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CHLORITE GEOTHERMOMETRY?—CONTAMINATION AND APPARENT OCTAHEDRAL VACANCIES

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Abstract—The large contents of octahedral vacancies in published formulae of chlorite from hydrothermal systems and clastic sequences are shown to be largely caused by inclusion of other minerals. Verification is provided by analytical electron microscope (AEM) analyses of chlorite in pelitic rocks from the Gaspé Peninsula, Quebec and the Gulf Coast, Texas. The Gaspé chlorite occurs as discrete crystals locally coexisting with corrensite, and the Gulf Coast chlorite is free of mixed layers other than local serpentine-like 7-Å layers. Unlike most electron microprobe analyses (EMPA), but like other AEM analyses, the reported chlorite formulae do not have significant octahedral vacancies, are not Si-rich and (Fe + Mg)-poor relative to classic metamorphic chlorite, and have nearly equal amounts of tetrahedral and octahedral Al. The studied chlorites and those in metabasites and clastic rocks that could be positively identified as containing no or minimal mixed layering or submicroscopic intergrowths have little or no Ca or alkalis. In contrast, EMPA of chlorite reported for other clastic sequences show variable amounts of Na + K + 2Ca that exhibit a poorly defined positive correlation with the proportion of octahedral vacancies. The EMPA of chlorite from the Salton Sea and Los Azufres geothermal fields that were suggested to contain temperature-dependent amounts of tetrahedral Al (and thus used as "chlorite geothermometers") show compositional characteristics similar to those reported for several saponite-chlorite transition series in metabasites.

Continuous increases in octahedral occupancy and tetrahedral Al with increasing metamorphic grade are attributed to decreases in abundance of mixed layers or fine-grained intergrown minerals that commonly occur as a result of increasing crystal size and homogeneity in prograde sequences. Use of "chlorite geothermometry" based on the proportion of apparent octahedral vacancies or tetrahedral Al is therefore unwarranted and leads to inaccurate temperature estimates.

Key Words—Analytical electron microscopy, Chlorite, Chlorite geothermometry.

INTRODUCTION

Trioctahedral chlorite is one of the most common minerals in diagenetic, low-grade metamorphic, and hydrothermally altered rocks. Variations in its composition may reflect changes in physical conditions and fluid chemistry among other variables. The characteristics of chlorite are therefore of great interest in studies of regional patterns and reaction mechanisms of alteration processes, petroleum production and migration, and ore-forming processes, particularly those involving fluid mixing and temperature-related variations.

Among several potential chlorite geothermometers, that using the tetrahedral Al content of trioctahedral chlorite has been increasingly used in low-grade regimes in recent years (Cathelineau 1988; Bevins *et al* 1991). However, chemical analysis of phyllosilicates in low-grade rocks is fraught with difficulty because of the small grain sizes, mixed layering, and complex intergrowths that exist at scales beyond the resolution limits of the electron microprobe and conventional analytical techniques (Peacor 1992; Warren and Ransom 1992). Major contamination of an analysis is usually easily detected. However, small numbers of mixed layers result in subtle changes in composition of an otherwise apparently homogeneous material that may be interpreted as caused by solid solution, including defects. Such confusion is especially likely where there is contamination by minerals that have similar formulae. Such subtle contamination may therefore lead to errors of interpretation where analytical data are interpreted to the limits of their accuracy.

Our attention was drawn to problems involving analyses of chlorite because of several reasons: (1) In some cases where electron microprobe analyses (EMPA) indicated the presence of octahedral vacancies, analyses by analytical electron microscopy (AEM) showed the presence of contamination resulting in large part from mixed layering at a scale not detectable by optical and scanning electron microscopy. (2) The work of Shau *et al* (1990) showed a direct relation between composition (vacancies, relative amounts of tetrahedral and octahedral Al, presence of Na, K, and Ca) and proportions of mixed layers, with effects on formulae of the kind common in the literature. (3) AEM analyses on areas shown by transmission electron microscopy (TEM) to be pure chlorite almost invariably normalize, within error, to vacancy-free formulae. (4) Reinspection of a carefully selected set of chlorite analyses (Foster 1962) that are commonly used as evidence for the probable

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existence of abundant octahedral vacancies showed that substantial impurities could have been included. (5) Structure analyses of trioctahedral chlorite are consistent with small proportions or a lack of octahedral vacancies (Zheng and Bailey 1989).

Previous studies have focused on discussions of the relation between geological variables such as temperature and composition of chlorite, rather than on the significant impact of contamination of analyses by mineral mixtures. We were therefore concerned that analyses of low-grade chlorite have been portrayed in a way exceeding their merits. Examination of EMPA for low-grade chlorite present in the literature generally confirms the occurrence of analytical contamination, a conclusion arrived at using AEM data. Although that relation was compelling, we have further verified it by obtaining new AEM analyses of chlorite occurring in pelitic rocks from the Gaspé Peninsula, Quebec and Texas Gulf Coast. The samples from the Gaspé Peninsula vary in grade from the zone of diagenesis through the epizone. Analyses of chlorite from the Texas Gulf Coast were obtained for direct comparison with EMPA data of Hillier and Velde (1991) for samples from the same region. The new data have been collated with analyses of chlorite from other localities, verifying that proportions of octahedral vacancies in chlorite, *sensu stricto,* are minimal in extent and implying that the so-called chlorite geothermeters based on them are invalid.

Background to the "chlorite geothermometer"

Foster (1962) suggested that the proportion of octahedral vacancies in trioctahedral chlorite increases as the number of octahedral trivalent and quadrivalent cations in excess of tetrahedral trivalent cations increases, as required for charge balance. That conclusion was based on 154 selected wet chemical analyses of metamorphic and hydrothermal chlorite. Subsequently, many EMPA of trioctahedral chlorite from clastic sedimentary rocks and hydrothermally altered rocks have also been reported to have significant proportions of octahedral vacancies that are directly correlated with tetrahedral Al content. The correlations were based on normalization to the ideal anion content, $O_{20}(OH)_{16}$ (McDowell and Elders 1980; Cavarretta *et al* 1982; Cathelineau and Nieva 1985; Humphreys *et al* 1989; Gustin 1990; Hillier and Velde 1991).

McDowell and Elders (1980) analyzed chlorite in sandstones from borehole Elmore No. 1 of the Salton Sea geothermal system using EMPA techniques and showed a systematic decrease in the proportion of octahedral vacancies and increase in Mg + Fe contents with increasing temperature. Such variations in composition were used to estimate alteration temperatures in the Larderello-Travale geothermal field (Cavarretta *et al* 1982). Subsequently, Cathelineau and Nieva (1985) proposed a chlorite "geothermometer" that is a function of tetrahedral Al content; it is based on the empirical correlation of observed well temperatures and EMPA of chlorite in hydrothermally altered andesites from the Los Azufres geothermal field. Cathelineau and Nieva noted that the tetrahedral Al content is negatively correlated with the number of octahedral vacancies and increases with increasing temperature. Cathelineau (1988) used the analyses of Cathelineau and Nieva (1985) and McDowell and Elders (1980) to conclude that the tetrahedral Al content of chlorite is a function of temperature, independent of lithology and fluid composition. This apparent temperature-dependent chemical variation was attributed to increasing amounts of dioctahedral components in chlorite solid solutions formed at lower temperatures (Cathelineau 1988). Kranidiotis and MacLean (1987) showed a similar result for chlorite from a hydrothermal rhyolitic massive sulfide deposit, but they modified the correlation line in the tetrahedral Al versus temperature diagram of Cathelineau and Nieva (1985) to correct for possible influences of bulk-rock compositions.

Other researchers cautioned against the use of such a "geothermometer" because of the uncertain effects of variables such as bulk-rock and fluid compositions, coexisting mineral assemblages, fO_2, mineral growth rates and times, and possible contamination by associated phases (Shau *et al* 1990; Hillier and Velde 1991; Jahren 1991; Velde *et al* 1991; Jahren and Aagaard 1992; de Caritat *et al* 1993). Using the correlation equation of Cathelineau (1988), de Caritat *et al* (1993) showed that the chlorite tetrahedral Al "geothermometer" overestimated the temperatures of formation of chlorite in several rock sequences by 75 to 215°C. They suggested that the non-stoichiometric trioctahedral chlorite is a metastable phase whose composition was strongly affected by factors other than temperature. Shau *et al* (1990) showed that the apparent proportions of octahedral vacancies in chlorites from metabasites were directly correlated with the degree of mixed layering with corrensite. They noted that their observations appeared to be typical of analyses of so-called chlorite from low-temperature environments.

SAMPLES AND METHODS

Two series of rocks were used in this study. The first includes five pelitic rocks (A419, A416, R299, 89-12, and R245) as part of a prograde sequence ranging from the diagenetic zone to the epizone (illite crystallinity indices = 0.19–0.58° $\Delta 2\theta$ for ethylene glycol solvated <2 μm fractions) in the Gaspé Peninsula, Quebec (Jiang and Peacor 1994). The diagenetic rocks (samples A419 and A416) contain discrete chlorite, and corrensite and illite that locally occur as intimate intergrowths with chlorite (Figure 1a). The higher grade chlorite is coarser grained and has relatively well-defined crystal boundaries but forms complex intergrowths with muscovite,

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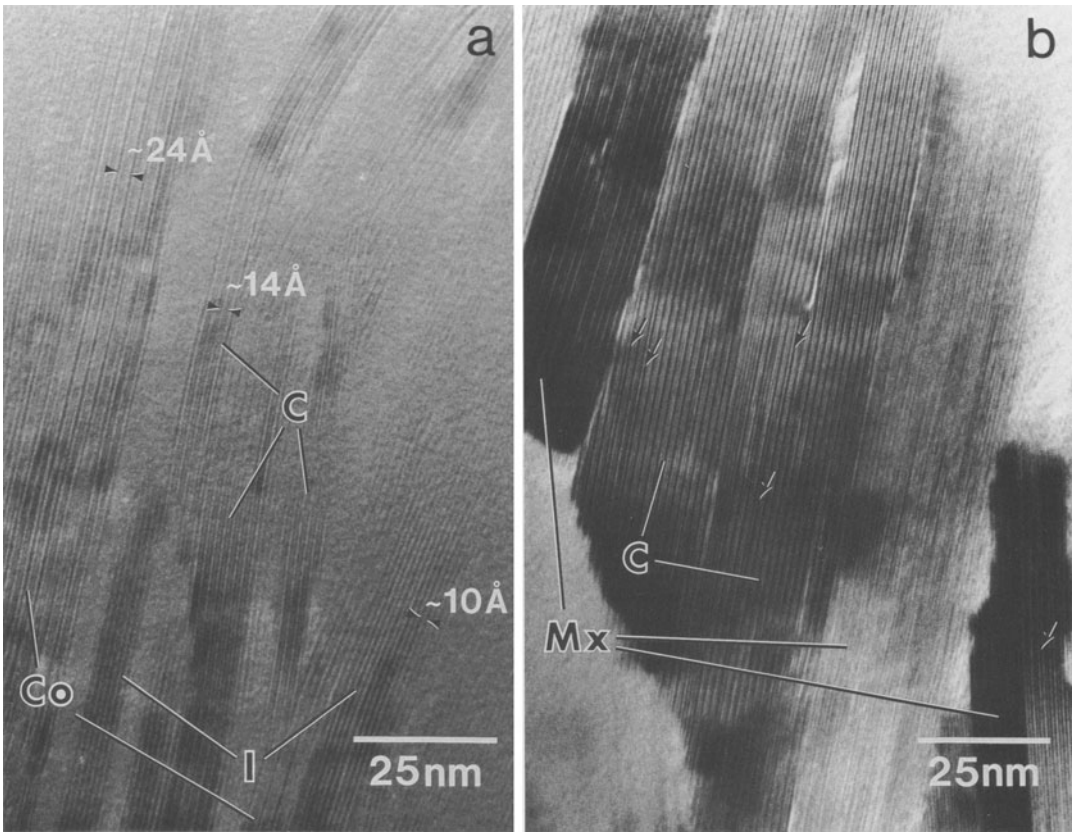


Figure 1. Transmission electron microscope images of (a) chlorite (C; d(001) ≅ 14 Å) coexisting with corrensite (Co; d(001) ≅ 24 Å) and illite (I; d(001) ≅ 10 Å) in sample A416 of the diagenetic zone of the Gaspé Peninsula, Quebec, and (b) aggregates of packets of chlorite (C) interstratified with local ~7-Å layers (black arrows) in a shale recovered from a depth of 4741.8 m; Pleasant Bayou #1 well, Brazoria County, Texas. Mx = mixed-layer 7-Å/14-Å phase.

quartz, and albite. Detailed descriptions of these samples were given and AEM analyses of chlorite were discussed with a different emphasis by Jiang and Peacor (1994).

The second set of rocks consists of four Gulf Coast mudstones recovered from (1) the Pleasant Bayou #1 well (three samples at depths of 4288.8, 4739.6, and 4741.8 m), Brazoria County, Texas (Freed, 1982), and (2) the Case Western Reserve University (CWRU) #6 well (one sample at 5745.4-m depth), Harris County, Texas (Hower *et al* 1976; Ahn and Peacor 1985a). The analyzed samples are from depths exceeding the smectite-to-illite transition zone (Freed and Peacor 1989). Chlorite is a minor phase in the samples. It occurs as aggregates of crystals, many of which are interstratified with serpentine-like 7-Å layers (Figure 1b).

None of the selected Gaspé and Gulf Coast samples provided authigenic chlorite crystals that are large enough to give uncontaminated analyses by EMPA. The temperature ranges of diagenesis and metamorphism are 140–170 and 80–260°C for the selected Gulf Coast and Gaspé rocks, respectively (Freed and Peacor 1989; Hesse and Dalton 1991), well within the temperature range in which trioctahedral chlorite was reported to have significant octahedral vacancies (Kranidiotis and MacLean 1987; Cathelineau 1988).

Carbon-coated, ion-milled specimens were analyzed using a Philips CM12 scanning transmission electron microscope fitted with a Kevex Quantum detector for X-ray energy-dispersive spectrometry (EDS) analyses. Chlorite crystals were first studied by electron diffraction and lattice-fringe imaging in order to minimize possible interferences from associated minerals. Still, more than half of the analyses were discarded because of possible overlap of the beam onto other minerals, as concluded by careful examination of TEM images and corresponding EDS analyses. Analytical procedures and instrumental settings are described by Jiang and Peacor (1994) and references therein. Normalization of structural formulae was based on the ideal anion formula, $O_{20}(OH)_{16}$, assuming all iron to be ferrous since AEM techniques cannot determine ferric/ferrous ratios and anion contents. Ferric iron generally is a minor constituent of low-grade chlorite (Cooper 1972;

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Table 1. Selected structural formulae of chlorite in pelitic rocks from the Gaspé Penninsula, Quebec.[1]

	Diagenetic zone				Anchizone				Epizone	
	A419	A419	A416	A416	R299	R299	8912	8912	R245	R245
Si	5.38	5.55	5.42	5.44	5.68	5.42	5.30	5.68	5.44	5.53
Al(IV)	2.62	2.45	2.58	2.56	2.32	2.58	2.70	2.32	2.56	2.47
Al(VI)	2.62	2.45	2.55	2.56	2.32	2.57	2.69	2.46	2.55	2.52
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	4.30	4.21	4.39	5.79	3.97	3.67	4.96	5.06	3.84	4.14
Mg	4.89	5.25	4.83	3.65	5.71	5.70	4.34	4.26	5.53	5.32
Mn	0.18	0.09	0.19	0.00	0.00	0.05	0.00	0.16	0.07	0.00
$\Sigma_{oct.}$	11.99	12.00	11.97	12.00	11.99	11.99	11.99	11.93	12.00	11.98
□[2]	0.01	0.00	0.03	0.00	0.01	0.01	0.01	0.07	0.00	0.02
Ca	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.02	0.00	0.00	0.01	0.02	0.01	0.01	0.00	0.01	0.00
K	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Na + K + 2Ca	0.02	0.01	0.09	0.01	0.02	0.01	0.02	0.00	0.01	0.00
$\frac{Fe}{Fe + Mg + Mn}$	0.46	0.44	0.47	0.61	0.41	0.39	0.53	0.53	0.41	0.44

[1] Normalization is on the basis of 20O + 16OH, and all iron is assumed to be ferrous. Two standard deviations based on counting statistics are 0.14–0.17 per formula unit (pfu) for Si and Al, 0.12–0.18 pfu for Mg, 0.07–0.12 pfu for Fe, ≤0.03 pfu for Mn, and ≤0.01 pfu for Ti, Ca, Na, and K.

[2] □ = apparent octahedral vacancies assuming 12 octahedral sites.

Black 1975; Shirozu 1978) and its presence in small amounts has little effect when compositions are compared, since all AEM analyses and EMPA were normalized using the same assumptions described above.

Analytical electron microscope analyses of chlorite

New analyses: chlorite from the Gaspé Peninsula and Texas Gulf Coast. The normalized formulae of Gaspé and Gulf Coast chlorite (Tables 1 and 2) contain few or no octahedral vacancies, contrary to most reported EMPA of diagenetic and low-grade metamorphic chlorite. There is no correlation between Na + K + 2Ca values and apparent octahedral vacancies (=12 − Σ octahedral cations) and tetrahedral Al content (Figure 2); such a lack of correlation is to be expected since the Na, K, and Ca contents are less or only slightly larger than two standard errors. The data verify that little or no K, Ca, or Na occur in the analyzed chlorite.

The AEM analyses of chlorite from the Gaspé Peninsula shown in Table 1 are typical of 123 analyses.

Table 2. Representative structural formulae of chlorite in shales from Texas Gulf Coast.[1]

	Pleasant Bayou #1 well Brazoria County						CWRU[2] #6 well Harris County	
Depth (m)	4741.8	4741.8	4739.6	4739.6	4288.8	4288.8	5745.5	5745.5
Si	5.30	5.34	5.19	5.41	5.26	5.21	5.22	5.15
Al(IV)	2.70	2.66	2.81	2.59	2.74	2.79	2.78	2.85
Al(VI)	2.95	2.99	2.82	2.83	2.90	2.93	2.92	2.87
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	5.58	5.93	6.09	6.32	6.07	5.83	6.12	5.87
Mg	3.28	2.82	3.00	2.63	2.84	3.10	2.84	3.17
Mn	0.06	0.07	0.07	0.09	0.11	0.06	0.06	0.07
$\Sigma_{oct.}$	11.87	11.81	11.99	11.87	11.92	11.93	11.93	11.98
□[3]	0.13	0.19	0.01	0.13	0.08	0.07	0.07	0.02
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.03
K	0.02	0.01	0.00	0.02	0.00	0.00	0.00	0.00
Na + K + 2Ca	0.02	0.05	0.00	0.02	0.00	0.00	0.00	0.03
$\frac{Fe}{Fe + Mg + Mn}$	0.63	0.67	0.66	0.70	0.67	0.65	0.68	0.64

[1] Normalization is on the basis of 20O + 16OH, and all iron is assumed to be ferrous. Two standard deviations based on counting statistics are 0.14–0.17 per formula unit (pfu) for Si and Al, 0.12–0.18 pfu for Mg, 0.07–0.12 pfu for Fe, ≤0.03 pfu for Mn, and ≤0.01 pfu for Ti, Ca, Na, and K.

[2] CWRU = Case Western Reserve University.

[3] □ = apparent octahedral vacancies assuming 12 octahedral sites.

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The tetrahedral and octahedral Al contents are nearly equal for the Gaspé chlorite, as required for charge balance in stoichiometric trioctahedral chlorite having no octahedral vacancies and containing only divalent octahedral cations with the exception of Al^{3+}. Approximately 96% of the analyses have <0.15 apparent octahedral vacancies and <0.05 (Na + K + 2Ca) per $O_{20}(OH)_{16}$ (Table 1 and Figure 2). The chlorite exhibits a wide range of Mg and Fe contents, with no regular trend with increasing degree of diagenesis and metamorphism, but the compositions of different crystals of a given specimen become more alike with increasing grade (Jiang and Peacor 1994).

The normalized formulae of chlorite from the Gulf Coast shown in Table 2 are selected from 42 analyses. The chlorite has a rather narrow range of Fe/Mg ratios that probably reflects a simple sediment source or formation path, having formed as a by-product of the smectite-to-illite reaction (Ahn and Peacor 1985a). Nearly 86% of the analyses of the Gulf Coast chlorite contain <0.25 apparent octahedral vacancies and <0.07 (Na + K + 2Ca) per formula unit (pfu). These values are greater than those of the Gaspé chlorite, probably because crystals in the Gulf Coast samples are smaller and some analytical overlap onto associated minerals occurs even by AEM. It is also possible that some of the ~7-Å mixed layers in the Gulf Coast chlorite are, in fact, kaolinite instead of the commonly assumed berthierine. Kaolinite coexists with chlorite and mixed-layer illite/smectite in Gulf Coast sandstones and mudstones (Ahn and Peacor 1985b; Burton *et al* 1987). Hillier and Velde (1992) studied chlorite in sandstones from the North Sea and showed that the chlorite that has excess octahedral vacancies actually may contain variable amounts of interlayered kaolinite, even though it appears to be well crystallized with euhedral outlines. However, there is no evidence to indicate the presence of interlayered kaolinite/chlorite in the Gulf Coast samples. The minor alkali and Ca contents in some analyses suggest that at least some contamination was caused by surrounding mixed-layer illite/smectite or feldspars.

The Gulf Coast samples provide a comparison of AEM data with the EMPA data of Hillier and Velde (1991), who published analyses of chlorite from several localities, including five from sandstones in Texas Gulf Coast sediments. Average values for their five samples include 0.93 vacancies on octahedral sites, Na + K + 2Ca = 0.12, and tetrahedral and octahedral Al values of 1.78 and 3.47, respectively, per $O_{20}(OH)_{16}$. Such values are typical for analyses of sedimentary chlorite, but they differ significantly from those obtained by AEM in this study. Hillier and Velde's analyses may have been contaminated by quartz or illitic clays. Still, we emphasize that different samples were used and, whereas the samples in our study are mudstones, Hillier and Velde analyzed sandstones. In addition, the

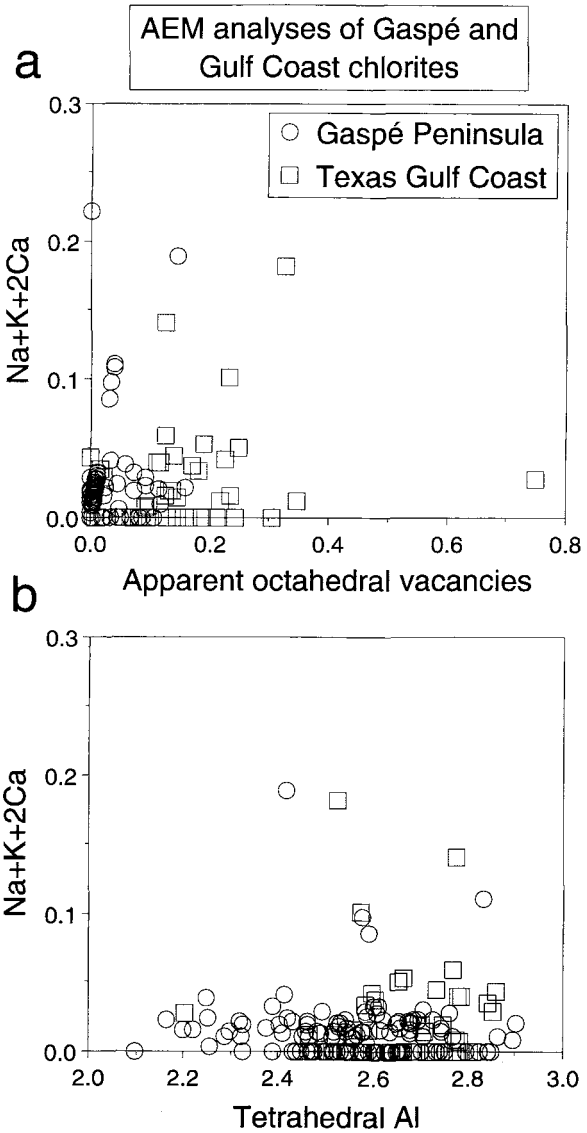


Figure 2. Correlation diagrams showing relations between Na + K + 2Ca values and apparent (a) octahedral vacancies and (b) tetrahedral Al content of chlorite in pelitic rocks from the Gaspé Peninsula and Texas Gulf Coast.

latter were obtained from depths of <3000 m, whereas those of this study were obtained at greater depths (temperatures) where defects are less likely. Comparisons may therefore be imperfect.

Other published AEM analyses of chlorite. We have compiled as many published AEM analyses of chlorite as possible. Some papers do not report alkali and Ca contents because those elements occur in negligible amounts; their presence is simply neglected in other cases. This oversight has important consequences for values of apparent tetrahedral Al and octahedral vacancies, as shown below. A plot of octahedral vacancies

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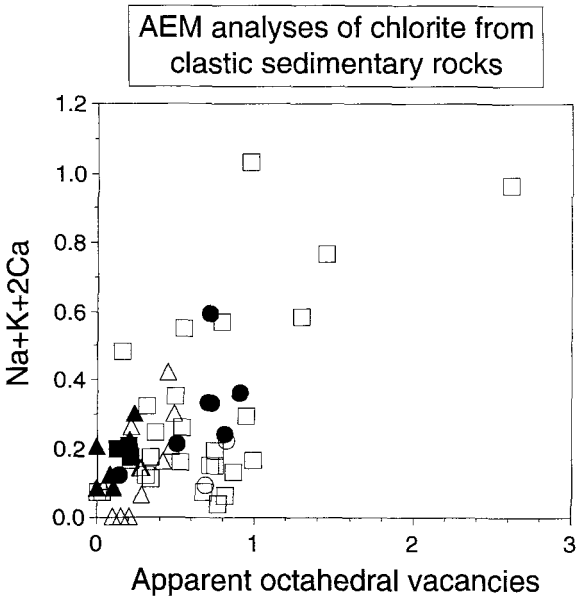


Figure 3. Relation between values of Na + K + 2Ca and apparent octahedral vacancies in published AEM analyses of chlorite in clastic sedimentary rocks (○ = Curtis *et al* 1984; □ = Curtis *et al* 1985; △ = Li *et al* 1994a; ● = Whittle 1986) and metabasites (■ = Shau *et al* 1990; ▲ = Shau and Peacor 1992).

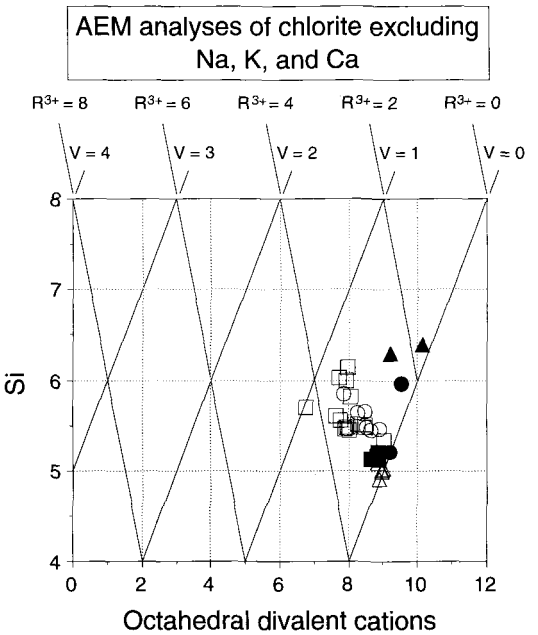


Figure 4. Plot of Si versus octahedral divalent cations (modified after Wiewióra and Weiss 1990) illustrating the extent of apparent octahedral vacancies in AEM chlorite analyses with alkali and Ca not reported (○ = Ahn and Peacor 1985a; □ = Jahren and Aagaard 1992; △ = Jiang *et al* 1992; ● = Kreutzberger and Peacor 1988; ■ = Li *et al* 1994b; ▲ = Yau *et al* 1988). R^{3+} = octahedral trivalent cations; V = apparent octahedral vacancies; the contours are based on 8 tetrahedral and 12 octahedral sites per $O_{20}(OH)_{16}$.

versus Na + K + 2Ca for those published analyses that include Na, K, and Ca is shown in Figure 3. There is no overall trend, but the number of apparent octahedral vacancies appears to increase with Na + K + 2Ca content, especially when individual sets of data are considered.

The analyses of chlorite in metabasites reported by Shau *et al* (1990) and Shau and Peacor (1992) have small amounts of octahedral vacancies and alkali and Ca cations caused by coexisting phyllosilicates including corrensite, talc, and saponite. Several analyses of chlorite from clastic sediments of the Nonesuch Formation at White Pine, Michigan contain relatively high values of Na + K + 2Ca and octahedral vacancies and minor Ti. Such analyses were obtained on samples that include residual biotite or smectite-like layers within chlorite that originated from alteration of detrital biotite (Li *et al* 1994a). Most of the analyses reported in these three studies contain minor alkali and Ca, even though they were obtained from crystals that had no impurities that could be identified by electron diffraction and lattice-fringe imaging.

The AEM analyses of chlorite in sandstones from the North Sea and several other localities exhibit a wide range of Na + K + 2Ca values and octahedral vacancies (Curtis *et al* 1984, 1985; Whittle 1986). Hillier and Velde (1992) suggested that the kaolinite that is interstratified with chlorite may in part account for the large proportion of apparent octahedral vacancies in formulae of chlorite from North Sea sandstones reported by Whittle (1986). Kaolinite, like berthierine, has d(001) ≅ 7 Å, and these minerals can therefore be distinguished from each other only with difficulty. Kaolinite is especially difficult to identify by TEM methods since it is rapidly damaged by interaction with the electron beam and becomes amorphous within a few seconds (Jiang and Peacor 1991). Curtis *et al* (1984, 1985) concluded that the presence of alkalis in their analyses implied contamination by admixed illite or residual smectite. The relatively large amounts of Ca in some of their analyses indicate that calcite may have been another source of contamination.

Figure 4 depicts the relation among Si content, octahedral divalent cations, and apparent octahedral vacancies, with values obtained from AEM-derived formulae for which Na, K, and Ca were not reported. The analyses of Jiang *et al* (1992), Kreutzberger and Peacor (1988), Li *et al* (1994b), and Yau *et al* (1988) were obtained for chlorite from a sulfide deposit, shaly limestones, mudstones, and shales, respectively. In those studies, the alkali and Ca contents were found to be negligible and excluded from the formulae normalizations. The numbers of octahedral vacancies are reasonably small (mostly <0.3 pfu) in those analyses. The analyses of Gulf Coast chlorite of Ahn and Peacor (1985a) are similar to those reported in this study and

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will not be discussed further. Jahren and Aagaard (1992) analyzed euhedral chlorite crystals from North Sea sandstones with (001) normal to the electron beam but did not report alkali and Ca values. Their analyses have relatively large numbers of octahedral vacancies. However, Jahren (1991) noted the presence of >10% illite in partially dissolved chlorite crystals and variable amounts of K in analyses of euhedral chlorite from North Sea sandstones. Lee *et al* (1984) showed that chlorite and illite can form fine-scale intergrowths ranging from interstratified layers to interlaminated stacks and analyses obtained for crystals with (001) normal to the electron beam may be contaminated.

In comparison with the previous analyses, 93% of the new analyses obtained here fall in the vicinity (<0.25 vacancies) of the zero vacancy line and have 5–6 Si pfu. The data collectively show that there are few or no octahedral vacancies in the analyzed chlorite and that there is no correlation between tetrahedral Al content and Na + K + 2Ca for analyzed regions that were verified to have little or no contamination by associated minerals (e.g., the chlorite studied here). In contrast, the analyses that show excess octahedral vacancies give petrographic and chemical evidence that suggests potential associations with mixed layers or fine-scale intergrowths.

Relations between mixtures of minerals and excess octahedral vacancies in chlorite

Many studies have shown that phyllosilicates can form a wide range of intergrowths in low-grade rocks. Mixed layering of chlorite with other phyllosilicates including illite, berthierine, tri- and dioctahedral expandable 2:1 minerals, and kaolinite, is common (Figure 1), especially in diagenetic rocks. Those same minerals occur as stacks of packets or randomly intergrown packets that are undetected by XRD because ordinary XRD techniques cannot characterize such textures. Because of the fine grain sizes and complex textural relations, it is extremely difficult if not impossible to obtain analyses of single phyllosilicate crystals in low-grade, fine-grained clastic rocks with EMPA techniques. Analyses of crystal aggregates invariably include extraneous materials. Mineral coatings, inclusions, mixed layers, and mineral interlaminations may occur at scales that cannot be detected by standard petrographic studies. Moreover, those features are typical of low-grade clastic rocks (Peacor 1992). Those problems are exacerbated in EMPA because the electron beam penetrates the surface of the sample being analyzed.

AEM/TEM techniques have two clear advantages over EMPA: (1) the area of analysis is up to two orders of magnitude smaller, and (2) the structure of the specific volume being analyzed can be characterized by electron diffraction. Nevertheless, AEM/TEM techniques have limitations, in part because of spurious scattering of beams in the area of the sample (Williams *et al* 1989). Specimen tilting may change the spatial relations of mineral aggregates with respect to the electron beam. Significant electron and X-ray scattering will occur in the TEM column if large apertures and intense beams are used. Intergrowths may not be identified unless proper crystal orientations are obtained. Cation diffusion, even of Al, may be a problem if care is not taken. The most serious limitation is that AEM analyses are based on X-ray intensity ratios, from which only concentration ratios can be obtained, thus further complicating the normalization process.

However, analyses by AEM obtained in the last few years (Peacor 1992 and references therein) with "clean" and carefully engineered analytical systems are much more accurate, precise, and lacking in contamination than those of earlier studies (Ahn and Peacor 1985a). That is, AEM data must also be evaluated cautiously, but with recent data generally being of higher quality.

Many EMPA of chlorite from low-grade clastic rocks have been reported in the literature, but only a small proportion are suitable for comparison and discussion here because alkali and Ca contents were not reported in most cases. Formulae derived from those analyses typically contain significant numbers of octahedral vacancies, some with values much larger than those described below. As will be evident from the following analysis, such exclusion of alkalis and Ca obscures the true nature of the analyzed material, whereas their inclusion serves as a test of sample purity.

Data from EMPA of chlorite (occurring primarily in sandstones) reported by Boles and Franks (1979), McDowell and Elders (1980), and Hillier and Velde (1991) are plotted in Figure 5. There is no apparent correlation between tetrahedral Al and Na + K + 2Ca contents, but there are as many as ~1.5 octahedral vacancies pfu. A plot of Si versus divalent cations pfu (Figure 5b) shows widely scattered points, with a poorly defined trend. This trend appears to indicate an increase of apparent octahedral vacancies toward higher Si values and lower totals of octahedral divalent cations, characteristic of diagenetic and low-grade metamorphic chlorite.

The same type of plot for EMPA of chlorite and mixed-layer chlorite/smectite that occur in metabasites and hydrothermally altered rocks clearly displays a trend (Figure 6). Such a trend would be produced by analyses affected by a specific type of contamination, as is generally the case in metabasites where chlorite commonly contains expandable trioctahedral layers (e.g., Shau *et al* 1990). This trend is apparently not the case for the overall data plotted in Figure 5. However, there are systematic variations for most data points if individual data sets are separately considered. Although the overall pattern in Figure 5 might be interpreted as a result of a lack of contamination, the following relations imply that contamination occurred.

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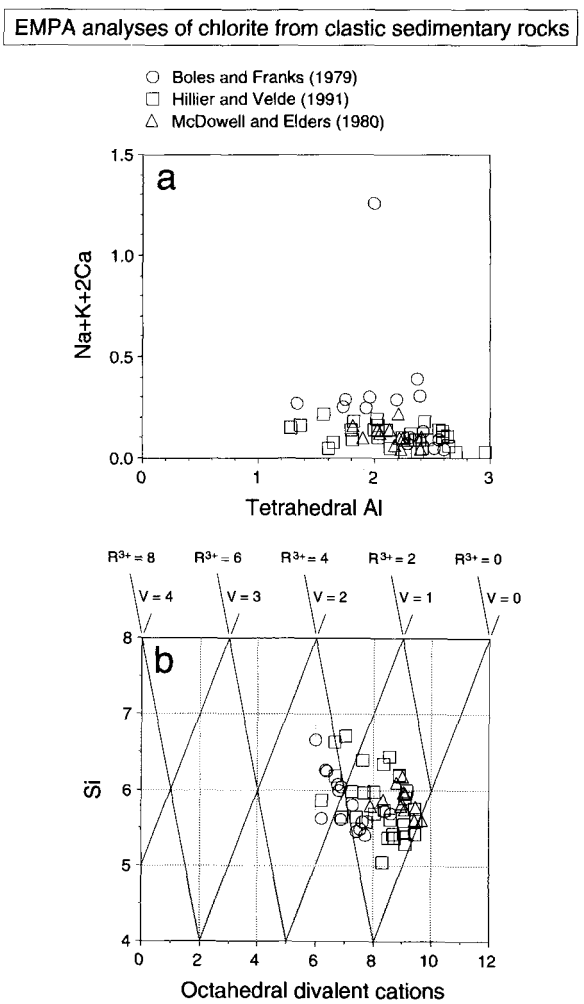


Figure 5. Diagrams displaying the relations (a) between tetrahedral Al and Na + K + 2Ca contents, and (b) among octahedral divalent cations, Si content, and apparent octahedral vacancies for published electron microprobe analyses of chlorite in clastic sedimentary rocks. R^{3+} = octahedral trivalent cations; V = apparent octahedral vacancies.

A common criterion for selection of EMPA is that $Na_2O + K_2O + CaO < 0.5$ wt. % (Foster 1962; Hillier and Velde 1991). Calculations show that the limiting value is attained with less than ~4 wt. % muscovite, ~6 wt. % illite, or ~12 wt. % saponite mixed with chlorite. However, the calculated effects on increases in Si and octahedral vacancies and decreases in tetrahedral Al are significant for those limits. For example, calculated trends of compositional variations in chlorite resulting from contamination by various minerals are illustrated in Figure 7 as a plot of Si versus octahedral divalent cations. The most significant result of mixing with dioctahedral phyllosilicates is a decrease of octahedral occupancy, as indicated by the slopes of the mixing lines for kaolinite, illite, and muscovite, which are roughly perpendicular to the lines indicating vacancy content.

Figures 8a and 8b are plots of Na + K + 2Ca versus tetrahedral Al contents and apparent octahedral vacancies, showing the effects of analyses by mixing chlorite with 4 and 10 wt. % of a number of minerals. Combinations of contaminating minerals result in widely scattered distributions, similar to those in Figure 5. Contamination by talc, kaolinite, rutile, or quartz gives a significant decrease in octahedral occupancy with no increases in alkali and Ca contents. A mixture of 4 wt. % quartz with 96 wt. % chlorite gives ~0.36 octahedral vacancies pfu, without Na, K, or Ca. Clearly the criterion of acceptance of analyses of $Na_2O + K_2O + CaO < 0.5$ wt. % provides no test for such contamination. These relations collectively suggest that small amounts of exotic minerals that may predictably be overlooked and included in EMPA of low-grade chlorite can have a significant impact on the proportions of octahedral vacancies and tetrahedral Al.

Octahedral vacancies and "chlorite geothermometry"

It has generally been accepted that trioctahedral chlorite has significant numbers of octahedral vacancies since Foster (1962) carried out her classic analysis of chlorite compositions. However, the analyses presented here suggest that there is no convincing evidence for significant numbers of octahedral vacancies in trioctahedral chlorite. Instead, our data, combined with those from the literature, suggest that formulae derived from verifiably pure chlorite have few or no octahedral vacancies. In contrast, formulae with significant proportions of vacancies are apparently not of pure chlorite, and using the mineral name "chlorite" for such materials is misleading. It has yet to be demonstrated that such data correspond to a well-defined single phase of chlorite, *sensu stricto*.

Cathelineau (1988) showed positive correlations between measured drillhole temperatures and values of tetrahedral Al and octahedral vacancies for chlorite from the Los Azufres and Salton Sea geothermal fields and suggested that such correlations can be used as a "geothermometer." Although Cathelineau considered Na, K, and Ca to be contaminants and did not consider them in normalized formulae, no compensation was made for other components. As shown in Figures 9a and 9b, those same data give excellent correlations between Na + K + 2Ca values and amounts of tetrahedral Al or numbers of octahedral vacancies. The correlation trends are much like those observed for chlorite that has mixed-layered chlorite/smectite and occurs in metabasites and hydrothermally altered rocks (Figures 9c and 9d). Those relations imply that the EMPA of the Los Azufres and Salton Sea chlorite were not obtained from pure chlorite and may have been contaminated by small quantities of another phase, probably smectite, but other minerals or mineral mixtures could give similar trends (Figures 7 and 8).

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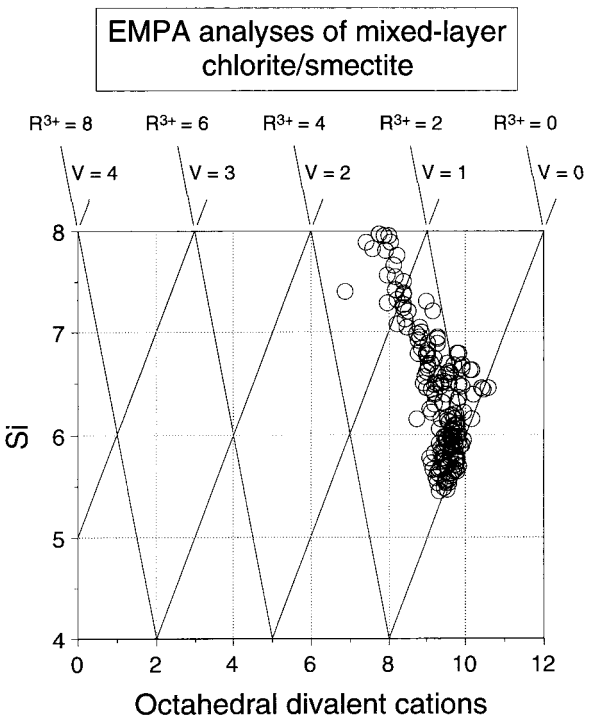


Figure 6. Plot of Si versus octahedral divalent cations exhibiting a trend given by the electron microprobe analyses of mixed-layer chlorite/smectite from the literature (see Figure 9 for references). R^{3+} = octahedral trivalent cations; V = apparent octahedral vacancies.

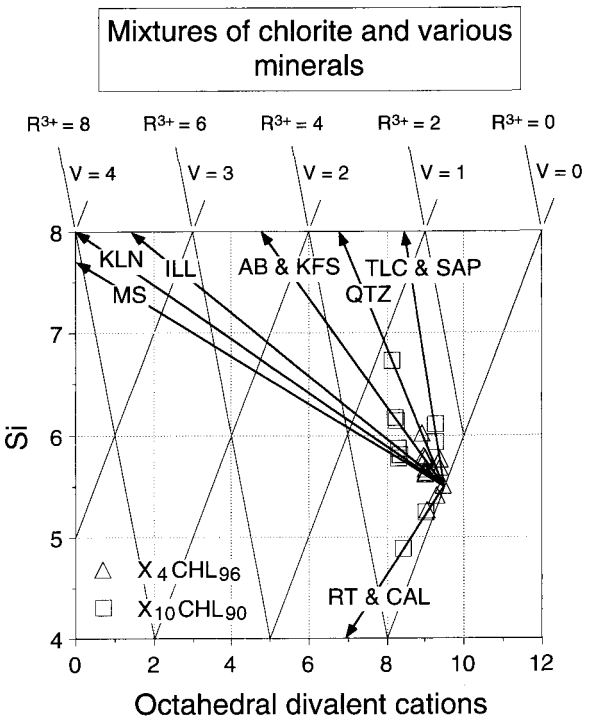


Figure 7. Plot of Si versus octahedral divalent cations displaying schematic trends of compositional deviations generated from mixtures of an assumed composition of chlorite (CHL; $Fe_{5.5}Mg_4Al_{2.5}Si_{5.5}Al_{2.5}O_{20}(OH)_{16}$) and other minerals. Triangles and squares represent the average compositions of 96 and 90 wt. % of the assumed chlorite plus 4 and 10 wt. % of quartz (QTZ; SiO_2), albite (AB; $NaAlSi_3O_8$), potassium feldspar (KFS; $KAlSi_3O_8$), calcite (CAL; $CaCo_3$), kaolinite (KLN; $Al_8Si_8O_{20}(OH)_{16}$), talc (TLC; $Mg_6Si_8O_{20}(OH)_4$), saponite (SAP; $Ca_{0.4}Na_{0.2}Mg_6Si_7AlO_{20}(OH)_4$), muscovite (MS; $K_2Al_4Si_6Al_2O_{20}(OH)_4$), illite (ILL; $K_{1.4}Al_4Si_{6.6}Al_{1.4}O_{20}(OH)_4$), and rutile (RT; TiO_2), respectively. R^{3+} = octahedral trivalent cations; V = apparent octahedral vacancies.

De Caritat *et al* (1993) reviewed three potential geothermometers that utilize the composition of chlorite to estimate temperatures of formation. They showed that there are large discrepancies among the temperatures estimated by those geothermometers and temperatures determined by other methods for several rock systems. They therefore suggested that none of those geothermometers can satisfactorily perform over a wide range of Al content, Fe/(Fe + Mg) ratios, coexisting mineral assemblages, and temperatures. Two of the geothermometers are concerned with tetrahedral Al content and octahedral vacancies relating to the dioctahedral component (Cathelineau and Nieva 1985; Walshe 1986). Both were calibrated and proposed on the basis of problematic analyses such as the EMPA of chlorite from the Salton Sea geothermal system (McDowell and Elders 1980) discussed above. This relation implies that contaminated analyses played an important role in the establishment of those potential temperature indicators, and on that basis alone the geothermometers are unacceptable. The inconsistent temperatures obtained by de Caritat *et al* (1993) are the predictable result of such relations.

Why, then, do the analytical data for chlorite from the Los Azufres and Salton Sea areas, or from other prograde sequences for that matter, appear to correlate with temperature? We can only speculate, as the original samples are not available to us. However, we have studied other samples from the Salton Sea Geothermal Field (Yau *et al* 1988), and found using older AEM techniques that pure chlorite does not contain alkalis and normalizes well with only few vacancies. In addition, textural relations for such samples are compatible with general trends in low-grade rocks that are characterized by complex mixed layering, high concentrations of defects, small crystal sizes, and other features that contrast with those of high-grade rocks. Indeed, as seen in part by well-documented changes in illite crystallinity with increasing grade (Merriman *et al* 1990), pelites tend to become more homogeneous as they approach states of chemical and textural equilibrium. Such changes occur commonly in prograde sequences of metamorphic rocks (Cashman and Ferry 1988) and even more clearly in low-grade rocks, especially with respect to clay minerals (Eberl *et al* 1990). These changes generally occur continuously as a function of grade, and chemical analyses therefore sample

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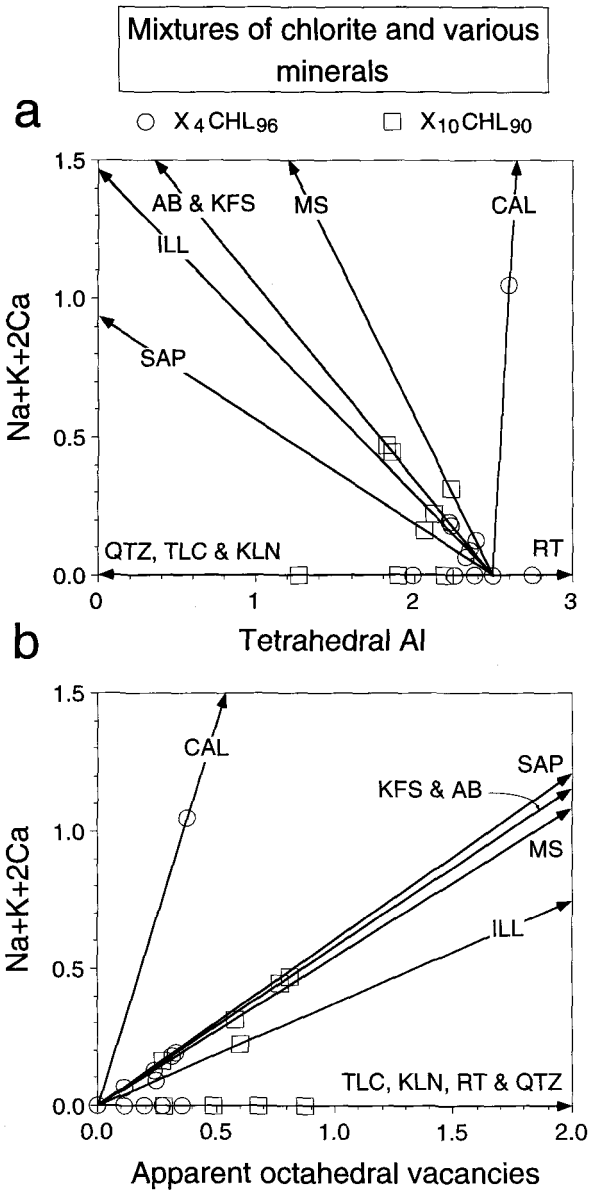


Figure 8. Diagrams showing the effects of mixing with other minerals on the values of Na + K + 2Ca, tetrahedral Al, and octahedral vacancies of chlorite. Notations and compositions for minerals are the same as those in Figure 7.

increasingly homogeneous, i.e., less contaminated, chlorite with grade. Indeed, the data of Cathelineau and Nieva (1985) and McDowell and Elders (1980) are consistent with that trend, namely toward vacancy-free chlorite with increase in grade.

Shau *et al* (1990) criticized the use of the "geothermometers" discussed here on the basis of their inference that analyses were contaminated by mixed layering. They noted that mixed layering represents a metastable state that depends on kinetic factors (e.g., water-rock ratio) that affect the degree to which metastable phases are able to transform to stable states. Mixed-layered materials exist as a function of many unconstrained variables and cannot be used as geothermometers. De Caritat *et al* (1993) criticized the use of such "geothermometers" on similar grounds, i.e., that the chlorite occurring at low grades is not in chemical equilibrium, even if pure. On the other hand, mixtures occurring on a scale larger than that of individual mixed layers, not necessarily in a coherent structural relation, simply give rise to direct contamination of analyses whether there is equilibrium or not. Data from such mixtures are clearly not useful as geothermometers.

Still, much can be learned from established trends that appear to occur as a function only of temperature, even where they do not represent reproducible equilibrium states and where they may appear to be a measure of one variable (e.g., vacancies in chlorite) but are a function of another (e.g., contamination of analyses). Such variables do serve as measures of the progress from one state (metastable) to another (stable). They are therefore useful in determining such progress, especially where the variables that affect such progress are well constrained. They should not, however, be used in the evaluation of specific temperatures, i.e., as geothermometers.

The possible geological causes of any compositional variations can be determined only when reliable analyses of well-characterized minerals have been obtained. The importance of recognizing potential problems involved in interpretations of analytical data cannot be overemphasized. Cautionary comments expressed in the past have often simply been ignored, in part, we believe, because it is so difficult to determine temperatures in low-grade rocks, and because functions such as a "chlorite geothermometer" are so appealing and easily used without proper safeguards.

We conclude that the use of a geothermometer based on the tetrahedral Al content of chlorite or related variable is clearly not appropriate at present because of the lack of well-defined analyses and compositional variations. There has been no demonstration of mineral equilibrium in those rocks where lack of equilibrium is the rule, reliable theoretical calculations of the effects of solid solution are approximations at best, and experimental calibrations, including extrapolations from higher temperatures, are problematic. Empirical applications of "chlorite geothermometry" are therefore not warranted. Our conclusion does not negate much of the value inherent in EMPA or other analytical data that are subject to low levels of contamination. However, the data must be selected and interpreted cautiously and not extended beyond their reliability, as in utilizing quantitative measures of octahedral vacancies as quantitative functions of other variables. Such data are, on the other hand, useful for many purposes, as in determination of average trends in Mg/(Mg + Fe) ratios as a function of grade or degree of

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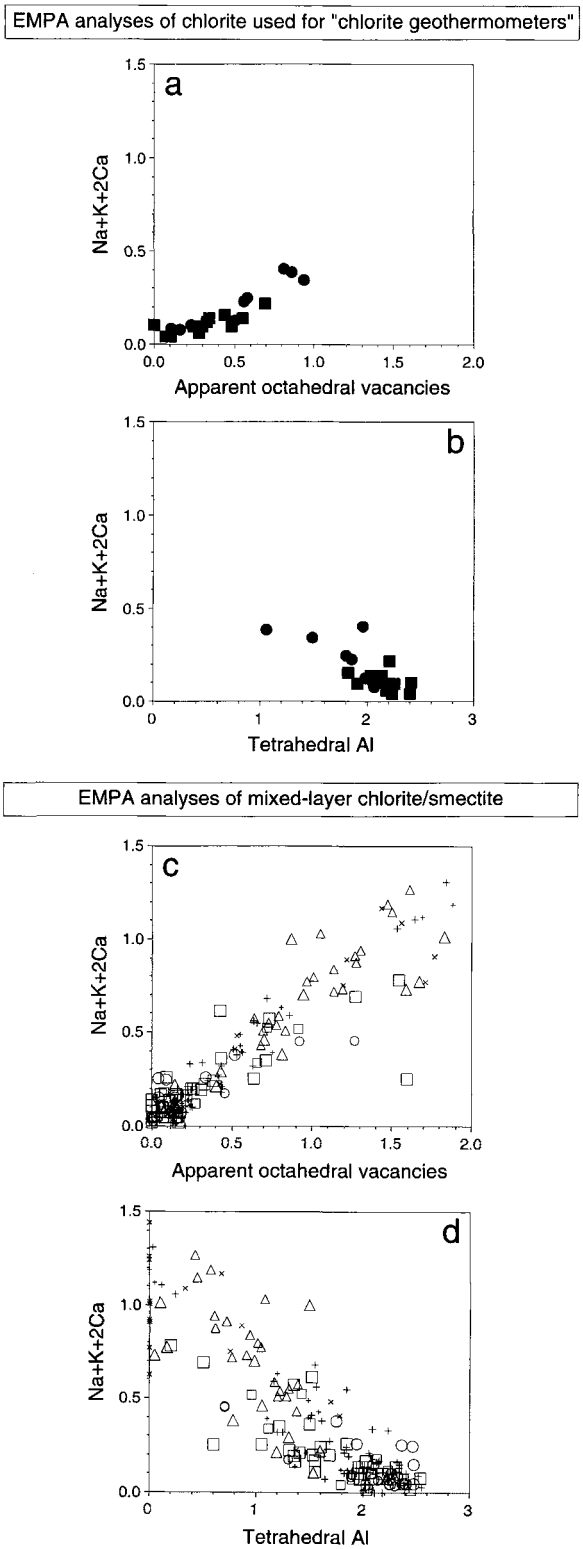


Figure 9. Diagrams showing positive and negative correlations between Na + K + 2Ca values and apparent octahedral vacancies and tetrahedral Al contents, respectively, for the electron microprobe analyses of chlorite given by McDowell and Elders (1980) and Cathelineau and Nieva (1985) (solid circles and squares in a and b) and those reported for chlorite and mixed-layer chlorite/smectite in metabasites (c and d; large ○ = Beiersdorfer 1993; large □ = Bettison and Schiffman 1988; large △ = Bettison-Varga *et al* 1991; large + = Bevins *et al* 1991; small ○ = Gills and Thompson 1993; small □ = Inoue and Utada 1991; small △ = Inoue 1985; small + = Robinson *et al* 1993; × = Schiffman and Fridleifsson 1991).

fluid mixing, for example. Our data do not exclude the possibility of establishing a chlorite geothermometer. Rather, we suggest that careful analytical work and interpretation are critical to an understanding of the relations among compositions, thermodynamic variables, and physical conditions of formation of chlorite.

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