

## Polytypism of cookeite in low-grade metapelites of the Cameros Basin, Spain: Lack of correlation of well-ordered polytypes with pressure

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### ABSTRACT

Cookeite occurs in low-grade, chloritoid-bearing metapelites of the Cameros Basin, northern Iberian Range, Spain, as thin coatings on poikiloblastic pyrite crystals <25 cm on edge. Textural relations imply formation via hydrothermal fluids in a syn- to late-regional metamorphic environment. Selected-area electron diffraction patterns of cookeite display a wide range of stacking order-disorder, from patterns with streaking parallel to  $c^*$  in  $k \neq 3n$  reflections to sharply defined reflections having one-, two-, and greater than two-layer periodicities. Well-ordered polytypes in crystals up to 0.1  $\mu\text{m}$  thick are of type *Ia*, as determined by powder X-ray diffraction. Coexisting chamosite likewise displays a range of order in polytypism from complete disorder to the well-ordered *I**b*** polytype which is typical of low-grade metamorphism.

Contrary to assertions that ordered cookeite polytypes are indicators of medium- to high-pressure metamorphism, the occurrence of ordered stacking sequences is direct evidence that, although ordered cookeite may occur in medium- to high-*P* environments, it is equally indicative of low-*P* environments. It can therefore not be used as an indicator of high pressure. The occurrence of several ordered and disordered polytypes in the same sample is compatible with the generally accepted notion that free-energy differences between polytypes are too small to be indicators of specific stable-equilibrium *P-T* conditions. The general occurrence of semirandom stacking is attributed to a lack of equilibrium in structure that is generally characteristic of phyllosilicates in low *P-T* environments of formation.

### INTRODUCTION

Jullien et al. (1996) correlated polytypism of cookeite from pegmatitic and metamorphic environments with increasing pressure. They tentatively suggested that cookeite polytypes may be organized into three classes as a function of pressure of formation: (1) semirandom stacking at low pressure, (2) increasing order of 1L and 2L types at medium pressure,  $5 < P < 10$  kbar, and (3) principally well-ordered 2L and 3L types coexisting with long-period polytypes (periodic stacking faults superimposed on ordered short-period repeats),  $P > 10$  kbar. Those relations imply that well-ordered polytypes of cookeite can be used as an indicator only of medium to high pressure.

Cookeite,  $(\text{Al}_4\text{Li}[\text{Si}_3\text{Al}]\text{O}_{10}(\text{OH})_8)$ , has been described as occurring in three very different environments: igneous, metamorphic, and hydrothermal. Cookeite is best known as occurring in pegmatites (Sahama et al. 1968; Černý 1970; Černý et al. 1971). Metamorphic cookeite has been considered as an index mineral in the Alpine domain of western Europe (Jullien et al. 1996, and references therein). Cookeite has also been described as a late mineral in low-temperature hydrothermal assemblages (Brammell et al. 1937; Shimada et al. 1985; Fischer et al. 1989; Ren et al. 1988; Miser and Milton 1964; Orliac et al. 1971). All of these occurrences imply a low-pressure origin for cookeite, but do not correlate formation conditions with type of polytypism.

Polytypism of trioctahedral chlorite (clinocllore-chamosite)

has been studied by Brown and Bailey (1962), Bailey (1969, 1988), Bailey and Lister (1989), and Schmidt and Livi (1999). It has also been used as an indicator of stability relations in low-grade metamorphic rocks (Hayes 1970; Walker 1989; Walker and Thompson 1990). Walker (1993) concluded that although type *II* chlorite is common in high-temperature rocks and type *Ib* in low-temperature assemblages, the former is also stable at  $<< 200$  °C, and the transition between *Ib* and *I**b*** polytypes cannot be considered as a geothermometer. Schmidt and Livi (1999) carried out a high-resolution transmission electron microscope (HRTEM) and selected-area electron diffraction (SAED) study of chlorite over the range from diagenesis to epizone and suggested that temperature is the most important factor affecting polytypism of chlorite. They concluded that *I**b*** polytypes and ordered stacking sequences occur in the epizone. The literature thus appears to show trends with respect to occurrence of chlorite polytypes as a function of temperature in low-grade metamorphic rocks, but no definitive relationship between *P-T* conditions and polytypism has yet been demonstrated.

Mata et al. (1991) described the occurrence of cookeite in the Cameros Basin, Spain, where it is associated with pyrite ore deposits in a very low-grade metamorphic environment. Mineral assemblages of the cookeite-bearing rocks resemble those described by Vrublevskaia et al. (1975), Jullien and Goffé (1993), Paradis et al. (1983), and Goffé et al. (1996), but the cookeite paragenesis is similar to those of the low-temperature hydrothermal sulfide deposits referred to above. This well-stud-

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ied environment, very low-grade regional metamorphism with overprinting via fluids, represents an ideal opportunity to correlate specific cookeite polytypes with qualitatively determined *P-T* conditions. We have therefore carried out a detailed study using SEM, EMPA, and TEM to determine the conditions of formation of cookeite, characterize polytypes, and thus correlate the state of polytypism with the conditions of formation.

### GEOLOGICAL SETTING

The Cameros Basin is comprised of an Upper Jurassic-Lower Cretaceous sequence, Kimmeridgian to Albian in age. These sediments, collectively termed "Wealdian," have a total thickness of about 9000 m. The structure is controlled both by Mesozoic extension (Guiraud and Séguret 1984 and Mata et al. 2001a) and early Cretaceous folding and Tertiary folding and thrusting (Casas-Sainz and Gil-Imaz 1998). The present-day northern border of the Cameros Massif is the E-W striking north-verging Cameros thrust over the Tertiary molasse of the Ebro Basin (Casas-Sainz 1993).

A thermal event, with an absolute age ranging between 86 and 108 Ma (Goldberg et al. 1988; Casquet et al. 1992), gave rise to a mineral assemblage of iron-rich chloritoid, muscovite, paragonite, iron-rich chlorite, and quartz in the deepest strata of the basin (Guiraud and Séguret 1984; Goldberg et al. 1988; Barrenechea et al. 1995; Mata et al. 2001a). *P-T* conditions were determined on the basis of mineral assemblages (Mata et al. 2001a), which suggest that a temperature of at least 350 °C was reached for strata buried at a minimum depth of 5600 m.

### MATERIALS AND METHODS

A preliminary study of cookeite in these rocks was carried out by Mata et al. (1991). They described it as a colorless sheet silicate that occurs as a thin coating on metamorphic pyrite crystals up to several cm in size. The cookeite of the Cameros basin was characterized by its negative elongation, 3.14 wt% Li<sub>2</sub>O content, *1a* polytypism, and X-ray diffraction (XRD) peaks. Powder XRD data included the values  $d(060) = 0.149$  to  $0.151$  nm, relatively small  $d(001)$  values, and large intensities for peaks with  $d = 0.23$  nm and  $0.426$  nm. These parameters are consistent with di-trioctahedral chlorite (Bailey and Lister 1989).

Representative samples of cookeite were selected from the Cidacos Valley (CV), Ambasaguas (AA), and Navajún (NJ). Samples from CV and AA are from pyrite quarries which are no longer active, whereas samples from NJ are from an active mine. The mineral assemblages of the pyrite-bearing rocks were determined by Mata et al. (1990, 2001a), Goldberg et al. (1988), Barrenechea et al. (1995), and Alonso-Azcárate et al. (1995, 1999). They are:

(1) quartz + chlorite + muscovite + paragonite + chloritoid ± calcite ± albite ± rectorite

(2) quartz + chlorite + muscovite ± paragonite ± pyrophyllite ± calcite ± albite ± rectorite

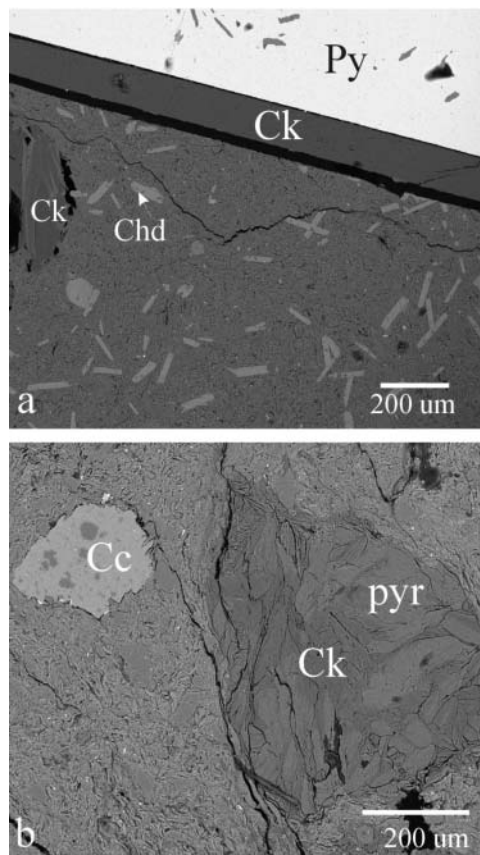
Mineral assemblage 1 is present in the deepest strata of the basin and can also be found in a NW-SE oriented area from CV to NJ. CV and NJ samples correspond to assemblage 1, and AA samples to assemblage 2.

Polished thin sections were prepared for both optical and scanning electron microscope (SEM) study using back-scattered electron (BSE) images and energy-dispersive spectral (EDS) analyses. Some images were obtained using the ion-milled surfaces of specimens prepared for scanning transmission electron microscope (STEM) study. SEM observations were made with a Hitachi S-3200N instrument fitted with a Noran microanalysis system at the University of Michigan. TEM samples were attached to areas where cookeite was detected by SEM. The TEM study was carried out with a Phillips CM12 instrument operated at 120 kV that was fitted with a KeveX Quantum detector for EDS analysis. Analyses were obtained in scanning mode over areas with a minimum size of 200 nm. Some observations were made with a Phillips CM20 TEM at the University of Granada. Standards and

conditions for STEM analysis were the same as those given by Jiang et al. (1990). Electron microprobe (EMP) analysis was performed with a CAMECA Camebax instrument at the University of Michigan.

### BSE OBSERVATIONS

Optical and BSE images show that cookeite occurs primarily as thin coatings on cubes and pyritohedra of pyrite up to 25 cm in size. The thickness of the coating is approximately proportional to the size of the pyrite crystals. Figure 1a shows a uniform cookeite coating on a pyrite crystal in a matrix of chamosite, muscovite, paragonite, quartz, and chloritoid. The pyrite crystals are poikiloblastic and have inclusions of chloritoid, chamosite, cookeite, muscovite, paragonite, berthierine, calcite, gypsum, anhydrite, monazite, and titanium oxide. Other minerals present in the coatings are quartz, barite, muscovite, pyrophyllite, kaolinite, and gypsum, the latter as a probable weathering product of pyrite. Cookeite also occurs in calcite-rich nodules finely intergrown with chamosite (NJ and CV samples), pyrophyllite (AA samples), or muscovite (all samples) (Fig. 1b). Other accessory minerals included in the nodules are anhydrite and amphibole crystals less than 5 μm in size, for which EDS analyses indicate the species edenite.



**FIGURE 1.** BSE images of polished thin sections. (a) Large pyrite crystal from NJ coated with cookeite. Chloritoid crystals occur in the matrix. (b) BSE image of cookeite and pyrophyllite intergrown in nodules of the matrix of an AA sample. Ck = cookeite, Chd = Chloritoid, Py = Pyrite, Cc = Calcite, and Pyr = pyrophyllite.

Chamosite crystals are included within cookeite, implying that it formed first. The poikiloblastic pyrite crystals include or have sharp contacts with chamosite (or pyrophyllite)-containing carbonate nodules and the fine-grained rock matrix. This implies that pyrite and cookeite formed subsequent to minerals in nodules and matrix.

### TEM STUDY OF COOKEITE

TEM images show that cookeite occurs in large crystals ( $<2\ \mu\text{m}$  thick), some of which are relatively free of defects and others which are strained with variable proportions of stacking faults and high-angle boundaries. Thick ( $>0.5\ \mu\text{m}$ ), defect-free crystals with straight layers are common. Figure 2 shows a typical lattice-fringe image of a 625 nm thick cookeite crystal comprised of straight and parallel 1.4 nm layers. Thick layer sequences are comprised of units 50 to 300 layers thick which are twinned by rotation about [001]. Packets (up to 100 nm thick) of cookeite occur with kaolinite, muscovite, paragonite, chamosite, berthierine, and pyrophyllite. No lateral transitions were observed between cookeite and kaolinite. Saliotite (mixed-layered cookeite-paragonite) with periodicities  $<2.4\ \text{nm}$  (Goffé et al. 1994) was observed intergrown with large areas of rectorite in NJ and AA samples (Mata et al. 2001b).

### SELECTED AREA ELECTRON DIFFRACTION DATA

Figures 3a to e show [100] SAED patterns of chamosite and cookeite. SAED patterns of chamosite (Figs. 3a and 3b) display features varying from streaking parallel to  $c^*$  in  $k \neq 3n$  reflections (Fig. 3a), to sharply defined reflections having one-layer periodicities (Fig. 3b). Streaking parallel to  $c^*$  in  $k \neq 3n$  reflections is very common, mainly in diagenetic and anchizonal chlorite, whereas sharply defined reflections with  $k \neq 3n$  have only been found in epizonal chlorite (Schmidt and Livi

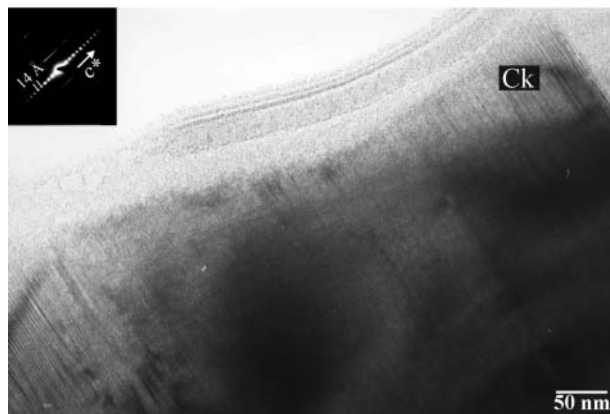


FIGURE 2. TEM image of a defect-free cookeite crystal. Inset: SAED pattern of cookeite.

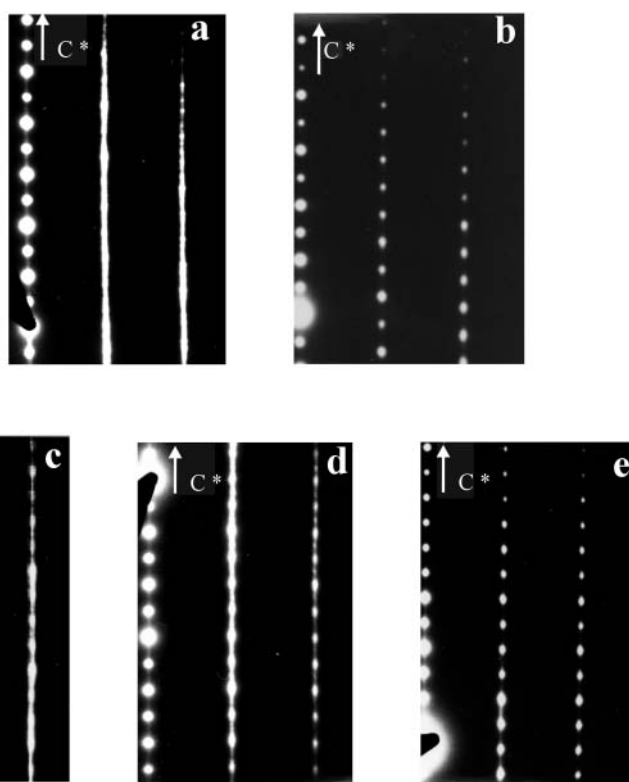


FIGURE 3. Representative [100] SAED patterns of chlorite (a, b) and cookeite (c, d, e). [100] SAED patterns of chamosite varying with streaking parallel to  $c^*$  in  $k \neq 3n$  reflections (a) to sharply defined reflections having one layer periodicities (b). SAED patterns of cookeite displaying a wide range of stacking order-disorder, varying from streaking parallel to  $c^*$  in  $k \neq 3n$  reflections (a), similar to a, to sharply defined reflections having one layer periodicity (e), similar to b.

1999). Where berthierine occurs interstratified with chamosite, streaking occurs along  $c^*$ , and 001 reflections with  $l = 2n + 1$  are weak and diffuse, as typical of randomly interstratified 1.4 and 0.7 nm layers.

SAED patterns of cookeite display features representing a wide range of stacking order-disorder even in the same sample. In all of the studied samples, SAED patterns of cookeite vary from having streaking parallel to  $c^*$  in  $k \neq 3n$  reflections (Fig. 3c) to sharply defined reflections. Many of the studied crystals seem to have little disorder, as indicated by weak streaks between  $k \neq 3n$  reflections. One-layer periodicity (Fig. 3c) is the most common kind in well-ordered crystals. Two-layer periodicity was detected in some patterns with streaking in  $k \neq 3n$  reflections. Long-period or complex stacking sequences, as described by Jullien et al. (1996) for high-grade metamorphic cookeites, were not detected in this study. Both chamosite and cookeite have the same kinds of stacking sequences in the same samples, from almost fully disordered with heavy streaking to ordered with sharply defined reflections.

### CHEMICAL COMPOSITION OF COOKEITE

The chemical compositions of cookeite crystals were obtained by EMP and EDS analysis. Table 1 shows the results of the EMP

**TABLE 1.** Electron microprobe analysis and structural formulae of cookeite

	1	2	3	4	5	6	*
SiO <sub>2</sub>	37.62	36.26	36.38	38.80	39.35	35.45	38.95
Al <sub>2</sub> O <sub>3</sub>	46.49	46.88	46.83	46.70	45.61	48.35	44.38
FeO	0.58	0.31	0.00	0.20	0.00	0.00	0.64
MgO	0.31	0.12	0.07	0.38	0.41	0.94	0.26
MnO	0.02	0.08	0.00	0.00	0.00	0.00	n.d.
K <sub>2</sub> O	0.00	0.02	0.01	0.02	0.02	0.00	0.29
CaO	0.10	0.03	0.03	0.22	0.09	0.08	0.21
Na <sub>2</sub> O	0.02	0.01	0.02	0.03	0.18	0.00	0.20
F	0.00	0.00	0.00	0.00	0.00	0.00	n.d.
Li <sub>2</sub> O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.14
Total	85.13	83.69	83.35	86.37	85.656	84.826	85.27
	1	2	3	4	5	6	*
Si	6.41	6.28	6.31	6.50	6.63	6.06	6.48
Al	1.59	1.72	1.69	1.50	1.37	1.94	1.52
Al(VI)	7.74	7.84	7.88	7.72	7.69	7.81	7.18
Fe	0.08	0.04	0.00	0.03	0.00	0.00	0.08
Mg	0.08	0.03	0.02	0.10	0.10	0.24	0.06
Mn	0.00	0.01	0.00	0.00	0.00	0.00	0.00
K	0.00	0.01	0.00	0.00	0.00	0.00	0.03
Ca	0.02	0.00	0.01	0.04	0.02	0.02	0.04
Na	0.01	0.00	0.01	0.01	0.06	0.00	0.06
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Li							1.44

Notes: The structural formulae were calculated on the basis of 13.5 O atoms without taking into account Li<sub>2</sub>O content. n.d. = not determined.

\* Chemical analysis of separated crystals by X-ray fluorescence and atomic absorption for Li<sub>2</sub>O content (Mata et al. 1991).

and EDS analyses. At the  $\mu\text{m}$  resolution scale of EMPA and SEM cookeite appears to be homogeneous; small variations in Na, K, and Ca contents and the Si/Al ratio are ascribed to contamination with paragonite, muscovite, pyrophyllite, kaolinite, and quartz as demonstrated by the BSE and TEM images. The apparent Fe content is likewise explained by contamination by berthierine and chamosite. The Li<sub>2</sub>O content (3.14 wt%) of separated crystals corresponds precisely with that of ideal cookeite (Mata et al. 1991).

## DISCUSSION

### Origin of cookeite in metapelites of the Cameros Basin

The samples described here correspond to a maximum temperature of 350 °C in the deepest strata within the basin (5600 m), and lithostatic pressure, corresponding to a depth of burial of <6 km, was <2 kbar, as corroborated by the mineral assemblages (Mata et al. 2001a).

Although pyrite is widespread in the Cameros rocks as small crystals, only in the described sites does it occur so abundantly as to serve as an ore (Alonso-Azcárate et al. 1999). Rectorite and kaolinite, which generally occur at significantly lower *P-T* conditions than those minerals corresponding to metamorphism of the deepest strata within the basin, occur only in close association with pyrite. These pyrite crystals, with which cookeite is clearly cogenetic, truncate metamorphic textures, and chloritoid crystals are included in the poikiloblastic pyrite crystals. Textural relations imply that cookeite and pyrite formed subsequent to chamosite and chloritoid, the latter two minerals being typical of an epizonal metamorphic assemblage. Alonso Azcárate et al. (1999) implied a hydrothermal origin of pyrite at *T* < 350 °C and *P* < 2 kbar.

The textural features involving cookeite, as observed by TEM, also support a post-metamorphic origin. Cookeite occurs as thick (up to 0.5  $\mu\text{m}$ ) defect-free crystals associated with dis-

crete packets of chamosite, berthierine, kaolinite, and paragonite and extensive areas of rectorite and saliotite. The assemblage with quartz, rectorite, and cookeite was also found by Miser and Milton (1964) and Orliac et al. (1971) in shales. Cookeite was also found with sulfides by Shimada et al. (1985), Brammall et al. (1937), Fischer et al. (1989), and Ren et al. (1988). In those studies cookeite occurred as films or filling veins and vugs in low-temperature, hydrothermal-alteration assemblages, many of them with pyrite. Those assemblages had not been affected by subsequent metamorphic events, some corresponding to anchizonal conditions (Merriman, pers. comm.). Although cookeite has been described by many authors as a common low-temperature metamorphic mineral (Jullien et al. 1996 and references therein), it must also be considered to be typical of hydrothermal alteration of pelitic rocks in association with sulfide or quartz veins. The conditions described above are in accord with the stability field of cookeite proposed by Vidal and Goffé (1991). They studied the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Li<sub>2</sub>O-H<sub>2</sub>O and defined a *P-T* field for cookeite and quartz between 260–480 °C, from low-pressure regimes to high-pressure conditions, in water-saturated systems.

### Petrological significance of stacking sequences in cookeite

Jullien et al. (1996) observed that pegmatitic and low-temperature greenschist-facies cookeite gives SAED patterns with highly disordered stacking sequences, metabauxites of the Ligurian Alps subjected to 10 kbar pressure (blueschist facies) give one- or two-layer perfectly ordered polytypes, and high-pressure metapelites from blueschist facies rocks give disordered two-layer polytypes. They concluded that pressure is the principal factor that affected stacking sequences in the samples studied.

Cookeite from the Cameros Basin exhibits a wide range of stacking order-disorder, with SAED patterns having features varying from streaking parallel to *c*\* in *k*  $\neq$  3*n* reflections to sharp reflections having one- or two-layer periodicity (Fig. 3).

The most common ordered sequence has one-layer periodicity, whereas where two-layer periodicity was observed, the sharp reflections were invariably superimposed on streaks parallel to *c*\*. Coexisting chamosite exhibits similar features. This is in accord with the powder XRD data of Mata et al. (1991), who concluded on the basis of characteristic powder XRD lines as described by Brown and Bailey (1962) that ordered polytypes are *Ia* for cookeite and *I**b*** for chamosite. Those conclusions relate to averages based on many crystals for which the two-layer polytypism of cookeite would be a minor component, rather than being for individual crystals as determined by SAED.

The data of this study therefore show that the ordered polytypes of chlorite occur in low-pressure rocks, which formed at grades below that of the greenschist facies, with the exception of long-period polytypes, which were found by Jullien et al. (1996) to correlate with medium to high pressure. In particular, the coexistence of domains in the same sample with semirandom order and well-ordered short-period polytypes correlates with the type of polytypism typical of the medium pressure range ( $5 < P < 10$  kbar) as defined by Jullien et al. (1996). The state of polytypism of cookeite can not therefore be used as a direct indicator of the magnitude of pressure. The collective data of Jullien et al. (1996) and this study do not imply that specific polytypes of cookeite cannot form at high pressure, but only

that their occurrence is not constrained by it.

There is a long history of attempts to correlate polytypism in trioctahedral chlorites, as determined largely by powder XRD, with temperature and pressure in a variety of environments (Walker 1993, and references therein). Type *II* chlorite coexists with dioctahedral mica over the entire range of grade spanned by the sequence of  $1M_d$  polytypism to the  $2M_1$  polytype, so it cannot be used as a geothermometer in low-grade metasediments. Walker concluded that many different factors can affect the presence of types of chlorite polytypes, including rock type and composition, and that transformations involving dissolution/recrystallization are determined by kinetic factors rather than stable equilibrium. In a recent HRTEM-SAED study, Schmidt and Livi (1999) found that disordered sequences are most common in trioctahedral chlorite of low-grade rocks of the Taveyanne sandstone ( $T = 210\text{--}250^\circ\text{C}$ ) and that both types of polytypes (*Ibb-Ibb*) can coexist. Nevertheless, in epizonal samples no streaking was observed in SAED patterns, and the *Ibb* polytype was the common one. They suggested that compositional variations and pressure are not significant in chlorite polytypism, temperature being the most important factor for trioctahedral chlorite. Merriman and Peacor (1999) have pointed out that disordered sequences are commonly the result of formation at low temperatures which favor a lack of approach to the state of ordered, stable equilibrium. For example, muscovite which forms in very low-grade shales almost invariably displays  $1M_d$  polytypism, whereas that which forms at higher grades is ubiquitously well ordered, usually as the  $2M_1$  or  $3T$  polytype. The disordered state of low-temperature samples simply reflects an inability to achieve equilibrium rather than implying an equilibrium state. That is, samples are invariably well ordered at high grades, but may be either ordered or disordered at low grades.

Several of the authors of the above papers and references suggested that polytypism can be related to several factors, including temperature, pressure, composition, crystal-growth mechanism, and deformational history. Verma and Krishna (1966) reviewed the factors affecting polytypism, noting that the differences in free energies are generally so small that small changes in any of a large number of variables may affect polytypic state. This is mitigated, to a limited degree, by the fact that the detailed structures of so-called polytypes of layer silicates such as mica and chlorite are not polytypes, *sensu strictu*, because there are small differences in atomic coordinates between repeating units except where they are related by symmetry. In addition, different polytypes may have slightly different compositions, for which Bailey (1984) suggested the term polytypoid. Nevertheless, repeating structure units of phases referred to as polytypes are identical to a first approximation.

The collective data therefore show that polytypic state is not useful either as a geothermometer or geobarometer because many factors can affect the relative stability of different polytypes. In particular, low-grade formation favors disorder, but does not require it, nor does such disorder reflect an equilibrium state. In general, free-energy differences between polytypes are so small as to be influenced by a large number of variables, no single variable having large enough influence to be used as an indicator of variables controlling stable equilibrium. In particular, the occurrence of well-ordered stacking sequences

in the low-pressure rocks of this study is direct evidence that, although ordered cookeite may occur in high-pressure facies, and even be favored by such conditions, it is equally indicative of low-pressure environments. It cannot therefore be used as an indicator of high pressure.

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