

Ireland. The chloritoids from the latter locality are very similar to those reported in this study although they are significantly coarser grained. Ottrelite was also reported in Upper Devonian epizone slates from S.W. England by Hutchings (1889), but electron microprobe analyses by Primmer (1984, 1986) have shown that this phase is, in fact, a near Mn-free chloritoid with < 1.1% MnO.

The chloritoid-bearing rocks reported here lie close to the upper anchizone–epizone boundary in Snowdonia as determined by Merriman and Roberts (1986) and Robinson and Bevins (1986) using illite crystallinity measurements and metabasite assemblages. It is possible that of all the occurrences of chloritoid reported in the literature, e.g. as summarized in Halferdahl (1961), Hoschek (1967), and Deer *et al.* (1982), this is one of the lowest grade occurrences to date.

KEYWORDS: chloritoid, pelitic rocks, Rhyd-Ddu, Gwynedd, Wales.

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[Manuscript received 2 April 1987;  
 revised 11 June 1987]

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MINERALOGICAL MAGAZINE, JUNE 1988, VOL. 52, PP. 396–9

## Al-chlorite as a hydration reaction product of andalusite: a new occurrence

MOST chlorites are trioctahedral, i.e. they are composed of two trioctahedral layers. Although the possible existence of di, dioctahedral chlorite, which consists of two dioctahedral layers, has been suggested by Brindley and Gillery (1961) and Grim (1964), the occurrence and chemistry of such chlorite is not well understood. We describe a new occurrence of a near-end-member di, dioctahedral Al-chlorite as a hydration reaction product of andalusite.

The altered andalusite is from the pegmatite at Szabo Bluff, Scott Glacier, Antarctica (86° 29' S, 144° 45' W) (Stump *et al.*, 1981). Andalusite occurs as columnar, radiating, reddish-brown crystals segregated in the interior zone of the pegmatite (Burt and Stump, 1984). In addition to andalusite, the interior zone is composed of K-feldspar, milky quartz, platy albite, tourmaline, muscovite, and ilmenite and other oxides.

Ion-thinned specimens were studied with a JEOL 200CX 200 kV transmission electron microscope (TEM) with a top-entry stage for high-resolution imaging and with a Philips 400T 120 kV TEM with a side-entry stage for analytical electron microscopy (AEM). The Philips 400T is equipped with a Gatan 607 electron energy-loss spectrometer and a Tracor Northern TN-2000 multichannel analyser for electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray analysis.

Optical-microscope observations indicate that andalusite is mainly altered to muscovite, primarily along irregular veinlets. Euhedral, dark-blue corundum occurs exclusively within muscovite aggregates, indicating that corundum is also produced by andalusite alteration. The occurrence of corundum is attributed to a local deficiency of silica in the fluid that caused the andalusite alteration (Rose, 1957; Burt and Stump, 1984).

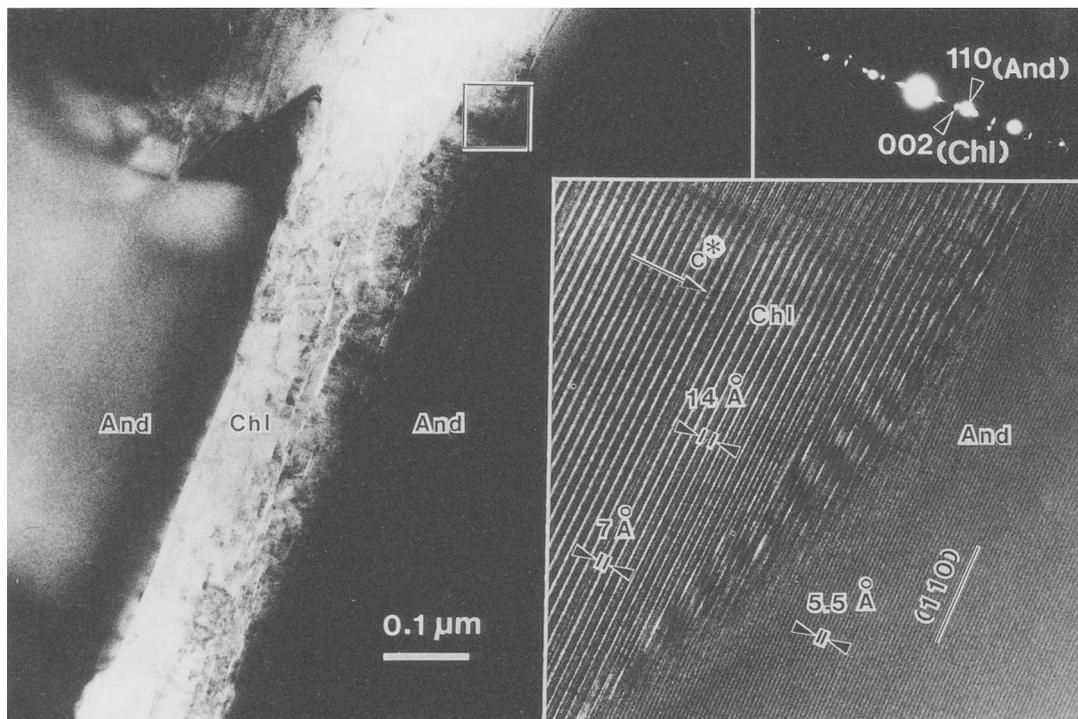


FIG. 1. TEM image of andalusite (And) partially replaced by Al-chlorite (Chl). The insets are an electron diffraction pattern and a high-magnification image of the interface between andalusite and Al-chlorite, which is indicated by a rectangle. (001) lattice fringes of Al-chlorite and (110) lattice fringes of andalusite are nearly parallel. Note that 7 Å layers are interlayered within 14 Å layers (Al-chlorite).

TEM observation reveals that most andalusite crystals were partly replaced by a chlorite occurring as 0.1 to 0.3  $\mu\text{m}$  thick lamellae intergrown within andalusite (Fig. 1). The boundaries between these two phases are irregular. However, electron diffraction patterns and TEM images show that {110} of andalusite and {001} of chlorite are parallel in many places where chlorite replaces andalusite (Fig. 1). Such replacement with preferential orientation may have been favoured as a result of the dominant {110} cleavage of andalusite.

Electron microprobe analysis of unaltered andalusite results in a chemical formula of  $\text{Al}_{1.99}\text{Fe}_{0.03}\text{Si}_{0.99}\text{O}_5$  (Table 1). The chlorite grains are too small for electron microprobe analysis, so AEM was used for chemical analysis. Al and Si are the only major cations, and they occur together with minor Fe. The elemental mole ratios of chlorite were determined by the thin-specimen analysis method (Cliff and Lorimer, 1970). Normalization of the Al, Si, and Fe mole ratios to  $\text{O}_{10}(\text{OH})_8$  anions results in the average chemical formula,  $\text{Al}_{4.32}\text{Fe}_{0.07}(\text{Si}_{2.83}\text{Al}_{1.17})\text{O}_{10}(\text{OH})_8$  (Table 1).

Diocahedral chlorites can be classified into di,triocahedral and di,diocahedral types (Eggleton and Bailey, 1967; Bailey *et al.*, 1979; Bailey, 1981) (Table 2). The former, which accounts for most diocahedral chlorite, consists of diocahedral 2:1 layers (pyrophyllite-like layers) and triocahedral interlayers (brucite-like layers). Therefore, in the strict sense, structural and chemical characteristics of di,triocahedral chlorite are intermediate between those of triocahedral and true diocahedral chlorite. In contrast, the di,diocahedral chlorite is composed of two diocahedral layers (pyrophyllite-like and gibbsite-like layers).

Brindley and Gillery (1961) suggested that chlorite with two diocahedral layers has the theoretical formula  $\text{Al}_{4+x/3}(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_8$ . The known occurrences of relatively pure Al-chlorite were limited to the hydrothermal ore veins of the Donetz Basin, USSR, and the name of donbassite has been used for them (Lazarenko, 1940). In addition, less well-crystallized hydrous minerals comparable to di,diocahedral chlorites occur as a component of mixed-layer clays and as a

**Table 1.** Andalusite and Al-chlorite analyses. Andalusite was analysed using the electron microprobe and chlorite was analysed using analytical electron microscopy.

|   | Andalusite <sup>1</sup> | Chlorite <sup>2,3</sup> |
|---|-------------------------|-------------------------|
| SiO <sub>2</sub>                            | 35.83                   | 32.23                   |
| Al <sub>2</sub> O <sub>3</sub>              | 61.18                   | 53.06                   |
| <sup>4</sup> Fe <sub>2</sub> O <sub>3</sub> | 1.50                    | 1.06                    |
| MgO   | 0.02                    | n.d.                    |
| TiO <sub>2</sub>                            | 0.06                    | n.d.                    |
| MnO <sub>2</sub>                            | 0.03                    | n.d.                    |
| <sup>5</sup> Cr <sub>2</sub> O <sub>3</sub> | 0.04                    | n.d.                    |
| <sup>5</sup> H <sub>2</sub> O               | n.d.                    | 13.65                   |
| <b>Total</b>                                | <b>98.66 wt%</b>        | <b>100.00 wt%</b>       |
| Si  | 0.99                    | 2.83                    |
| Al  | 1.99                    | (IV) 1.17<br>(VI) 4.32  |
| Fe <sup>+3</sup>                            | 0.03                    | 0.07                    |
| Mg  | 0.00                    | n.d.                    |
| Ti  | 0.00                    | n.d.                    |
| Mn  | 0.00                    | n.d.                    |
| Cr  | 0.00                    | n.d.                    |
| <b>Total</b>                                | <b>3.01</b>             | <b>8.39</b>             |
| Al/Si                                       | 2.01                    | 1.94                    |

1. Andalusite was normalized to five oxygens.
2. In AEM analysis, andalusite was used for obtaining proportionality constants ("k" factors) of Al and Fe relative to Si, based on the electron microprobe data of andalusite from the same specimen. The chlorite values represent an average of six analyses.
3. The elemental mole ratio of chlorite was normalized to anion O<sub>10</sub>(OH)<sub>8</sub>, and oxide weight percentages (wt%) were calculated from the resulting chemical formula.
4. All Fe was assumed to be ferric.
5. The H<sub>2</sub>O content of chlorite was calculated stoichiometrically.
6. n.d. = not determined.

mixture with other minerals (Eggleton and Bailey, 1967; Müller, 1967; Baylis and James, 1981).

The chlorite analysed in this study has an average of 4.32 total octahedral cations per formula unit, and it can be classified as donbassite, a di,dioctahedral chlorite (Bailey *et al.*, 1979; Bailey, 1981) (see Table 1). The minor Fe (<0.1 per formula unit) of Al-chlorite was apparently derived from the precursor andalusite, which contains a

similar small amount of Fe (Table 1). Minor Fe<sup>3+</sup> is common in andalusite as a result of substitution for Al (Deer *et al.*, 1982).

The possible presence of Li, which cannot be detected by energy-dispersive X-ray analysis, was checked by EELS. No Li was detected, excluding the possibility of this being a Li-chlorite such as cookeite, which occurs as a result of hydrothermal alteration in Li-bearing pegmatites (Černý, 1970). This lack of Li is consistent with the fact that no other Li-bearing minerals occur in this pegmatite (Burt and Stump, 1984).

Electron diffraction patterns of the di,dioctahedral Al-chlorite show streaking for reciprocal lattice rows with  $k \neq 3n$ , indicating that the stacking sequence of pyrophyllite-like and gibbsite-like layers is disordered by a shift of  $\pm b/3$  or by rotation of  $n(120)^\circ$ . Such semi-random stacking disorder is also common in trioctahedral chlorites (Brown and Bailey, 1962; Veblen, 1983; Spinnler *et al.*, 1984; Ahn and Peacor, 1985).

The Al/Si ratio of the Al-chlorite is approximately 1.94, which is similar to that of the andalusite ( $\approx 2.01$ ). This similarity, as well as replacement textures shown by TEM, indicate that alteration occurred through a hydration reaction and that the Al/Si ratio is nearly preserved. In places 7 Å layers are interlayered within Al-chlorite (Fig. 1). AEM examination of areas rich in 7 Å layers does not indicate an increased concentration of Mg or Fe, suggesting that the interlayered 7 Å layers are likely to be kaolinite rather than a serpentine-group mineral.

Although the stability relations of minerals in the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O have been extensively studied (Roy and Osborn, 1954; Zen, 1969; Holdaway, 1971; Hass and Holdaway, 1973; Day, 1976; Perkins *et al.*, 1979; Hemley *et al.*, 1980), the stability field of Al-chlorite was not determined.

**Table 2.** Schematic classification of chlorites\*

| Structural types  | Octahedral cations per O <sub>10</sub> (OH) <sub>8</sub> | Examples   |
|-------------------|--|--|
| Trioctahedral     | $\approx 6.0$  | clinochlore:<br>(Mg <sub>5</sub> Al)(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub><br><br>chamosite:<br>(Fe <sub>5</sub> Al)(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub> |
| Di, trioctahedral | $\approx 5.0$  | sudolite:<br>(Al <sub>3</sub> Mg <sub>2</sub> )(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub> \   |
|                   |  | cookeite:<br>(LiAl <sub>4</sub> )(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub>   |
| Di,dioctahedral   | 4.0 - 4.5  | donbassite:<br>Al <sub>4+x/3</sub> (Si <sub>4-x</sub> Al <sub>x</sub> )O <sub>10</sub> (OH) <sub>8</sub>   |

\* The classification scheme is based on that of Eggleton and Bailey (1967), Bailey *et al.* (1979), and Bailey (1981).

Al-chlorite presumably becomes unstable where K is present, and it may readily react to muscovite + corundum. These minerals are, in fact, the dominant alteration products of andalusite in the Szabo Bluff pegmatite. However, the possible presence of such Al-chlorite as a stable phase under appropriate conditions cannot be excluded.

Although andalusite is anhydrous, some published chemical analyses of andalusite indicate minor amounts of H<sub>2</sub>O (Simpson, 1931; Hietanen, 1956; Pearson and Shaw, 1960). In addition, infrared spectroscopy has also indicated the possible presence of OH in some andalusites (Beran and Zemmann, 1969; Wilkins and Sabine, 1973). The present study suggests that a partial hydration reaction of andalusite should be considered in interpreting the detection of H<sub>2</sub>O from andalusite, and the submicroscopic replacement by Al-chlorite may be widespread. Although the intergrowth of muscovite can be easily recognized by the detection of K, the presence of Al-chlorite in andalusite would be difficult to recognize from chemical analysis because the two minerals can have the same Al/Si ratio.

An implication of this study is that the andalusite polymorphs, sillimanite and kyanite, as well as topaz could also directly alter to Al-chlorite by hydration reactions, given a sufficiently alkali-free environment. This study suggests further investigation of these aluminous minerals and also the possible presence of Al-chlorite as a stable phase in the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O.

*Acknowledgements.* We are grateful to D. M. Burt for providing samples and valuable comments on the manuscript. We also thank B. Miner and J. H. Rask for assistance with the EELS measurements and J. C. Clark for microprobe analysis. This study was supported by NSF grant EAR-8408168, and electron microscopy was performed at the Facility for High Resolution Electron Microscopy in the Center for Solid State Science at Arizona State University.

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[Manuscript received 23 June 1987;  
 revised 10 August 1987]

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KEYWORDS: chlorite, andalusite, electron microscopy, Szabo Bluff, Antarctica.

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