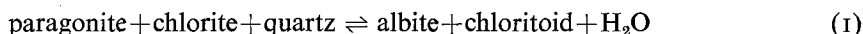# The occurrence of paragonite in chloritoid schists from Stonehaven, Scotland

E. BALTATZIS AND B. J. WOOD

Department of Geology, The University, Manchester M13 9PL

SUMMARY. Paragonite has been found in two chloritoid–chlorite–mica schists from the Dalradian, north of Stonehaven. The principal bulk-chemical constraints on the occurrence of this mineral within the chloritoid zone appear to be the ratios of soda to potash and the Al_2O_3 contents of the rock. The composition of paragonite coexisting with muscovite indicates a crystallization temperature of 550 °C for rocks some way above the chloritoid isograd. Although this result is supported by other mineral equilibria, the muscovite compositions suggest a temperature of 690 °C, which is too high because the mineral assemblage chloritoid–paragonite is unstable above about 600 °C. By combining data on the breakdown of the chloritoid–paragonite assemblage with a mineral equilibrium for the assemblage garnet–plagioclase–muscovite–biotite, it has been deduced that rocks close to the staurolite isograd crystallized at about 7·5 kb and 600 °C.

THIS paper arose from an investigation of the reactions that produced chloritoid in the Dalradian metapelites north of Stonehaven, Aberdeenshire. Although he was not able to find low-grade rocks of similar composition to the chloritoid schists, Chinner (1967) considered that the chloritoid isograd *may* have arisen from reaction between paragonite and chlorite:

$$\text{paragonite} + \text{chlorite} + \text{quartz} \rightleftharpoons \text{albite} + \text{chloritoid} + H_2O \qquad (1)$$

The extent of the occurrence of paragonite in Dalradian rocks is, however, poorly documented. Although the mineral has been found in Argyllshire (McNamara, 1965) it had not, prior to the present investigation, been observed in the Stonehaven area. It was necessary, therefore, for the authors to determine whether or not paragonite occurs in this region in order for the validity of the model reaction (1) to be established. Many microprobe analyses of white micas in rocks from above and below the chloritoid isograd have been made and paragonite has not, as yet, been found in any low-grade rocks. It has, however, been detected in the two chloritoid-bearing schists whose approximate localities are shown in fig. 1. This paper describes the occurrence of paragonite in chloritoid-zone rocks and discusses the implications of its presence in terms of the physical conditions of metamorphism.

Mode of occurrence. Paragonite occurs in two schists, which contain the common mineral assemblage chloritoid, chlorite, muscovite, albite, and quartz. Two generations of muscovite growth are shown by large plates whose (001) planes are parallel to S_1 and smaller fibrous flakes parallel to S_2. Paragonite occurs as small fibrous crystals and as intergrowths with muscovite of the second generation.

Rock and mineral analyses. Rock analyses were performed by XRF methods and correction procedures described by Brown et al. (1973). Mineral compositions were determined with a Cambridge Geoscan microprobe using a range of metal and silicate standards; full ZAF corrections were applied to these data.

An initial comparison of the compositions of paragonite-bearing and paragonite-free rocks of the same grade (Table I) indicates that the Na_2O content, or the Na /(Na+K) ratio is, as might be expected, the principal chemical constraint on the occurrence of this mineral. From
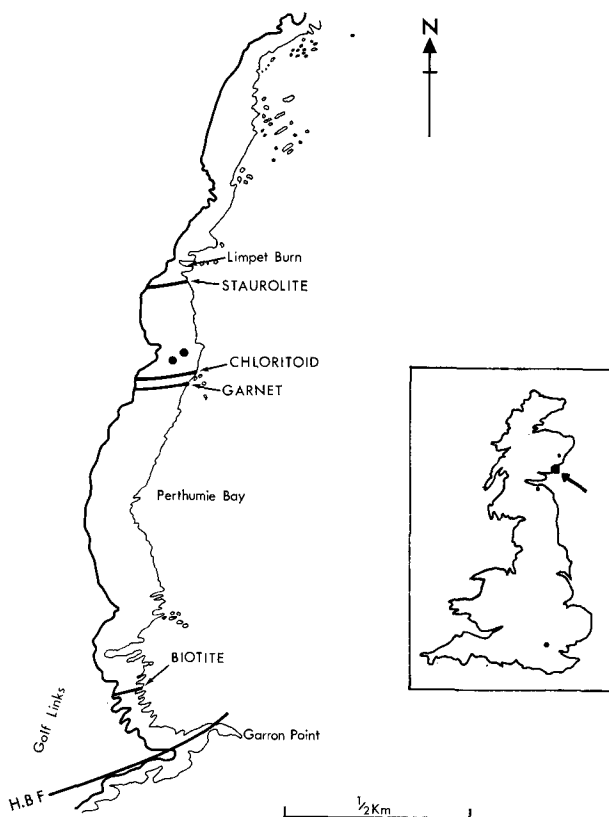
FIG. 1. Localities of chloritoid–paragonite assemblages described in the text from the region north of Stonehaven. *Solid* line indicated with an arrow corresponds to approximate first appearance of the mineral concerned in the area between high and low water marks. HBF refers to the Highland Boundary Fault.

TABLE I. *Analyses of chloritoid-bearing rocks*

	D20	D21	St18	St19	St23
SiO_2	56.28	57.59	60.70	53.11	51.99
Al_2O_3	23.60	23.19	20.34	24.13	25.16
Fe_2O_3	1.02	0.97	1.41	1.81	1.59
FeO	5.54	5.18	5.08	5.75	4.62
MgO	1.72	1.66	1.99	1.79	1.96
CaO	0.14	0.26	0.28	0.78	0.95
Na_2O	1.68	1.44	0.70	0.49	0.61
K_2O	3.29	3.70	4.09	5.54	5.96
TiO_2	0.88	0.61	0.75	0.87	0.78
MnO	0.09	0.09	0.07	0.09	0.10
P_2O_5	0.07	0.15	0.04	0.07	0.05
Ign. loss	5.04	4.54	3.99	4.92	5.57
Total	99.35	99.38	99.44	99.35	99.33
Na/(Na+K)	0.44	0.37	0.20	0.10	0.11

Mineral assemblages

D20, D21:   Chloritoid, chlorite, muscovite, paragonite, quartz, albite.
St18, St19: Chloritoid, chlorite, muscovite, biotite, garnet, quartz, albite.
St23:   As St18, St19, without biotite.

the analyses given in Table I it may be seen that the mole ratio $Na/(Na+K)$ necessary to produce paragonite in the chloritoid schists is less than 0·37 and greater than 0·20. These figures are in good agreement with those derived from microprobe analyses of coexisting muscovite and paragonite (Table II), which indicate that muscovite is, at this grade, saturated with paragonite once its mole ratio of $Na/(Na+K)$ is greater than 0·33.

TABLE II. *Mineral analyses*

Sample No.	D20		D21		D20	D21
	Parag	Musc	Parag	Musc	Ctd	Ctd
SiO_2	45.92	44.17	45.21	44.68	24.46	24.83
TiO_2	0.08	0.18	0.05	0.20	–	–
Al_2O_3	39.29	36.57	40.28	36.46	41.60	42.02
FeO*	0.41	1.02	0.61	0.93	24.74	24.92
MgO	n.d	0.23	0.16	0.48	2.24	2.18
NnO	n.d.	0.02	0.01	0.01	0.86	0.79
CaO	0.20	0.01	0.22	n.d.	–	–
Na_2O	7.24	2.55	6.39	2.57	–	–
K_2O	0.80	7.86	0.79	7.76	–	–
Total	93.94	92.62	93.70	93.10	93.90	94.75

* Total iron as FeO

Number of ions on the basis of 22 oxygens					Ions to 24 oxygens	
Si	5.960	5.999	5.872	6.028	3.988	4.007
Al^{iv}	2.040	2.001	2.128	1.972	7.994	7.993
Al^{vi}	3.970	3.853	4.038	3.826		
Ti	0.007	0.019	0.004	0.020	–	
Fe	0.045	0.116	0.066	0.105	3.373	3.364
Mg	–	0.046	0.031	0.096	0.543	0.525
Mn	–	0.003	–	0.002	0.118	0.408
Ca	0.027	0.002	0.030	–	–	–
Na	1.820	0.672	1.609	0.672	–	–
K	0.133	1.362	0.130	1.336	–	–
mol $Na/(Na+K)$	0.93	0.330	0.925	0.334	–	–

Errata: Col. 1, *for* NnO *read* MnO; last col., *for* 0.408 *read* 0.108.

Apart from the ratio $Na/(Na+K)$ the compositional parameter that is likely to have greatest effect on paragonite occurrence is the alumina content of the rock. From Table I it can be seen that paragonite coexists with the two ferromagnesian minerals, chloritoid and chlorite. Paragonite is unlikely, however, to coexist with garnet or biotite provided that chloritoid is stable. The occurrence of chloritoid–albite assemblages implies that the following reaction might occur between garnet and paragonite in the chloritoid zone:

$$\text{garnet} + \text{paragonite} \rightleftharpoons \text{chloritoid} + \text{albite} + H_2O \qquad (2)$$
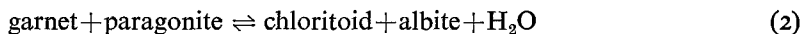
The probable relationship between chloritoid-bearing assemblages with paragonite and those without paragonite is illustrated in the AFM diagram of fig. 2. Although not strictly quantitative, this figure has been constructed by correcting Al_2O_3 contents of the rocks for Na_2O (in albite) and CaO and MnO (both in garnet). The paragonite-bearing rocks have compositions that project (from muscovite) on the Al_2O_3-rich side of the chloritoid–chlorite tie line in the three-phase assemblage garnet–chlorite–chloritoid. Rocks without paragonite plot inside the garnet–chloritoid–chlorite triangle.

Paragonite may, therefore, occur in rocks of the chloritoid zone provided that the $Na/(Na+K)$ ratio of the rock is greater than 0·33 and garnet and biotite are absent. There are, as

yet, insufficient data available for us to know the proportion of chloritoid-bearing rocks that fall in this category.

It is of interest to note that all of the mineral phases involved in reaction (1) occur in specimens D20 and D21, both of which were collected from some way above the chloritoid isograd. It seems unlikely, therefore, that reaction (1) is an adequate model for the initial chloritoid-producing reaction in the Stonehaven area.

Muscovite–paragonite geothermometry. Since the muscovites and paragonites that coexist in D20 and D21 are close to binary $KAl_3Si_3O_{10}(OH)_2$–$NaAl_3Si_3O_{10}(OH)_2$ solid solutions it should be possible to apply experimental data on the muscovite–paragonite solvus to estimate
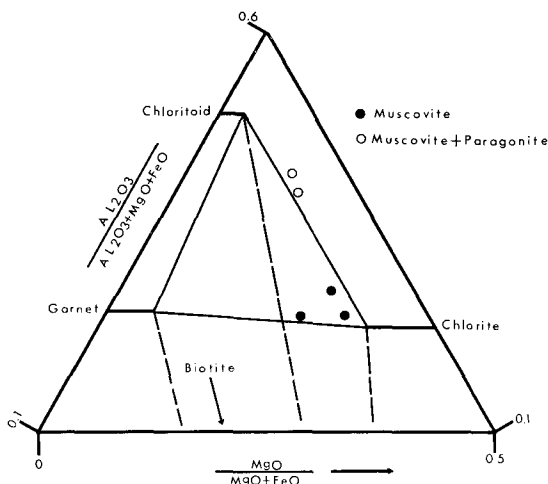
FIG. 2. Part of the triangle Al_2O_3–FeO–MgO in the tetrahedron K_2O–Al_2O_3–FeO–MgO showing the approximate positions of paragonite-bearing and paragonite-free rocks and the compositions of coexisting garnet, chlorite, and chloritoid.

the temperatures of crystallization of these assemblages. Comparison of the mineral analyses of Table II with the solvus of Eugster *et al.* (1972) yields temperatures of about 550 °C from the paragonite limb and 690 °C from the muscovite limb. The discrepancies between the two sets of results, although discouraging, are in agreement with other observations on natural assemblages. Eugster *et al.* (1972) noted that the compositions of muscovite coexisting with paragonite in the Gassetts schist, Vermont, implied a crystallization temperature of 740 °C; this temperature is 210° greater than that obtained from oxygen isotope fractionation data. Rumble *et al.* (1975) observed a discrepancy between oxygen isotope and 'muscovite' temperatures of 155 °C for a rock from the Clough formation, Black Mountain, New Hampshire. Since temperatures obtained from oxygen isotope data and from paragonite compositions disagree by similar amounts with temperatures obtained from muscovite compositions it is probable that temperatures derived from the paragonite limb of the solvus are more accurate than those derived from the muscovite limb. In this case the temperature of 550 °C obtained from analyses of paragonite coexisting with muscovite is in reasonable agreement with that estimated from solid–fluid equilibria (see below).

P–T estimate from mineral equilibria. With increasing grade staurolite appears in the chloritoid schists approximately $\frac{1}{4}$ km north of the chloritoid–paragonite-bearing assemblages described in this paper. Although plagioclase is not abundant in chloritoid-bearing rocks, large feldspar crystals occur in most staurolite and chloritoid–staurolite schists. Thus, although

the reactions that give rise to staurolite are incompletely known, the appearance of this mineral and its coexistence with plagioclase must be associated with instability of the chloritoid–paragonite assemblage discussed here:

$$4FeAl_2SiO_5(OH)_2 + 5NaAl_3Si_3O_{10}(OH)_2 + 4SiO_2 \rightleftharpoons 2Fe_2Al_9Si_4O_{23}(OH) + 5NaAlSi_3O_8 + 8H_2O$$

$$\text{chloritoid} \qquad \text{paragonite} \qquad \text{quartz} \qquad \text{staurolite} \qquad \text{plagioclase} \qquad \text{fluid}$$

(3)
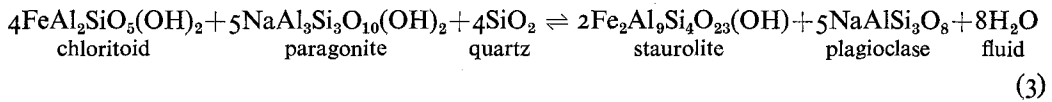
Given equilibrium mineral compositions, thermodynamic data for reaction (3) may be used to estimate the P–T conditions of the staurolite isograd and to obtain maximum temperatures for the chloritoid–paragonite assemblages discussed previously.
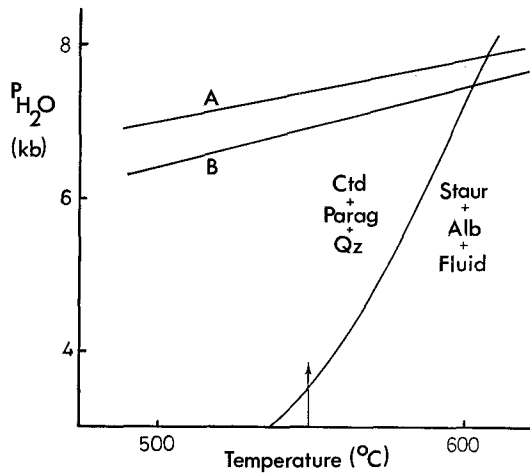
FIG. 3. Lines denoted A and B were calculated for two garnet–biotite–muscovite–plagioclase rocks from close to the staurolite isograd using data for equilibrium 6. Vertical arrow corresponds to paragonite solvus temperature just above the chloritoid isograd. The calculated breakdown of chloritoid+paragonite+quartz should take place at the staurolite isograd; the intersection of this curve with A and B gives for $P_{H_2O} = P_{total}$, pressure and temperature of crystallization at the point where staurolite appears.

The requisite thermodynamic data were obtained by combining information for the aluminosilicate polymorphs (Robie and Waldbaum, 1968) with enthalpy and entropy changes obtained from experimental studies of the two reactions

$$NaAl_3Si_3O_{10}(OH)_2 + SiO_2 \rightleftharpoons NaAlSi_3O_8 + Al_2SiO_5 + H_2O \quad \text{(from Chatterjee, 1972)} \quad (4)$$

$$\text{paragonite} \qquad \text{quartz} \qquad \text{albite} \qquad \begin{array}{c}\text{andalusite/}\\\text{kyanite}\end{array} \quad \text{fluid}$$

$$4FeAl_2SiO_5(OH)_2 + 5Al_2SiO_5 \rightleftharpoons 2Fe_2Al_9Si_4O_{23}(OH) + SiO_2 + 3H_2O \quad \text{(Richardson, 1968)} \quad (5)$$

$$\text{chloritoid} \qquad \text{sillimanite} \qquad \text{staurolite} \qquad \text{quartz} \quad \text{fluid}$$
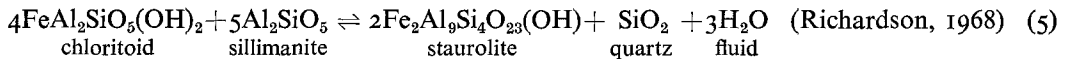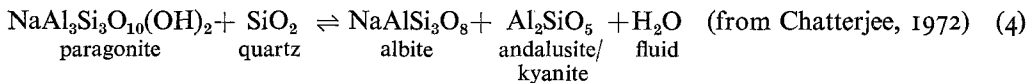
After having corrected for the appropriate Al_2SiO_5 polymorphs, combination of (4) and (5) yields values of $\Delta H^0_{1\,bar}$ and ΔS^0 for reaction (3) of $+185 \cdot 0$ kcal and 335 e.u. respectively. These data enable construction of an equilibrium curve for coexistence of the phases, all pure, associated with reaction (3). The appropriate curve, constructed for the condition of P_{H_2O} equal to P_{total} is shown in fig. 3. Assuming that the experimental results we have used are correct, the true position of this curve should be within ± 30 °C of that shown in the figure.

In order to apply equilibrium (3) to rocks it is, of course, necessary to take account of the presence of additional components in the natural multicomponent assemblages. We corrected

the curve shown in fig. 3 by taking analyses of mineral phases present in rocks close to the staurolite isograd and assuming that each mineral behaves as an ideal ionic solution. It was found, however, that the resultant shift in the curve for reaction (3) is only 5 °C; the correction was therefore ignored.

If metamorphic temperature is known from reaction (3), an approximate estimate of the pressure of crystallization close to the staurolite isograd may be obtained from the assemblage garnet–plagioclase–biotite–muscovite. For this assemblage one may use the equilibrium:

$$3CaAl_2Si_2O_8 + KMg_3AlSi_3O_{10}(OH)_2 \rightleftharpoons Ca_3Al_2Si_3O_{12} + Mg_3Al_2Si_3O_{12} + KAl_3Si_3O_{10}(OH)_2 \quad (6)$$

plagioclase   biotite   garnet   muscovite

Although there are no experimental data for reaction (6) we were able to obtain approximate values of the equilibrium constant from the work of Schmid and Wood (1976). These authors reported a pressure of 8·1 kb at 640 °C derived from a rock that contained the above minerals together with sillimanite and for which they were able to use the experimentally determined reaction:

$$3CaAl_2Si_2O_8 \rightleftharpoons Ca_3Al_2Si_3O_{12} + 2Al_2SiO_5 + SiO_2 \quad (7)$$

plagioclase   garnet   sillimanite   quartz

We calibrated (6) against (7) for the assemblage in question and made a small temperature extrapolation (assuming $dP/dT = 20·9$ bar deg^{-1}) so that it could be applied to appropriate Stonehaven rocks. Two rocks from close to the staurolite isograd gave the P–T curves (A and B) derived from equilibrium (6) that are shown in fig. 3. The intersection of A and B with the curve for reaction (3) gives (assuming $P_{H_2O} = P_{total}$) a pressure of about 7·5($\pm \sim 2$) kb and a temperature of 600 °C at the point where staurolite appears.

These results may be compared with the petrogenetic grid constructed by Harte (1975) for pelites from the eastern Dalradian by assuming that the rocks under consideration were metamorphosed at conditions close to the invariant point garnet–chlorite–chloritoid–biotite–staurolite–fluid. Harte's estimate of the position of this invariant point, about 6 kb and 600 °C ($P_{H_2O} = P_{total}$), is in good agreement with our calculations.

Conclusions. Paragonite may occur in the chloritoid schists of Stonehaven provided that the molar ratio Na/(Na+K) for the rock is greater than 0·33 and garnet and biotite are absent. The mineral has not, thus far, been found in Stonehaven rocks of lower than chloritoid grade. The composition of coexisting paragonite and muscovite from between chloritoid and staurolite isograds imply temperatures of 550 °C (paragonite limb of the solvus) or 690 °C (muscovite limb). The results obtained for paragonite agree better with temperatures obtained from other mineral equilibria than do those for muscovite. The physical conditions of metamorphism close to the staurolite isograd were (assuming $P_{H_2O} = P_{total}$) about 600 °C and 7·5 kb.

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