Kimberlitic chlorites from Sierra Leone, West Africa: unusual chemistries and structural polytypes

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Abstract
Chlorites occur as ovoid discrete nodules (1–4 cm), as anhedral macrocrysts (0.20 mm) and euhedral crystals (0.05 mm) in kimberlite, and as cleavage replacement products of high Fe (reversely pleochroic), low Ti + Cr phlogopites. The nodules are severely deformed and four textural groups are recognized (fibrous, platy, tectonized, multiple cleavage) that consist of intergrown chlorites and vermiculites of variable compositions. Major chemical types in the nodules are classified as high Fe (25 wt.%), intermediate Fe (15 wt.%), and low Fe (8 wt.%) varieties with a subgroup consisting of low Fe and high K (0.8–2.3 wt.% K2O). The chlorites have high SiO2 (46.6 wt.% max) and MgO (28 wt.% max), and low Al2O3 (<12 wt.%) contents. High Fe3+ and later alteration result in vacancies (corroborated by electron densities) in the interlayer sheet. The chlorites and vermiculites are dominantly of the rare 1a structural type, intergrown with more typical 1b chlorite in some specimens. Two-layer “s” and “t” stacking sequences identified in 1a chlorites and vermiculites suggest alteration from parent 1M and 2M1 phlogopites, respectively. Chloritization of peridotitic phlogopite nodules and macrocrysts took place at relatively low P–T conditions concurrent with, or followed by crystallization of primary magmatic chlorite in the kimberlite groundmass.

Introduction
Chlorite is a common constituent of many rock types and a characteristic component of low grade greenschist facies metamorphism. It is, however, stable over a range of temperature, pressure, and volatile conditions (Albee, 1962). Primary igneous chlorite occurs in some diabases (Lehmann, 1965) and Fawcett (1965) reports chlorite in residual liquids from basalts in Mull. Quenched chlorite is noted by Schreyer and Yoder (1964) in experiments at 5 and 10 kbar at temperatures above the cordierite solidus in the system Mg-cordierite-H2O. Diamond inclusion studies support the notion of hydrous phyllosilicates in the upper mantle, and phlogopite (Prinz et al., 1975; Sobolev, 1977), biotite (Giardini et al., 1974), and type 1b chlorite (Mitchell and Giardini, 1977) have been reported. Nixon and Kreston (1973) describe green kimberlitic chlorite and phlogopite cored by chlorite in the Khabes dike, Lesotho. A green pleochroic chlorite occurs along the outer three meters of a kimberlite from the De Beers Mine (Ferguson et al., 1973). These may be late-stage alteration products of phlogopite associated with, or resulting from fluidization and kimberlite emplacement (Kreston, 1973). McGechin et al. (1973) have characterized three pleochroic types of chlorites resulting from variations in Cr2O3 content from the Moses Rock kimberlite and the Cane Valley carbonatite dikes, Utah. Diopsidic pyroxenes from spinel lherzolite are considered to be the precursors to these chlorites via reactions with a volatile-rich fluid phase during kimberlite-carbonatite as-
cent. Chlorite replacement of phlogopite along cleavage planes is also described from the Mir pipe in Siberia (Frantsesson, 1970), and this appears to be directly associated with carbonatitic activity in the pipe.

Chlorite was first recognized as a constituent of the Koidu kimberlite complex in Sierra Leone by Grantham and Allen (1960), but few details are provided. Systematic sampling of the complex (Tompkins, 1983; Tompkins and Haggerty, 1983a,b) now shows that chlorite is abundant and is present in three modes: as large (up to 4 cm) discrete megacrystic nodules, as a primary crystalline component of the kimberlite, and as a replacement product of phlogopite. Chlorites most similar to these are reported from only one other kimberlite locality, the Mbuji-Mayi complex in Zaire (Fieremans and Ottenburgs, 1979). The analytical data, however, are not directly applicable because large concentrations of quartz are present in bulk chemical analyses. The present study was undertaken to characterize the Koidu chlorites, compositionally and structurally, in an attempt to define more accurately their genesis and petrological affinities, and to establish whether chlorite is a viable mineral host for volatiles in the upper mantle.

**Geological setting**

The Cretaceous-Jurassic kimberlite field in the Leo uplift of eastern Sierra Leone is comprised of three kimberlite pipes, a ring-dike structure, and multiple sets of en-echelon kimberlite dikes intruded into Archean age granitic rocks (Hall, 1970). This district forms part of a larger kimberlite province that includes other bodies in Liberia, Guinea, Mali, and the Ivory Coast (Bardet, 1974). The pipes at Koidu are multiple intrusions and several facies of kimberlite are recognized (Tompkins and Haggerty, 1983a,b). Kimberlites at Pipe 1 are typically coarse grained and brecciated, whereas those at Pipe 2 are finer grained and have carbonatitic affinities based on major and minor element bulk chemistries (Tompkins, 1983). The dikes are massive and distinctly basaltic in appearance. Chlorite replacement of phlogopite along cleavage planes is also described from the Mir pipe in Siberia (Frantsesson, 1970)) and this appears to be directly associated with carbonatitic activity in the pipe.

Chlorite was first recognized as a constituent of the Koidu kimberlite complex in Sierra Leone by Grantham and Allen (1960), but few details are provided. Systematic sampling of the complex (Tompkins, 1983; Tompkins and Haggerty, 1983a,b) now shows that chlorite is abundant and is present in three modes: as large (up to 4 cm) discrete megacrystic nodules, as a primary crystalline component of the kimberlite, and as a replacement product of phlogopite. Chlorites most similar to these are reported from only one other kimberlite locality, the Mbuji-Mayi complex in Zaire (Fieremans and Ottenburgs, 1979). The analytical data, however, are not directly applicable because large concentrations of quartz are present in bulk chemical analyses. The present study was undertaken to characterize the Koidu chlorites, compositionally and structurally, in an attempt to define more accurately their genesis and petrological affinities, and to establish whether chlorite is a viable mineral host for volatiles in the upper mantle.

**Analytical procedures**

**Terminology**

Nodule is used in the sense generally applied to polyminerall xenoliths hosted in kimberlite, and megacrysts are large (usually >2 cm) discrete nodules of a single mineral. Because of the genetic implications implied by phenocrysts and xenocrysts these terms are only used in specific instances and the term macrocryst is employed where there are uncertainties in origin. Primary igneous is used for mineral melt derivatives whereas replacement (or secondary) implies a solid state reaction derived from deuteristic processes or post-consolidation activity.

**Optical techniques**

Chlorite nodules were examined and classified in hand specimens and under a binocular microscope. Thick polished mounts were found to be more useful than polished-thin-sections in revealing subtleties in cross fiber relations. Transmitted and reflected light microscopy was used for the study of kimberlites.

**Chemistry**

Chemical analyses of mineral assemblages and intergrowths were determined using an ETEC automated electron microprobe at the University of Massachusetts. Accelerating voltage was 15 kV, with a beam diameter of 5 μm and a specimen current of 0.03 nA. Matrix correction factors are those of Bence and Albee (1968) and Albee and Ray (1970). Synthetic (s) and natural (n) standards used are as followed: pyrope garnet, P-130 (n) for Fe, Al; Mn-ilmenite (n) for Ti, Mn; Fo130, P-130 (n) for Mg; kyanite (n) for Si; chromite, Cr-cats (s) for Cr; jadeite, Jd-35 (s) for Na, Ca; sandidine (n) for K.

Iron was determined by microbeam analysis but ferrous iron was determined on discrete nodules by wet chemical analyses following the Wilson cold digestion procedure as outlined by Maxwell (1968). Triplicate analyses were compared with two standards, BCR-1 and Knippa-1. These standards are routinely used in XRF analyses at the University of Massachusetts; the USGS analyses are given in Flanagan (1976). Deviations of the standards from the mean were no greater than ±0.10 wt.%. The wet chemical ferrous iron determinations of chlorite nodules represent bulk compositions. Ferrous and ferric iron contents were calculated from weighted averages based on chlorite modal analyses in those nodules having more than one compositional type.

**X-ray crystallography**

Four chlorite nodules were studied by X-ray powder and single crystal techniques. Samples CHK-1 and CHK-6 were selected as representative of the fibrous chlorites and CHK-2 and CHK-13 of the platy and tectonized chlorites. Gandolfi patterns were taken of individual fibers and plates as well as Debye-Scherrer patterns using crushed material in capillary tubes with FeKa radiation. From three to six individual fibers or plates from each nodule were also studied by precession and Weissenberg methods to determine the precise stacking sequence of layers. The 00l intensities for crystals from samples CHK-1 and CHK-2 were measured on a single crystal diffractometer, corrected for Lp and absorption factors, and used to calculate one-dimensional electron density maps.

**Chlorite occurrence and mineral associations**

**Discrete chlorite nodules**

The discrete chlorite nodules (Fig. 1) are similar to other members of the megacryst suite (pyroxene, garnet, ilmenite) at Koidu with respect to size (1-4 cm) and their oval and abraded appearance. In hand specimen the nodules are dark forest green in color with veinlets of...
Fig. 1. A representative collection of the four discrete chlorite nodule groups identified at Koidu. Textural types from left to right are: back row, all group F; front row, groups T, P, C; center, group F.

mustard yellow serpentine. Their habit is variable and four major groups are recognized. Group F (fibrous) chlorites are cohesive and consist of nodules with a filiform to bladed habit. Group P (platy) are characterized by chlorites that form books or plates typical of phyllosilicate minerals. Group T (tectonized) are characterized by single distinct parting planes. Textures are platy to fibrous and many nodules are bent or multiply contorted. Group C (multiple cleavage) are composed of nodules with two distinct parting directions. Examples of a selection of these groups are illustrated in Figure 2a-f. Anastomosing networks of crosscutting fibers (Fig. 2a-d) are present in some nodules and these crossfibers form distinct subparallel groups. Typically, one set of crossfibers is observed but two sets may also be present (Fig. 2d). Compositionaly, these fine cross-fibers are usually similar to the host phase. In Figure 2d, however, hardness, reflectivity, and chemical differences are evident and the harder and darker cross-fibers are selectively replaced by serpentine (highly reflective phase). In Figure 2e-f the flame-like structures are two compositionally distinct chlorites intergrown along the same cleavage planes. Kink banding perpendicular to the cleavage disrupts this parallism giving the appearance of cross-cutting fibers. These textures are interpreted to result from deformation and rehealing along brittle fracture planes and are very similar to those described by Boyd and Nixon (1978) for lherzolitic phlogopites from kimberlites in South Africa.

Macrorcrysts and groundmass chlorite

When calcite is the major matrix mineral, groundmass chlorite is found with only minor modal amounts of Ti, Cr-rich phlogopite. In those kimberlites where matrix serpentine is predominant, however, groundmass Ti, Cr-rich phlogopite is abundant and chlorite is sparse or absent. Large (0.25–0.5 cm) chlorites are anhedral and xenocrystic in appearance but finer grained groundmass chlorites are present as perfect euhedral platelets (Fig. 3a) averaging =0.05 mm in cross-section. They occur either as disseminated crystals in the carbonatitic-kimberlite groundmass or as aggregate platelets (Fig. 3b) in carbonate rich pockets of less carbonated kimberlite. In some cases the platelets are optically zoned (Fig. 3a). These chlorites as well as the others are strongly pleochroic in deep blue-green with abnormal blue interference colors and a small negative 2V(=15°). Occasional decomposition of macrorcrystic chlorite results in the formation of admixtures of goethite + hematite + complex intergrowths of finely disseminated calcite and silicate minerals (Fig. 3c). Expansion of the sheet silicate and swelling and distortion of the chlorite takes place.

Replacement chlorite

Reversely (R) pleochroic phlogopites (α > γ, where α = tan, and γ = colorless) form cores to normally (N) pleochroic phlogopites (α < γ, where α = colorless and γ = tan in color). The early phlogopites (R) are preferentially replaced by chlorite along cleavage planes (Fig. 3d). The phlogopites are consistently >0.1 mm in longest dimension, and phlogopites (R) similar to these have been described from a number of kimberlites in South Africa (Farmer and Boettcher, 1981).

Mineral chemistry

Representative averages of electron microbeam analyses of the Koidu chlorites are listed in Tables 1-3. Previously published kimberlitic chlorite compositions are also presented and have been recalculated based on a theoretical 28 oxygen formula cell. In most of the Koidu chlorites studied, two, three, or in some cases four distinct compositions were determined. Some of the components are evident in the photomicrographs in Figure 2 but others are not illustrated and are on a much finer scale.

Major elements

The unusual chemistry of the chlorites is distinguished by their low Al₂O₃ (8–12 wt.%), high SiO₂ (28.97–41.65 wt.%), and MgO (19.0–28.0 wt.%) values coupled with high Fe (up to 29.5 wt.% as FeO). Nodules (CHK-1, 2, and 3) with two compositional types in groups F, D, and T (Table 1) have hosts with low FeO₄(=7 wt.%), high SiO₂(=41 wt.%), and Al₂O₃ averaging 11.5 wt.%. This compositional type is referred to as low iron chlorite. By contrast, the high iron chlorites average 21.5 wt.% FeO₄, are lower in SiO₂ (31.7 wt.%), and lower in Al₂O₃ (8.6 wt.%). The average MgO contents in both the high and low iron chlorites is 26 wt.%. Nodules CHK-7 (group F) has three compositional types (Table 2), a high iron chlorite host (the inverse of CHK-1, 2, and 3), a low Fe chlorite (8.7 wt.% FeO₄), and a chlorite of intermediate FeO₄ (13.1 wt.%) content. Aluminum and SiO₂ vary sympathetically and MgO ranges from 24–28 wt.%.
Nodule CHK-13 (group T) has four compositional components (Table 2) of which three are approximately in equal proportions. Here again, low and high iron chlorites are present, but in addition there are two intermediate iron chlorites having 10 and 15 wt.% FeO.<br><br>Compositions of five additional nodules (CHK-4, 1B, 3B, 4B, and 9) are given in Table 2, representing groups F, T, and C. These nodules have not been characterized in the same detail but the major compositional host phases are high, low, or intermediate iron chlorites, similar in major element compositions to those described above. The replacement chlorites (Fig. 3d) in phlogopite...
as well as the groundmass chlorites (Fig. 3a-b, Table 3) are high Fe compositional types.

Considering the bulk compositions of the entire group, the three chemical chlorite types may now be defined as low (7–10 wt.% FeO), intermediate (12–14 wt.% FeO), and high (17–20 wt.% FeO) iron varieties.

In order to maintain charge balance, a large amount of ferric iron is required for the higher Fe chlorite varieties in the absence of major concentrations of other trivalent cations. Even though the low Fe varieties contain higher octahedral Al, considerable Fe³⁺ or octahedral vacancies are necessary assuming a formula fit to theoretical chlorite. The low Fe varieties, however, yield a reasonable cation total to a theoretical vermiculite formula of 22 oxygens and these phases may indeed be vermiculite or interstratified vermiculite/phlogopite (i.e., CHK-13, analysis D) or vermiculite/chlorite. Because of probable multicomponent complexities in these phases the theoretical 28 oxygens is used. This is a reasonable assumption for most chlorites (Foster, 1962) but it is possible that some oxygen has replaced (OH); this increases the cation total but decreases tetrahedral Al which in many cases is already fairly low. Variations in Al, Fe²⁺, and Mg are shown in Figure 4 and are compared to chlorites from other kimberlites. A well-defined trend is apparent for the Koidu and Mir chlorites and for some of the Utah samples; a few of the latter are enriched in Mg and are slightly removed from the arcuate trend displayed by the remaining groups.

Minor elements

The Koidu chlorites have minor concentrations of MnO (0.09 wt.% max), Cr₂O₃ (0.51 wt.% max), and TiO₂ (0.14–0.43 wt.%). There is a tight cluster of the latter two oxides around 0.1 wt.% Cr₂O₃ and 0.2 wt.% TiO₂ (Fig. 5). The few anomalously high contents are associated with groundmass chlorites and one of the chlorite nodules. The minor element concentration of the Koidu chlorites are markedly different from those of the Utah specimens, which are high chromium chlorites (0.23–3.90 wt.% Cr₂O₃). The chlorite from the Mir pipe, however, is similar to the Koidu samples having 0.26 wt.% Cr₂O₃, and 0.32 wt.% TiO₂.

Na, K, and Ca

Sodium contents are minimal in all Kimberlithic chlorites with a maximum of 0.07 wt.% Na₂O for those at Koidu to 0.03 wt.% Na₂O for the Utah and Siberia samples. Potassium, however, is present in concentrations of up to 2.31 wt.% K₂O, and CaO contents up to 0.25 wt.% were detected for Koidu. The modal proportions of the high

Table 1. Compositions of discrete chlorite nodules.

<table>
<thead>
<tr>
<th>X</th>
<th>CHK-1 (g)</th>
<th>CHK-2 (g)</th>
<th>CHK-3 (g)</th>
<th>CHK-6 (g)</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.10</td>
<td>48.12</td>
<td>48.14</td>
<td>48.16</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.15</td>
<td>0.16</td>
<td>0.17</td>
<td>0.18</td>
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<tr>
<td>Al₂O₃</td>
<td>10.89</td>
<td>10.90</td>
<td>10.91</td>
<td>10.92</td>
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<tr>
<td>Fe₂O₃</td>
<td>3.12</td>
<td>3.13</td>
<td>3.14</td>
<td>3.15</td>
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<tr>
<td>MgO</td>
<td>5.54</td>
<td>5.55</td>
<td>5.56</td>
<td>5.57</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>CaO</td>
<td>0.15</td>
<td>0.16</td>
<td>0.17</td>
<td>0.18</td>
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<tr>
<td>Na₂O</td>
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<td>0.02</td>
<td>0.03</td>
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<td>K₂O</td>
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<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>FeO</td>
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<td>8.03</td>
<td>8.04</td>
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<td>Fe²⁺</td>
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<td>Mg²⁺</td>
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<td>3.47</td>
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<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
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<tr>
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<td>Ta⁵⁺</td>
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<td>H₂O</td>
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<td>OH</td>
<td>3.12</td>
<td>3.13</td>
<td>3.14</td>
<td>3.15</td>
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</table>

(X) sample number and textural type.
* Based on the unit cell assuming theoretical (OH) content.
+ Based on the difference obtained by wet chemical analysis for FeO
# Number of analyses averaged together.
* Estimated modal percent used in bulk analysis computation.
Table 2. Compositions of discrete chlorite nodules.

<table>
<thead>
<tr>
<th>Chlorite Analysis</th>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHK-7 (F)</td>
<td>41.00</td>
<td>0.19</td>
<td>12.02</td>
<td>8.67</td>
<td>27.54</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>86.86</td>
</tr>
<tr>
<td>CHK-13 (T)</td>
<td>37.73</td>
<td>0.19</td>
<td>10.91</td>
<td>7.06</td>
<td>27.95</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>82.08</td>
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<tr>
<td>CHK-14 (C)</td>
<td>43.93</td>
<td>0.22</td>
<td>8.12</td>
<td>6.17</td>
<td>27.51</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>82.55</td>
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<tr>
<td>CHK-18 (B)</td>
<td>41.35</td>
<td>0.20</td>
<td>11.26</td>
<td>5.76</td>
<td>25.54</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>83.08</td>
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<tr>
<td>CHK-38 (T)</td>
<td>41.35</td>
<td>0.20</td>
<td>11.26</td>
<td>5.76</td>
<td>25.54</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>83.08</td>
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<tr>
<td>CHK-18 (C)</td>
<td>37.20</td>
<td>0.20</td>
<td>10.27</td>
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<td>24.66</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>79.95</td>
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<td>CHK-9 (F)</td>
<td>34.62</td>
<td>0.20</td>
<td>10.86</td>
<td>4.52</td>
<td>24.66</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>77.78</td>
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</table>

K2O chlorites are 2% (CHK-3, group T, analysis C, Table 1), 50% (CHK-6, group F, analysis B, Table 1), and 34% (CHK-13, group T, analysis D, Table 2). These are all low Fe chlorites. Both K and Ca are considered to be incompatible with the chlorite structure (Pauling, 1930; Foster, 1962). It is likely that the K (+Ca) is present either in an interstratified phlogopite-(chlorite and/or vermiculite) phase or in incompletely replaced phlogopite crystals.

Combined elemental relations

In order to consider all elements on a single two-dimensional plot, the compositional space shown in Figure 6 is useful and is adopted from Robinson et al. (1982). All kimberlitic chlorite analyses are plotted including those from the Cane Valley diatreme, the Moses Rock dikes, and the Mir pipe. Ideal trioctahedral ("Tri") chlorite is shown and with increasing substitution of Al ideal chlorite compositions plot along the clinochlore-amosite join (Fig. 6). Ideal chlorite compositions with Al substitution less than that of ideal chlorite plot towards serpentine and away from clinochlore. Data for kimberlitic chlorites from Utah and Siberia lie along this trend. Displacements from this join and towards olivine-spinel (ol-sp) indicate that ferric iron is present. Similarly, chlorites plotting to the right of this join have variable degrees of octahedral vacancies. The Koidu chlorites show an enrichment of Si relative to ideal clinochlore and two subtle groups are present. One group consists of the high Fe chlorites (i.e., softer lighter phase, Fig. 2c and light flame-like phase Fig. 2e-f) plotting to the left of the clinochlore-serpentine join. When ferric iron is considered, these chlorite compositions move towards the "Tri-Di" octahedral region parallel to the join clinochlore-"Di". The second group is defined by the low Fe and high Si (±K2O) chlorites (i.e., crossfibers, Fig. 2c and the dark phases in Fig. 2e-f). These compositions plot towards talc (vermiculite) with ferric iron having less influence. Compositions are displaced to the right of these data after consideration of Fe3+ in the analyses.

Naturally occurring chlorites with octahedral vacancies were summarized by Eggleton and Bailey (1967) and are plotted as a field in Figure 6. Natural dioctahedral chlorites show a range in Si-R3* with Al being the dominant trivalent cation. "Di-Tri" octahedral chlorites show an enrichment of Si relative to ideal compositions and again the trivalent cation is predominantly Al. No naturally occurring "Tri-Di" octahedral chlorites have yet been found (Bailey, 1980). In chlorites, the lower the Si and the higher the tetrahedral Al values, the stronger will be the resulting interlayer bonding (Foster, 1962). Ideally, octahedral R3+ cations should equal tetrahedral Al3+ cations, but this rarely happens in nature. For the high Fe chlorites, tetrahedral Al is far in excess of octahedral Al (Tables 1–3). In order to maintain charge balance some...
**Chlorite structural types**

X-ray study shows that the layer-interlayer assemblages are dominantly of the Ia type in all four samples examined. This terminology is from Bailey and Brown (1962), in which the symbol I means that the directions of stagger of the octahedral sheets in the 2:1 layer and the interlayer are the same, and a means that interlayer cations project normal to the layers onto tetrahedral cations in the 2:1 layers above and below (Shirozu and Bailey, 1965). The close approach of interlayer and tetrahedral cations in the a position leads to cation-cation repulsion and consequent instability relative to the alternative b position. This accounts for the fact that Ia chlorites were the least abundant among the 303 chlorite specimens included in a survey of the abundances of structural types in nature by Bailey and Brown (1962). On the other hand, the Ia structural type is the only one found to date in vermiculite, where enhanced stability is gained primarily by having relatively few interlayer cations and secondarily by cation order patterns that achieve local charge balance (Shirozu and Bailey, 1966). Interlayer vacancies would enhance the stability of the Ia structural type in chlorite also, and it is noteworthy that Hayes (1970) tentatively concluded that Ia chlorites found in sedimentary rocks are transitional to vermiculite. This is the case in the Koidu chlorites also, where significant numbers of interlayer vacancies in all of the samples have been inferred from the chemical data of the preceding section and interlayer vacancies have been confirmed in two of the samples (CHK-1, and CHK-2) based on electron density measurements (Fig. 7).

Figure 7 was constructed using 28 00I reflections for each crystal after least-squares refinement of z-coordinates, cation multiplicities, and isotropic B values. The electron density in the interlayer sheet at zlc = 0° is very low (about 13 e- in CHK-I and 22 e- in CHK-2) relative to that of the octahedral cation plane in the 2:1 layer at zlc = 180° (about 44 e- and 46 e-). The densities for the tetrahedral cation plane at zlc = 110.9° suggest substitution of 0.1 atoms of tetrahedral Fe³⁺ per formula unit in CHK-1 and 0.2 atoms in CHK-2.

The low interlayer cation electron density and the broad peaks in the map of CHK-1 suggest that this specimen approaches true vermiculite, whereas specimen CHK-2 is slightly more chloritic. This has been confirmed by heating tests. Pieces of specimens CHK-1, CHK-2, CHK-6, and CHK-13 were ground under acetone, prepared as oriented slides, and heated at 600°C in a muffle furnace for one hour. X-ray powder diffractograms obtained in a dry air environment showed that the 14Å spacings of the untreated samples had collapsed completely to 10Å in specimens CHK-1 and CHK-6 and about 60% had collapsed to 10Å in specimens CHK-2 and CHK-13. The complete collapse of specimens CHK-1 and CHK-6 relative to the two other Koidu specimens is in accord with the differences observed in their 00I intensi-
Fig. 3. a) Euhedral groundmass chlorite from section KD-80-5. Microprobe analyses of this grain are given in Table 4. Transmitted light, air objective. b) Stacked chlorite platelets in groundmass kimberlite from section KD-80-5. Transmitted light, air objective. c) Chlorite (center) alteration to goethite and hematite (highly reflective phase), from section KD-80-13. Microprobe analyses are not given. Transmitted and reflected light, air objective. d) Early reversely pleochroic (R) phlogopite rimmed by late stage kimberlitic phlogopite with normal pleochroism (N), from section KD-80-7, area A, grain 3. Dark areas in the core phlogopite are chlorite. Microprobe traverse analyses across this grain are given in Tompkins and Haggerty (1983b). Transmitted light, air objective. Scale bars (a-b : 0.05mm; (c-d) = 0.2mm.

ties. Vermiculite samples CHK-1 and CHK-6 have extremely strong 14Å intensities, which are a consequence of the small amount of scattering power present in the interlayers. The 14Å peaks in the other two samples are intensified also, but not to the same degree. For example, the 14Å/7Å intensity ratio for the untreated CHK-1 sample is 37.0 and for the CHK-2 sample is 1.8.

Although stacking of adjacent 14Å structural units is often semi-random in chlorite, this is not the case in the Koidu specimens. The fibrous vermiculite specimens CHK-1 and CHK-6 were found to be the same, for the fibers sampled, and to have the fibers oriented parallel to crystallographic Y. All fibers have a 2-layer structure of the type labeled “s” by Mathieson and Walker (1954), in which there is an L type shift within each 2:1 layer (−a/3 parallel to the symmetry plane) and adjacent layers are also shifted by +b/3 and −b/3 relative to one another. No second phase was found by either powder or single crystal patterns of the CHK-1 and CHK-6 samples for the fibers studied.

Shirozu and Bailey (1966) refined the structure of a 2-layer “s” type vermiculite from Llano County, Texas, and consider the “s” sequence to be the most stable structure for vermiculite. De la Calle et al. (1976) and De la Calle et al. (1978) determined experimentally that the “s” structure occurs only as a result of vermiculitization of phlogopite-M. The transformation is reversible in the laboratory. They designate the “s” structure as the V₁ type and illustrate identification of different vermiculite structures by means of the diagnostic 02/ reflections. They point out that the observed diffuseness of these reflections in V₁ indicates a semi-ordered structure having mistakes in the regularity of the +b/3 and −b/3 shifts, relative to the ideal regular “s” model, such that there is equal probability of a given layer having a +b/3 or −b/3 shift.

Specimen CHK-2 is platy. One of the four platelets studied by precession photography showed a superposition of Ia and IIb type patterns. The other platelets showed only the Ia single crystal pattern, but abundant
extraneous streaks from other incoherently oriented phase(s) also are present. Powder patterns of the bulk sample confirmed the presence of Ia and IIb materials. The Ia material in this specimen has a 2-layer sequence labeled "t" by Mathieson and Walker (1954). They found this sequence in a vermiculite from Kenya, which they believed to be the average result of the equal probability of adoption of the 2-layer sequences "q" and "r". In both of these structures adjacent layers are related by 120° rotations, but differ in the sense of the b/3 shifts. De la Calle et al. (1976) and De la Calle et al. (1978) determined experimentally that the vermiculite "t" structure (V II in their terminology) transforms only to phlogopite-2M₁, which also incorporates 120° layer rotations in its structure and is considered the parent material. Both phlogopite-2M₁ and vermiculite "t" = V II are rare in nature. De la Calle et al. (1976) and De la Calle et al. (1978) conclude from the modulated streaks along the 02l row line that V II also is a semi-ordered structure in which there is an equal probability of a +b/3 or a −b/3 shift of a given layer. Instead of describing it as an average structure of the regular "q" and "r" sequences, therefore, V II is better described as semi-ordered with a layer sequence given by +120° ± b/3, −120° ± b/3, 120° ± b/3, etc. It is
not known in specimen CHK-2 whether or not the Ia stacking sequence is restricted to the collapsible vermiculitic layers and the IIb sequence to the chloritic layers, but this is a possibility.

Plates from specimen CHK-13 readily break into fibers upon cutting. Six fibers were found to give superposition of Ia and IIb chlorite patterns on precession photographs. This overlap prevented determination of the precise stacking sequence of layers in each phase. The IIb chlorite is the most abundant structural type and is believed by Bailey and Brown (1962) to be the most stable chlorite. It is the only chlorite to be synthesized to date, and is the only chlorite structural type found in the greenschist metamorphic facies, except in clearly retrograde reactions. Thus it is considered the higher temperature form of chlorite, somewhat analogous to the 1M polytype in the phlogopite system and the 2M1 polytype in the muscovite system. It is not known whether or not the Ia stacking sequence is restricted to the collapsible layers in specimen CHK-13.

Discussion

Experimental studies on the alteration of phlogopite to vermiculite, or vice-versa, (De la Calle et al., 1976; De La Calle et al., 1978) show without exception that 2-layer type V1 (="s") structures form from 1M phlogopites, and that type V11 (="t") structures result from 2M1 phlogopites. Neither of these 2-layer structures has been recognized previously in chlorite and may be restricted to the vermiculite phases. Soboleva et al. (1982) studied phlogopites from the Yakutian kimberlites and determined that all specimens they examined are 1M polytypes. These data coupled with the selective replacement of early macrocrystic phlogopites by chlorite at Koidu suggests that the precursor phase to the discrete chlorite nodules was probably phlogopite and that the ultimate end product would be vermiculite. This sequence of kimberlite pre and post emplacement alteration (phlogopite—chlorite—vermiculite) is consistent with that proposed by Kreston (1973).

The phlogopite (R)—chlorite macrocrysts lend strong support in favor of a similar phlogopite composition for the discrete nodules; some xenocryst-like chlorites in the groundmass may represent disaggregated nodules. Identical Cd2O3 and TiO2 contents between the chlorite nodules and core phlogopites (R) are observed (Tompkins, 1983). Such low Cd2O3, TiO2, and Al2O3 values represent growth in a highly depleted environment. Deformation kink bands in the nodules (Fig. 2) and chemical homogeneity of the core (R) phlogopites (Tompkins and Haggerty, 1983a) is compatible with crystal growth in a mantle source region prior to incorporation in the kimberlite host (Boyd and Nixon, 1978; Farmer and Boettcher, 1981).

Experimental studies on the oxidation state of Fe in potassium rich melts show that Fe is dominantly in the trivalent state, and that Fe3+ behaves as a tetrahedral species in peralkaline conditions (Dickenson and Hess, 1981). Potassium will act as an efficient charge balancing species and tetrahedral Al3+ expands the framework to allow the substitution of Fe3+ in the tetrahedral site. The early core phlogopites (R) are reversely pleochroic, most probably due to the effects of tetrahedral Fe; they represent crystallization from a depleted potassium-rich source in which tetrahedral Fe3+ played an important role in the absence of sufficient Al3+. Late stage reactions of disseminated early phlogopite nodules with the kimberlite liquid has permitted the nucleation and growth of Ti and Cr enriched phlogopites.

Forbes and Flower (1974) have demonstrated experimentally that Ti-rich phlogopites are more stable under mantle conditions than Ti-free phlogopites. If Ti acts as a stabilizer to the phlogopite structure then the preferential replacement of the reversely pleochroic phlogopites by chlorite may result from Ti depletion and Fe enrichment. The other possibility is that chlorite replacement occurred during a “chlorite event” as the rising kimberlite magma passed through the chlorite stability field. Late stage precipitation of Ti-rich groundmass phlogopite unaltered by, and in conjunction with chlorite (Fig. 3) further emphasizes the stabilizing effect of Ti on phlogopite and the probable primary occurrence of groundmass chlorite.

Water-CO2 activity appears to be the driving mechanism for chloritization in the kimberlite. Vermiculite is present only in weathered kimberlite (Fairbain and Robertson, 1966) under hydrous and post emplacement conditions. When CO2 activity is low, phlogopite (R+N) is more stable and chlorite is present in minor amounts. Some core phlogopites may even remain totally unaffected by chloritization. As phlogopite becomes unstable under conditions of increasing carbonitization, the reaction to chlorite requires the formation of brucite and the release of interlayer K. Magnesium ions must, therefore, be in abundance and readily available for linkage with hydroxyl molecules. In the carbonatic kimberlites, olivine is pseudomorphed by calcite, and chlorite is stable relative to phlogopite (Tompkins and Haggerty, 1983b). The carbonitization of olivine is, hence, a probable source to produce the required flux of Mg ions required for brucite formation. The XH2O/XCO2 ratio or changes in P-T conditions would be required to decrease sufficiently, subsequent to carbonitization, to permit the formation of brucite and the ultimate demise of phlogopite. This is necessary because positively charged brucite layers replace the interlayer K ions. Highly mobile K ions can be more readily transported in volatile rich fluids and may precipitate to form other late-stage K-bearing phases. Erlank and Rickard (1977) and Erlank et al. (1982) consider K-metasomatism to be widespread in the upper mantle and although we have no direct evidence that K-mobilization is related to the processes we invoke, the removal of K is nonetheless required for the transformation of phlogopite to chlorite. It is possible that the high K-chlorites
contain a vestige of earlier phlogopite and in this sense represents incipient transformation to chlorite and/or vermiculite. Primary, euhedral groundmass chlorite is Fe-enriched and these are comparable in most respects to the most Fe-rich chlorite nodules.

The formation of phlogopite was at lower P-T conditions than the diamond/graphite transition in the depleted portion of the peridotite mantle (Farmer and Boettcher, 1981). Phlogopite intergrowths with diamond (Prinz et al., 1975) are typically very high in TiO$_2$ (10.8 wt.%) consistent with growth from an evolved liquid. MARID suite rocks (which are most similar to the core phlogopite (R) in composition) are considered to have equilibrated under relatively shallow depths resulting from early plutonic kimberlite pulses (Dawson and Smith, 1977). In the system MgO-SiO$_2$-CO$_2$-H$_2$O the subsolidus formation of brucite and carbonate from forsterite and vapor occurs with decreasing temperature and/or increasing pressure and H$_2$O/CO$_2$ values (Ellis and Wyllie, 1980). Based on the stability of K-richerite (Kushiro and Erlank, 1970), the MARID suite nodules are considered to have crystalized at depths of 75–100 km. At these depths the chlorite dehydration reaction curve (Jenkins, 1981) intersects the Precambrian shield geotherm and is also coincident with the depth where CO$_2$ ceases to be a dominant solidus component (Wyllie, 1980), implying that high fluxes of CO$_2$ vapor are present.

Experimental and theoretical studies of the Mg end-member clinohlore (Jenkins, 1981; Obata and Thompson, 1981) show that chlorite (type IIb) can be stable at low temperatures (<900°C) up to ~75 km in the upper mantle and an alternative possibility is that some of the Koidu chlorites (types Ia, and Ia/IIb) are not pseudomorphs after phlogopite. Chlorite in diamond inclusions (type Ib; Mitchell and Giardini, 1977) are similar to our low Fe chlorite compositional type in FeO, SiO$_2$, and Al$_2$O$_3$ contents only. In the two inclusions reported, one is exceptionally enriched in CaO (10.7 wt.%) and probably represents an overlap with coexisting clinoxyroxene, the other is a high magnesium variety (40.3 wt.%) with almost twice the concentration of MgO than those from Koidu. Although the most stable chlorite polytype is type IIb it is interesting to note that the diamond inclusion is not a IIb but type Ib. Whether type Ia chlorites are stable at mantle P and T's under appropriate conditions is uncertain. Given these uncertainties it is still possible that the Koidu chlorite nodules are indeed primary upper mantle phases. The experimental data are not entirely appropriate to the compositions we discuss and data are clearly required to evaluate the high pressure stability of low Al$_2$O$_3$, high Mg-Fe chlorites.

**Conclusions**

Chlorite is present in three modes of occurrence in the Koidu kimberlite complex: (1) discrete nodules with fibrous, platy, tectonized, or multiply cleaved textural habits; (2) coarse anhedral macrocrysts and small euhedral platelets in kimberlite groundmass; and (3) as preferential replacement products of reversely pleochroic phlogopite. The chlorites are compositionally distinctive, high in SiO$_2$ and MgO and low in Al$_2$O$_3$ contents. Three dominant compositional types are designated as high (25 wt.% FeO), intermediate (15 wt.%) and low (8 wt.%) FeO varieties, with a minor type that is low in iron but high in K$_2$O. Compositions, comparisons with ideal chlorite, and electron density measurements, suggest extensive vacancies in the interlayer sheet. Fibrous specimens are Ia structural types, ubiquitous in vermiculite but among the least abundant of the chlorites found in nature. There is evidence for nearly complete transformation to vermiculite and for phlogopite as a precursor. Platy chlorites are intergrown Ia and IIb structural types, the latter being of relatively high temperature origin, the most stable among chlorites, and the most abundant structural type in nature.

Euhedral kimberlite groundmass chlorites are unequivocally of primary magmatic origin and high TiO$_2$ contents are consistent with crystallization from a residual melt. Carbonatite associations or high calcite contents, and the alteration of phlogopite to Ia chlorite implies chloritization under high XCO$_2$ activity. This condition prevailed in a volumetrically minor component of Pipe 2 and in many of the kimberlite dikes, suggesting that CO$_2$ volatilization was impaired, possibly because these facies were passive intrusions. By contrast, the dominant diatreme facies were explosive and enriched in H$_2$O, and this resulted in serpentine + phlogopite. Although eclogites are the only lithic nodules identified at Koidu that can be directly linked to a fertile asthenosphere, it is also possible that metasomatized lithosphere was sampled in the form of phlogopite nodules that are now completely transformed to chlorite.

The chlorites we describe may not be of mantle origin; additional chemical and crystallographic data are required on these and chlorites in other kimberlites. Experimental data appropriate to these compositions are also needed to determine the conditions required for Ia and IIb type chlorite formation, and to address the problem of chlorite stability in the upper mantle.

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