	-	-	-	0.007	0.003	0.003
Mg	0.127	0.151	0.140	0.117	0.094	0.081	0.083
Ca	1.507	1.476	1.518	1.530	1.537	1.489	1.580
Na	0.446	0.382	0.446	0.385	0.346	0.414	0.447
K	0.003	0.005	0.063	0.006	0.003	0.008	0.003
Total X	1.96	1.86	2.03	1.92	1.89	1.91	2.03
Total Y	4.17	4.23	4.13	4.21	4.17	4.19	4.13

*All iron treated as Fe²⁺

1 : 62568 MARG 2; 2 : 62568 MARG 3; 3 : 62568 MARG 8; 4 : 62569 MARG 7; 5 : 62569 MARG 2; 6 : 62573 MARG 1; 7 : 62573 MARG 2.

Sample localities shown on Figure 1. Sample numbers refer to the collection at the Department of Geology and Geophysics, University of Sydney.

and chromium are assumed to be in the trivalent state. In specimen 62568 V_2O_3 content reaches about 1%, and Cr_2O_3 reaches 0.37% in specimen 62573. Vanadium-bearing margarite has not to my knowledge been reported before, although chromium-bearing varieties are known (Cooper, 1980; Schreyer *et al.*, 1981). Y values of analyses in Table 1 are slightly high (about 4.2) but this is typical of natural margarite, which shows a slight trioctahedral character (Frey *et al.*, 1982), and they have no dependence on the content of V+Cr. Fig. 3 is a plot of Al^{vi} against V+Cr, and an inverse relationship exists, with Al^{vi} decreasing as V+Cr increases. Ionic radii of V^{3+} and Cr^{3+} in six-fold coordination are similar to that of Al^{3+} , namely, 0.72Å for V^{3+} , 0.70Å for Cr^{3+} and 0.61Å for Al^{3+} (Whittaker and Muntus, 1970). The substitution (V^{3+}, Cr^{3+}) = Al^{3+} does not involve any charge imbalance hence the interlayer cations would not be affected by the introduction of vanadium and chromium.

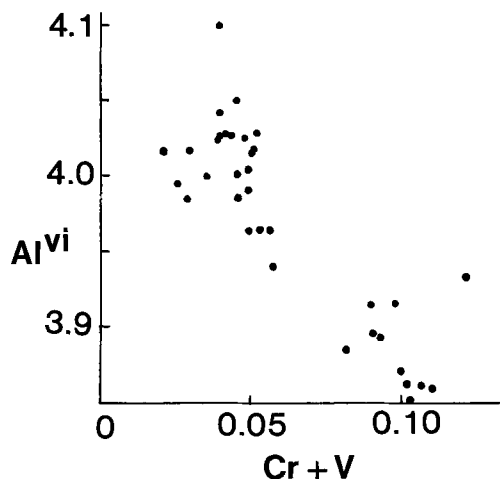


FIG. 3. Plot of Al^{vi} against (Cr+V) for 35 analyses of margarite.

Other elements present in small amounts are Fe and Mg, with Mg more abundant than Fe. Ti and Mn occur in insignificant quantities. This appears to be typical of margarite replacing andalusite from other localities (e.g. Guidotti and Cheney, 1976; Guidotti *et al.*, 1979; Teale, 1979). As with most natural margarite, the K content is very low, mostly less than 0.02 atoms per formula unit. There is thus little solid solution between margarite and muscovite. On the other hand there is a significant

Table 2 Analyses of phengitic mica replacing andalusite

Analysis	1	2	3
SiO_2	45.19	46.54	45.03
TiO_2	0.18	0.13	0.18
Al_2O_3	35.10	37.78	35.32
V_2O_3	1.05	0.40	0.21
Cr_2O_3	0.08	0.07	0.40
FeO^*	0.15	0.19	1.25
MnO	-	0.00	0.05
MgO	0.67	0.42	1.97
CaO	-	0.01	0.01
Na_2O	0.59	0.61	0.54
K_2O	9.91	9.33	10.49
BaO	1.46	-	-
Total	94.38	95.48	95.45
Number of cations on the basis of 22 oxygens			
Si _{iv}	6.113	6.096	6.012
Al^{iv}	1.887	1.904	1.988
Al^{vi}	3.707	3.928	3.572
Ti	0.018	0.013	0.018
V	0.114	0.042	0.022
Cr	0.009	0.007	0.042
Fe	0.017	0.021	0.140
Mg	0.134	0.082	0.392
Mn	-	0.000	0.006
Ca	-	0.002	0.002
Na	0.154	0.153	0.140
K	1.709	1.559	1.787
Ba	0.077	-	-
Total X	1.96	1.71	1.93
Total Y	4.00	4.09	4.19

*All iron treated as Fe^{2+}

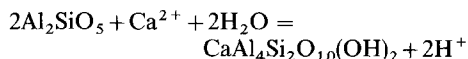
1 : 62568 MUSC 4; 2 : 62569 MUSC 4;

3 : 62573 MUSC 1.

paragonite component in both margarite and white mica replacing andalusite (Table 2).

Discussion

In order for margarite to replace andalusite Ca must be brought into the andalusite grain from elsewhere in the rock where some Ca-bearing phase is breaking down. The only Ca-bearing phase likely to be in these black slates is plagioclase and, although no plagioclase has been observed in any black slate from the area, it is surmised that there are scattered grains throughout the rocks. Frey and Orville (1974) reported that plagioclase is commonly present in margarite-bearing rocks. Since margarite occurs in only minor amounts, plagioclase need only occur in minor amounts also in order to provide Ca for margarite formation. On the scale of individual andalusite grains there has been metasomatism of Ca and H_2O into andalusite to form margarite, both minerals having the same Al to Si ratio. A reaction such as the following (Guidotti *et al.*, 1979) must have occurred:



This is an example of a local reaction similar to the metasomatic Al-constant sub-reactions discussed by Carmichael (1969).

The above equation is a simplified one, and the significant amounts of Na in this margarite must also have been derived from the matrix.

The presence of V and Cr in margarite in these rocks appears to be a result of V and Cr being present in the andalusite which it replaces. There is up to 1.31% V₂O₃ and up to 0.44% Cr₂O₃ in this andalusite (Table 3). Relative and absolute values of V and Cr in margarite from each specimen differ greatly (e.g. margarite from specimen 62568 has negligible Cr) and this can be attributed to differing amounts of these elements in the parent andalusite grains, which in turn depend to a large extent on the V and Cr contents of the whole rock. Within the one layer of black slate V and Cr contents vary from one locality to another (Morand, 1984).

Table 3 Analyses of andalusite

Analysis	1	2	3
SiO ₂	36.57	36.87	37.37
TiO ₂	0.06	0.09	0.07
Al ₂ O ₃	61.73	62.18	61.59
V ₂ O ₃	1.31	0.40	0.23
Cr ₂ O ₃	0.24	0.09	0.44
Fe ₂ O ₃ *	0.06	0.09	0.07
MnO	0.02	0.01	0.00
MgO	0.07	0.05	0.04
Total	100.06	99.78	99.81
Number of cations on the basis of 20 oxygens			
Si	3.956	3.997	4.047
Al	7.891	7.944	7.863
Ti	0.005	0.006	0.006
V	0.113	0.035	0.019
Cr	0.021	0.008	0.038
Fe ³⁺	0.005	0.006	0.005
Mg	0.011	0.007	0.007
Mn	0.002	0.001	0.000

*All iron treated as Fe³⁺
 1 : 62568 AND 2 ; 2 : 62569 AND 1 ;
 3 : 62573 AND 1.

Because the assemblage margarite + quartz does not occur in these rocks, even though they are quartz-rich, it is suggested that during margarite formation, i.e. D2, the temperature was above the margarite + quartz stability field and below the margarite breakdown temperature. This constrains the temperature to between about 450 °C and 530 °C at a pressure of 3 kbar (assuming $a_{\text{H}_2\text{O}} = 1.0$) (Chatterjee, 1976). 3 kbar is considered to be the pressure under which the Abercrombie Beds were metamorphosed during D2 (Morand, 1984).

Paragonite solid solution in margarite would raise the breakdown temperatures of margarite and margarite + quartz, because paragonite is stable to higher temperatures (Chatterjee, 1974). On the

other hand, methane was probably an active fluid phase in these carbon-rich rocks and would have had the effect of lowering $a_{\text{H}_2\text{O}}$ and hence lowering reaction temperatures. These two effects would tend to cancel each other.

The Abercrombie Beds display both a chlorite and a biotite zone, but margarite is the only mineral in this sequence of rocks which provides a reasonable estimate of the temperature of regional metamorphism in the area. This demonstrates the significance of margarite as an indicator of regional metamorphic conditions there.

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