

# Stability of chlorite–quartz assemblages in rocks south and west of Keswick, Cumbria

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## Abstract

Chlorite minerals from six distinctive chlorite–quartz parageneses in central Borrowdale have been studied. All specimens were 14 Å (IIb) chlorites. Cell parameters and  $\beta$  refractive index exhibit an approximate linear dependence on composition for the range  $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.46$  to 0.84. The data indicate an apparent trend that chlorite iron content increases with temperature. This is in conflict with experimental studies (Flemming and Fawcett, 1976), and it is inferred that the observed compositional variations reflect the availability of iron in the veins rather than a dependence on temperature.

KEYWORDS: chlorite, chlorite–quartz parageneses, Keswick, Cumbria.

## Background to the paper

DR R. G. J. STRENS, former member of Council of the Mineralogical Society and Editorial Board of Physics and Chemistry of Minerals, died suddenly in 1980. A memorial is published in *American Mineralogist* 66, 1095–6 (1981). Some time after Dr Strens' death a partly drafted manuscript on chlorites from Borrowdale was found amongst his papers. This article is based largely upon the work of Dr Strens but it has been extended and updated by R.F. and R.J.F. Optical determinations, rock and mineral analyses were done by Dr Strens when he was a postgraduate student at Nottingham University. The methods used are described in his Ph.D. thesis (Strens, 1962). Hydrothermal experiments were performed by R.G.J.S. in 1979.

## Introduction

Experimental work on subsystems of the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  has often been hindered

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by the failure of structurally complex phases, including 14 Å chlorite and anthophyllite, to nucleate in the time available for reaction. The best approach to the problem of establishing the stability fields of phases in this system may thus lie in a combination of petrographic studies, which define equilibrium reactions and assemblages, experimental work on phase equilibria, which can provide accurate ( $P, T$ ) coordinates for the reactions, and thermodynamic calculations.

The occurrence in central Borrowdale (Strens, 1962, 1964, 1965) of six distinctive chlorite–quartz parageneses, formed over a wide ( $P, T$ ) range in rocks of well defined chemical composition provides an excellent opportunity of studying such experimentally intractable problems as the relative stability of 7 Å and 14 Å chlorites, the identity of the stable layer types, the effects of pressure and temperature on the range of stable compositions, and the status of phases (such as montmorillonite) which often appear in hydrothermal runs, but which are much less common in rocks.

The succession in the title area, Fig. 1, comprises

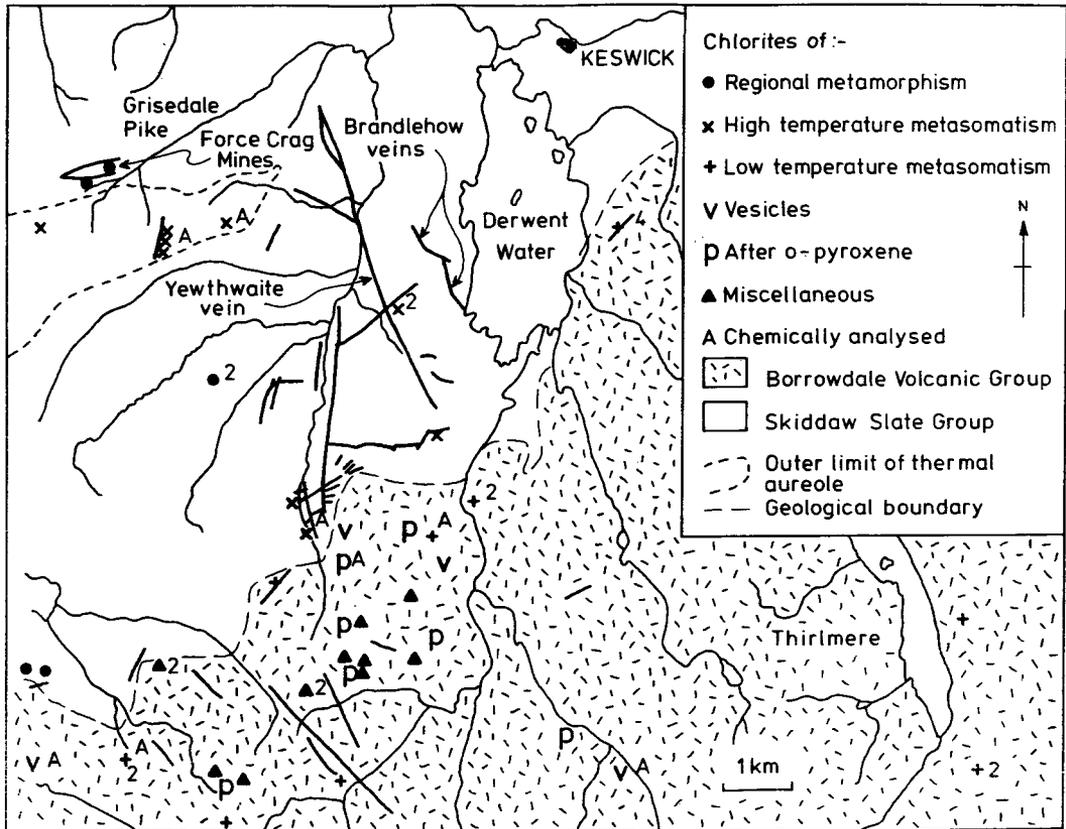


FIG. 1. Map showing the location and classification of the chlorite samples. The map was compiled by R. J. Firman from maps, data and grid references in Strens (1962). In addition to the locations shown, low-temperature metasomatic chlorites were also collected from the wall rock of the Yewthwaite (3 samples), Brandlehow and Force Crag veins and 4 samples from Grisedale, but references were not cited.

mudstones, siltstones and sandstones (Skiddaw Group) and the lower part of predominantly andesitic Llandelo volcanics (Borrowdale Volcanic Group) 1.3–3.0 km thick in the area mapped (Fig. 1). The Skiddaw Slates reacted under conditions of low grade regional metamorphism (see Bevens *et al.*, 1985, for discussion of low-grade metamorphism in the Lake District) to assemblages containing over 95% of chlorite, hydromuscovite and quartz. The Borrowdale Volcanics are considered to have suffered some contemporaneous alteration on extrusion and were thought by Strens (1962) to have been chemically little affected by the Caledonian regional metamorphism (but see Thomas *et al.*, 1985, for further discussion). Both rock types were cut and extensively chloritised by high-temperature copper and low-temperature lead-zinc veins, which structural evidence suggested were of late Caledonian and Hercynian ages respectively. The evidence for

these proposed ages was subsequently strengthened by K–Ar ages obtained by Ineson and Mitchell (1974) from wallrock alteration. The suggestion that the graphite and associated veins were pre-Bala (Strens, 1962, 1964, 1965) is less well supported and, in view of re-interpretation of pre-Bala structures (Soper and Moseley, 1978) and the K–Ar wall alteration dates (Ineson and Mitchell, 1975), is now suspect, a late Caledonian age being more likely (see also Stanley and Vaughan, 1982, for fuller discussion of the ages of mineralisation). The alteration mechanisms in the two rock types differed. Chloritisation of the basic members of the Borrowdale Volcanic Group involved the complete destruction of the early high-temperature assemblage (orthopyroxene + labradorite + magnetite ± garnet, clinopyroxene), and its replacement by chlorite, with loss of lime and alkalis (Strens, 1962), whilst the Skiddaw Slates were altered, possibly by

ion-exchange. This raises the possibility that the identity of the chlorite polytype which formed would be determined by a 'memory' of the pre-existing metamorphic chlorite which they replaced, rather than free energy considerations. Detailed studies of the veins (Strens, 1962) suggest that a dynamic equilibrium was established between the ore solutions and the wall rocks with components leached from the hot parts being redeposited in the cool extremities.

**Mineralogy and chemistry**

A total of 60 chlorite specimens were collected from the Borrowdale area. All were characterised optically in terms of colour,  $\beta$  refractive index, birefringence and pleochroism. For selected specimens partial analyses were obtained by wet chemical methods, densities were determined, cell parameters refined from powder X-ray diffraction photographs and infra-red absorption spectra were recorded. A number of host rocks were also analysed. Full details are given in Strens (1962) and are summarised below. Estimated pressures and temperatures of formation of the six chlorite-quartz paragenesis are given in Table 1 and partial bulk rock analyses are shown in Table 2.

**Optical properties**

Fig. 2 shows the dependence of the  $\beta$  refractive index on  $(Fe + Mn)/(Fe + Mn + Mg)$  ratio for some 10 of the 60 specimens collected in 1960. Despite the scatter there is satisfactory agreement with the relationships obtained by Hey (1954) for natural chlorites and McOnie *et al.* (1975) for synthetic chlorites. For convenience all 60 of the  $\beta$ - $\delta$  values are displayed (Fig. 3) on a 'composition grid' (after Hey, 1954). With the exception of chlorites from lead-zinc veins in the Borrowdales (in which the optics indicate that the  $Fe^{2+}/Fe^{3+}$  ratio varies considerably), the indices of each group cluster closely about the mean. Small variations correlate with the difference in the FeO/MgO ratio of the rock (Strens, 1962).

In both rock types there appears to be a tendency for the higher temperature chlorites to be richer in iron than the low-temperature chlorites. On a local scale, a systematic increase in iron content with increasing temperature of formation is confirmed by the steady reduction in  $\beta$ -index between the high- and low-temperature parts of wall rock adjacent to individual vein systems (Strens, 1962, 1965). This reduction occurs irrespective of the original composition of the wall rock.

TABLE 1 Chlorite - quartz paragenesis of central Borrowdale (Strens, 1962)

Rock Type	Origin	P(kb)	T(°C)	Samples	$\beta$	$\delta$	Composition
SKIDDAW GROUP	lead-zinc veins	(0.1)	(110-130)*	8	1.613±4	0.003±3	Fe <sub>4.9</sub> Mg <sub>5.6</sub> Al <sub>1.5</sub>
	regional metamorphism	2-3	(250-350)+	5	1.631±5	0.005±2	Fe <sub>6.4</sub> Mg <sub>4.0</sub> Al <sub>1.6</sub>
	copper veins	2-3	(200-350)*	10	1.652±6	0.007±2	Fe <sub>8.2</sub> Mg <sub>1.9</sub> Al <sub>1.9</sub>
BORROWDALE VOLCANIC GROUP	lead-zinc veins	(0.1)	(110-130)*	12	1.612±12	0.003±2	Fe <sub>4.8</sub> Mg <sub>5.7</sub> Al <sub>1.5</sub>
	deuteric alteration	(0.1)	(250-350)+	12	1.625±5	0.003±2	Fe <sub>5.7</sub> Mg <sub>4.5</sub> Al <sub>1.6</sub>
	copper, graphite veins	(1)† (2)	(200-350)*	13	1.642±8	0.003±2	Fe <sub>6.8</sub> Mg <sub>3.0</sub> Al <sub>2.2</sub>

Pressures are based on estimates of rock thicknesses and actual cover at the time of mineralisation.

† 1 kb if pre-Bala, 2 kb if Caledonian. \* According to Stanley and Vaughan (1982).

+ According to Thomas *et al.* (1985).

TABLE 2 Bulk Rock Compositions

	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	$\frac{Fe^{3+}}{\Sigma Fe}$	$\frac{Fe^{2+}}{Fe^{2+} + Mg}$	$\beta$
Skiddaw Group (a)	1.62	6.89	2.20	0.17	0.64	1.632 (c)
Borrowdale Volcanics (b)	2.50	5.01	3.41	0.31	0.45	1.625 (d)

a Average of 7 analyses (Strens, 1962)

b R.L. Oliver (1961) 76961/1

c Metamorphic chlorite

d Autometasomatic (deuteric) chlorite

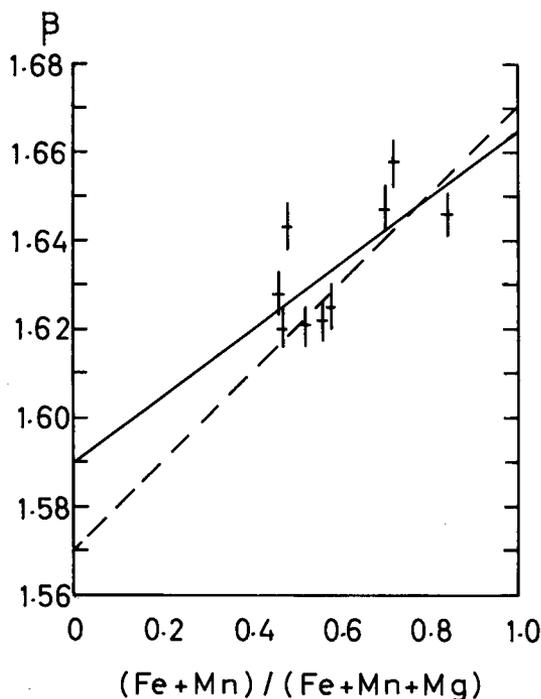


FIG. 2.  $\beta$  refractive indices as a function of composition for chlorites from the title area. The solid line represents a linear regression of the data. The broken line is based upon the relationship obtained by Hey (1954).

#### Layer type and unit cell parameters

Powder diffraction data were obtained for at least four samples from each of the groups listed in Table 1. All were 14 Å chlorite, indicating that the 7 Å chlorites which have often been produced in experimental work at low pressures and temperature (McOnie *et al.*, 1975; Flemming and Fawcett, 1976; Cho and Fawcett, 1986) are metastable over the composition and ( $P, T$ ) ranges represented in Borrowdale. Indeed the recent work of Cho and Fawcett (1986) confirmed that 7 Å chlorites can persist metastably for a very long time (e.g. over 72 days at 600 °C and 2 kbar). Similarly, the occurrence of montmorillonite in hydrothermal runs on magnesian chlorite compositions at temperatures below 450 °C contrasts with its absence from low-grade metamorphic rocks, pointing to metastable crystallisation. Within the limitations imposed on their identification by the use of powder diffraction photographs, all the natural chlorites studied were of the IIb layer type of Brown and Bailey (1962). Unit cell parameters exhibit a simple linear dependence on  $(\text{Fe} + \text{Mn})/(\text{Fe} + \text{Mn} + \text{Mg})$

ratio, as shown by the examples of  $b_0$  and volume in Fig. 4. The linear relationships may be described in terms of

$$b_0 = 9.193(\pm 0.032) + 0.174(\pm 0.050)X$$

$$v_0 = 695.4(\pm 4.6) + 19.5(\pm 7.2)X$$

where  $X = (\text{Fe} + \text{Mn})/(\text{Fe} + \text{Mn} + \text{Mg})$ . Although the small data populations only span a restricted range of composition, the regression parameters compare favourably with the values reported by McOnie *et al.* (1975) for synthetic chlorites extending from clinocllore to daphnite.

#### TX stability of 14 Å (FeMgAl) chlorite

Burnell and Rutherford (1984) noted that experiments on the stability of chlorite showed that, in the absence of other phases, the Fe-free Mg-chlorite is stable to higher grades than intermediate members of the solid-solution series. Furthermore, the addition of quartz to the system tends to restrict the stability range of both Fe- and Mg-chlorite (Fawcett and Yoder, 1966; James *et al.*, 1976; Chernosky, 1978). Attempts by Flemming and Fawcett (1976) to define the upper stability limit of chlorite + quartz at 2 kbar showed that it was virtually independent of Fe/Mg ratio and Al content in the chlorite. In contrast, Burnell and Rutherford (1984) concluded, from experimental studies, that in pelitic rocks containing excess muscovite and quartz, the chlorite of intermediate Fe/Mg ratios would persist to higher grades than the Fe and Mg end-members. These systems are not directly comparable, but in certain cases there appear to be distinct differences between the behaviour of the end-members and the intermediate members of the Fe-Mg chlorites.

In the present study field and laboratory evidence (Table 1) seems to indicate a slight trend of chlorite iron increasing with temperature. To test whether a stability maximum exists in the (FeMgAl) chlorite + quartz system a series of experimental runs was performed.

#### Experimental

As a preliminary survey of the problem, hydrothermal experiments were carried out at various ( $P, T$ ) in the Department of Earth Sciences, University of Cambridge, by R.G.J.S. in 1979. Mixtures of natural materials comprising 75% chlorite ( $\text{Fe}_{7.4}\text{Mg}_{2.6}\text{Al}_{2.0}$ ), 25% quartz, and a trace of anthophyllite seed (which acts as a nucleus for cumingtonite but is distinguishable from it) were sealed in 3 mm I.D. gold capsules and run in standard cold seal pressure vessels. The buffering provided was approximately nickel-nickel oxide.

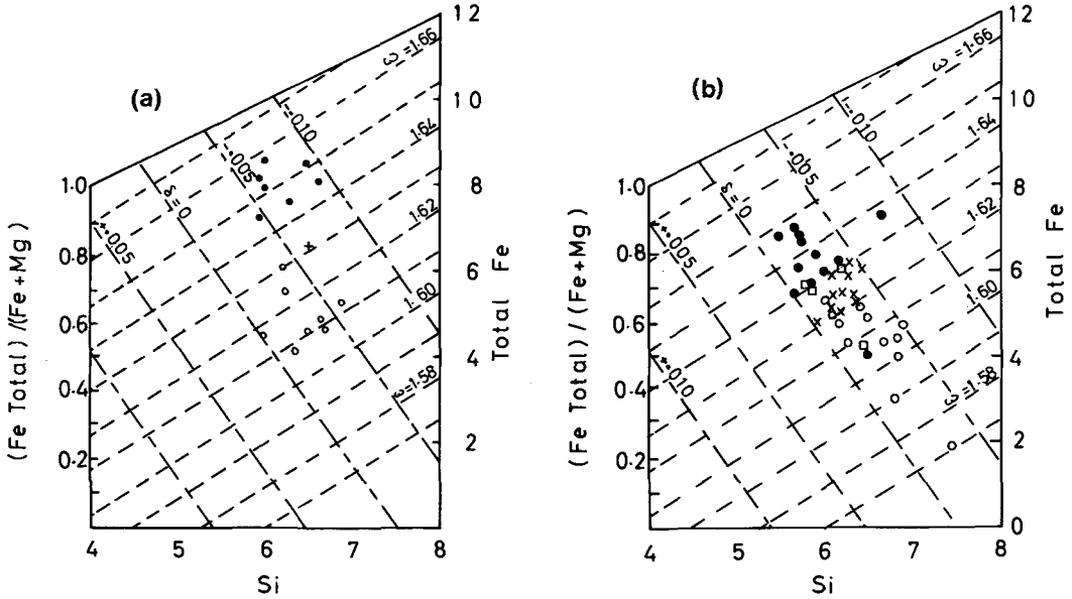


FIG. 3. Chlorites from central Borrowdale plotted in terms of their refractive index and birefringence on a composition grid (after Hey, 1954). (a) Chlorites from Skiddaw Group. Specimens of: regional metamorphism (+); high-temperature metasomatic origin (●); low-temperature metasomatic origin (○). (b) Chlorites from Borrowdale Volcanic Group. Specimens of: vesicles and after orthopyroxene (×); high-temperature metasomatic origin (●); low-temperature metasomatic origin (○); miscellaneous origin, mainly Longthwaite Group, (◻). Some data have been displaced slightly for clarity.

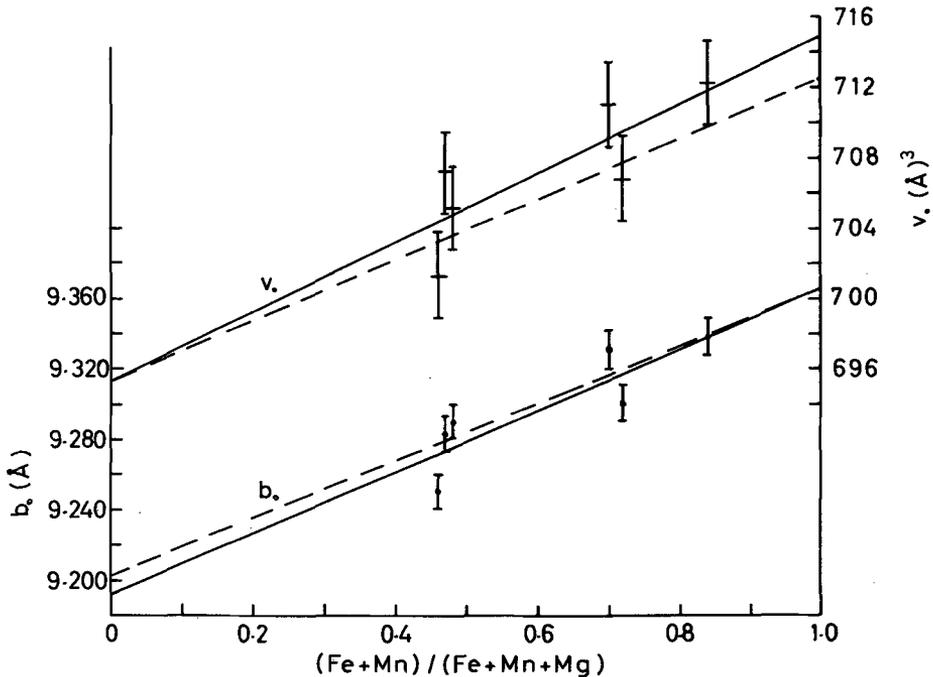


FIG. 4. Cell parameter ( $b_0$ ) and cell volume as a function of composition for chlorites from central Borrowdale. Solid lines indicate trends for these data, and broken lines the data of McOnie *et al.* (1975) for synthetic chlorites.

Pressures were controlled to  $\pm 50$  bars, and temperatures to  $\pm 4^\circ\text{C}$ .

In experiments of one month's duration at 2 kbar there were no reactions at 598 and 619°C, partial reaction at 635°C, and complete reaction to cordierite + cummingtonite at 660°C. On the basis of these data alone the stability limit for this intermediate chlorite appears to be  $627 \pm 10^\circ\text{C}$ . This is higher than the values reported for clinoclhire + quartz (582°C, Fawcett and Yoder 1966; 527°C, Chernosky, 1978), daphnite + quartz (600°C, Turnock 1960), and chlorite (of all Fe/Mg ratios) + quartz (595°C, Flemming and Fawcett, 1976). However, Fawcett (pers. comm., 1985) suggests that longer duration experiments would bring about a downward revision of the 627°C temperature to something closer to that of the 595°C determined by Flemming and Fawcett (1976). A detailed investigation of the problem would need to demonstrate reaction reversals. It is of interest to note that with starting materials of Fe-rich chlorite + muscovite + quartz, Burnell and Rutherford (1984) were able to achieve reversals of 600°C in times as short as 18 days, whilst in the system Fe-rich chlorite + quartz, Flemming and Fawcett (1976) employed run times up to 27 weeks to confirm reversals.

### Discussion and conclusions

If the preceding interpretations are correct, the stability field of 14 Å (Iib) chlorite with 1.5 to 2.5 Al in tetrahedral sites and 4–8 Fe per unit formula extends over the entire (*P, T*) range represented in the Borrowdale rocks. The montmorillonites and 7 Å chlorites which form and persist for long periods in hydrothermal experiments are thought to be metastable experimental products, the formation of which could presumably be suppressed by using mixtures of natural chlorite with its reaction products in place of glasses, gels, or mixed oxides (Fyfe, 1960; Cho and Fawcett, 1986).

Across the restricted composition range of total Fe/(Fe + Mg) = 0.46–0.84 for which optics and XRD data are available for Borrowdale chlorites, the  $\beta$  refractive indices and unit cell parameters vary approximately linearly with composition, in agreement with the data of McOnie *et al.* (1975) for synthetic chlorites.

From field, XRD and optical data there is an apparent trend that chlorite iron content increases with temperature. This is in conflict with the work of Flemming and Fawcett (1976) on the system synthetic chlorite + quartz, who found that at 2 kbar the upper stability limit was essentially independent of the Fe/Mg content of the chlorite. Complementary experimental studies using natural

chlorite from the title area proved inconclusive. In the absence of additional evidence it is inferred that the observed variation in chlorite iron (Table 1) possibly reflects the availability of iron in the veins rather than any temperature dependence. In fact the recent study of Cathelineau and Nieva (1985) suggests that the bulk composition of the rock could be the major control on Fe/Mg ratio in chlorite.

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