

## **Titanian clinohumite in the carbonatites of the Jacupiranga Complex, Brazil: Mineral chemistry and comparison with titanian clinohumite from other environments**

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### **ABSTRACT**

Titanian clinohumite (TiCl) occurs in the carbonatites of the Jacupiranga Complex, Brazil, either as the result of alteration of olivine (Mitchell, 1978) or in the reaction rock developed in the contact of the carbonatites and the host magnetite pyroxenite, where it may not be related to olivine. Lamellae of titanian chondrodite (TiCh) are found, and the presence of lamellae of polysomes representing  $n > 4$  is inferred. The TiCl samples contain TiO<sub>2</sub> up to 3.78 wt%, FeO up to 3.09 wt%, and F up to 2.34 wt%. Fe and Ti show a positive correlation. Complex zoning is always present. The only consistent trend is that of increasing TiO<sub>2</sub> toward the margins, but even this trend is only observed in the crystals of the reaction rock. The partitioning of Fe and Mg between TiCl and olivine indicates enrichment of Mg in the TiCl and is different for samples from the three sovites. The characteristics of the TiCl are thought to derive from a changing metasomatic environment, and all TiCl so far reported from carbonatite complexes is possibly of metasomatic origin. The Jacupiranga TiCl is similar in composition to TiCl from marbles, an observation that cannot be extended to TiCl from carbonatites in general. Samples of TiCl from kimberlites have compositions similar to those from some Alpine peridotites. Fluorine TiCl is certainly stable in the upper mantle, but because of its rarity it is considered a mineral of no importance to mantle geology.

### **INTRODUCTION**

Titanian clinohumite (TiCl) is not an abundant mineral in the Earth's crust but is the most abundant species of the humite group. Special attention was paid to it when in 1976 Aoki et al. suggested that it could be a storage location of H<sub>2</sub>O in the mantle. However, later studies generated contrary evidence (Smith, 1977; Mitchell, 1978; Engi and Lindsley, 1980; Trommsdorff and Evans, 1980). Dymek et al. (1988) returned to the problem, suggesting that titanian chondrodite (TiCh) and not TiCl "ought to be evaluated further as a possible upper mantle mineral, as it is the expected high-pressure phase."

The crystal structure of the TiCl has been studied by Robinson et al. (1973), Kocman and Rucklidge (1973), Fujino and Takéuchi (1978), Ribbe (1979), and Abbott et al. (1989), and TEM studies of this mineral were carried out by Muller and Wenk (1978) and White and Hyde (1982). Experimental work on the stability of the hydroxyl-TiCl has been performed by Merrill et al. (1972), Yamamoto and Akimoto (1977), and Engi and Lindsley (1980). Reviews of the humite group minerals can be found in Ribbe (1980) and Deer et al. (1982).

Clinohumite was reported in the Jacupiranga carbonatites by Melcher (1966), and one analysis of it was presented by Mitchell (1978). TiCl occurs in the Jacupiranga carbonatites as a product of alteration of olivine or in a rock that resulted from the reaction of the carbonatites

and the host magnetite pyroxenite (Gaspar and Wyllie, 1983). Microprobe analyses are presented in this contribution, and some structural and petrological implications are discussed. Analytical results are compared with those from other geological environments, and some considerations regarding TiCl occurrence in the upper mantle are briefly presented.

### **THE JACUPIRANGA COMPLEX**

Melcher (1966) presented the geology of the Jacupiranga Complex including the carbonatites. Gaspar and Wyllie (1983) summarized the available knowledge about the complex and presented new data on the carbonatites. Five different carbonatite intrusions were recognized (C1 to C5, from the oldest to the youngest). C1, C3, and C4 are sovites (calcite rock), C2 is a dolomitic sovite, and C5 is a rauhaugite (dolomite rock). Based on mineral chemistry, a sequence of magmatic evolution from C2 to C5 was established, but C1 represents a chemically separate intrusion (Gaspar and Wyllie, 1983, 1987). Roden et al. (1985) determined the Sr and Nd isotopic composition of the Jacupiranga carbonatites and found that C1 to C3 are isotopically different from C4 and C5, and magma contamination is evoked. Gaspar (1989) presented a comprehensive study of the geology and mineralogy of the complex.

### The reaction rock

A reaction that developed between carbonatites and the host magnetite pyroxenite formed a rock that is composed of an alternation of carbonate and silicate-rich bands, millimeters to centimeters in width. The whole banded rock may reach more than 2 m in width. The silicate bands are composed mainly of brown phlogopite, acicular alkali amphibole, and magnetite with platy exsolution lamella of ilmenite. Calcite and apatite are also common. TiCl and serpentine pseudomorphs after olivine may be present. Near the magnetite pyroxenite contact, the grain size is submicroscopic, becoming larger near the carbonatite bands. Locally, meters-wide pockets of pegmatitic recrystallization occur where phlogopite crystals may reach up to 40 cm in diameter. In these portions, many other mineral species may be found, but augite, perovskite, and several zeolites are the most common. The carbonate bands are composed of calcite with accessory brown phlogopite, apatite, and amphibole.

### Clinohumite

The Jacupiranga TiCl is orange to red-brown in color and displays a light yellow to colorless pleochroism in thin sections. It has two different types of occurrence. The first is as reaction rims or patches in olivine crystals in the three sovites of the complex where some olivine crystals may be completely replaced (Mitchell, 1978). Rare coarse-grained samples of the C1 sovite contain no relicts of olivine. It was in these crystals that rims of chondrodite have been found during the analysis, and no optical discontinuity has been observed. In C4, the olivines are strongly serpentinized and only small patches of TiCl are found. The second type of occurrence is in the reaction rock. In this case, the crystals are well developed and locally very abundant, and they have diameters up to 2 mm. Habits vary from anhedral to euhedral short prisms, and inclusions of magnetite, ilmenite, and calcite are common. In a few cases the TiCl is poikilitic to these minerals.

### ANALYTICAL PROCEDURE

EDS analyses were carried out using an ARL/EMX automated microprobe. WDS analyses were performed in a Camebax Microbeam automated microprobe. Standard analysis conditions were used for both methods. Identical results were obtained by the two methods for major elements (Si, Ti, Fe, and Mg), with some differences for Mn and Ca. As would be expected, the EDS analyses failed to detect Mn and Ca or gave inaccurate results for them because of their low concentrations (Table 1). Data collection was done on crystal cores and rims. Four to six analyses were carried out on each crystal except in the chemical profiles. Averages were made according to the homogeneity of  $M_{Ti}/Si$  in each crystal (see below).

### ANALYTICAL RESULTS

The microprobe results of the Jacupiranga TiCl are presented in Table 1. The most remarkable feature of the

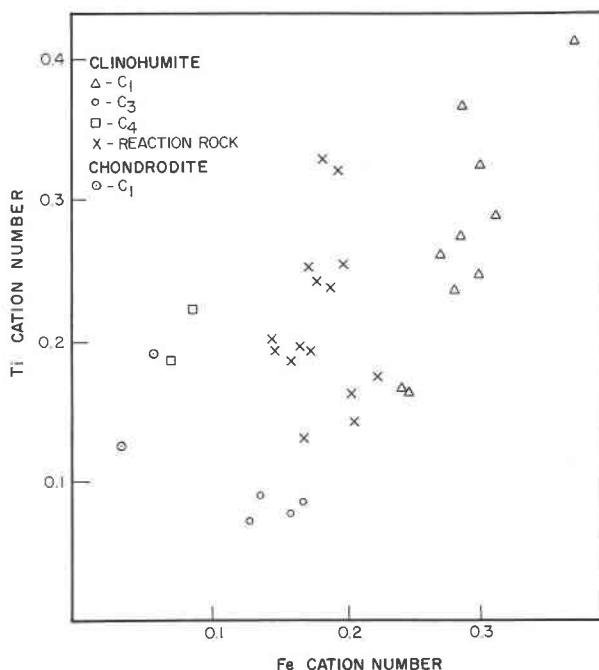


Fig. 1. TiCl and TiCh analyses (Table 1) showing a general positive correlation of Ti and Fe. Different total cation numbers used for normalizations (see discussion in the text) make comparisons based on absolute values meaningless.

TiCl is the variable metal to Si ratios ( $M_{Ti}/Si$ ) as discussed below. The highest FeO content is 3.09 wt%, and the highest  $TiO_2$  is 3.78 wt% for the TiCl and 4.43 wt% for the TiCh. The Ti/Si ratio in TiCh is higher than that of coexisting TiCl but not by a factor of 2 as would be expected in coexisting TiCh and TiCl (Aoki et al., 1976; Ehlers and Hoikens, 1987; Dymek et al., 1988). This factor of 2 results because chondrodite contains twice as many  $Mg(OH)F$  "layers" as does clinohumite. The  $Mg(OH)F$  "layer" is the part of the structure that contains the M3 site where Ti replaces Mg (Ribbe, 1979). It is apparent from Figure 1, despite some scattering of the data, that Ti and Fe show a positive correlation in the TiCl of the Jacupiranga carbonatites, a behavior already observed by Evans and Trommsdorff (1983) in the TiCl from an Alpine recrystallized garnet peridotite. In detail, however, TiCl from the reaction rock does not display this positive correlation: increasing Ti is accompanied by almost constant Fe.

The F contents (2.34–1.13 wt%) are in reasonable agreement with observations by Lapin (1982) that clinohumite from carbonatite environments reach 1.5–2.0 wt%. The highest F contents of the TiCh (3.0 and 4.43 wt%) do not represent higher  $X_F$  contents ( $\approx 0.35$ ) than those of the TiCl (0.3–0.6).  $X_F$  does not have a well-defined and constant negative correlation with Ti as would be expected from a substitution of the type  $MgF_2 = TiO_2$  (Evans and Trommsdorff, 1983; Dymek et al., 1988).  $Mg(OH)_2 = TiO_2$  is certainly the substitution mecha-

TABLE 1. Microprobe analytical results of clinohumite and chondrodite samples

	C1											
	1 (4)	2 (4)	3 (4)	4 (4)	5C (5)	5R (2)	6C <sub>1</sub> (2)	6C <sub>2</sub> (3)	6R (2)	7 (3)	8C (2)	8R (1)
SiO <sub>2</sub>	37.35	37.55	37.85	37.80	38.74	35.30	38.85	38.47	35.00	38.47	38.60	38.10
TiO <sub>2</sub>	3.45	3.26	2.05	2.08	3.36	4.43	3.55	3.78	2.93	2.54	2.93	2.97
MgO	53.20	53.20	54.40	54.35	53.84	55.10	53.00	53.63	56.50	53.40	53.35	53.50
FeO*	3.04	2.93	2.73	2.67	2.70	1.25	2.88	2.58	0.76	2.67	2.88	3.09
MnO	0.10				0.28	0.46	0.32	0.18	0.24	0.26	0.26	0.24
CaO	0.06		0.16	0.09	0.03	0.09	0.02	0.03	0.24	0.06		0.07
F	nd	nd	nd	nd	1.37	3.05	1.13	1.25	3.46	1.70	1.75	2.33
H <sub>2</sub> O**					0.91	2.73	0.60	0.87	2.92	0.92	0.81	1.04
Total	97.20	96.95	97.19	96.99	101.24	102.42	100.37	100.78	102.07	100.02	100.59	101.34
O = F					0.58	1.28	0.48	0.52	1.46	0.71	0.74	0.98
Total	97.20	96.95	97.19	97.00	100.66	101.14	99.90	100.26	100.61	99.30	99.85	100.36
Si	3.982	4.009	4.002	4.004	4.996	2.020	5.989	4.979	1.999	5.024	5.022	4.028
Ti	0.277	0.262	0.163	0.166	0.326	0.191	0.412	0.368	0.126	0.249	0.287	0.236
Mg	8.455	8.467	8.575	8.583	10.351	4.701	12.181	10.350	4.811	10.397	10.348	8.433
Fe <sup>2+</sup>	0.271	0.262	0.241	0.237	0.292	0.060	0.372	0.279	0.036	0.291	0.313	0.273
Mn	0.009				0.031	0.022	0.042	0.020	0.012	0.029	0.029	0.021
Ca	0.007		0.018	0.010	0.004	0.006	0.004	0.004	0.015	0.009		0.008
Total	13.000	13.000	13.000	13.000	16.000	7.000	19.000	16.000	7.000	16.000	16.000	13.000
F					0.560	0.556	0.558	0.516	0.627	0.701	0.722	0.785
OH†					0.788	1.062	0.619	0.748	1.121	0.801	0.704	0.743
M <sub>n</sub> /Si	2.265	2.243	2.248	2.247	2.202	2.465	2.172	2.213	2.501	2.185	2.186	2.227

	C3					C4			R				
	1 (4)	2C (2)	2R (2)	3 (4)	4 (4)	1 (2)	2 (3)	1C (2)	1R (2)	2C (2)	2R (2)	3C (2)	
SiO <sub>2</sub>	38.75	39.00	39.30	38.90	38.47	38.50	37.77	37.90	37.90	38.30	37.70	38.10	
TiO <sub>2</sub>	0.72	0.81	0.76	0.73	0.91	2.28	2.32	2.46	3.21	2.45	3.19	1.64	
MgO	55.90	56.00	56.00	56.40	55.55	55.50	55.10	55.20	54.40	55.00	54.30	55.70	
FeO*	1.17	1.47	1.30	1.17	1.25	0.78	0.81	1.65	1.89	1.89	2.20	1.90	
MnO					0.33	0.18	0.22						
CaO	0.38	0.35	0.19	0.25	0.03	0.05	0.02		0.12				
F	nd	nd	nd	nd	2.34	1.23	2.24	nd	nd	nd	nd	nd	
H <sub>2</sub> O**					1.01	1.23	1.24						
Total	96.92	97.63	97.55	97.45	99.89	99.76	99.72	97.21	97.52	97.64	97.39	97.34	
O = F					0.98	0.52	0.94						
Total	96.92	97.63	97.55	97.45	98.90	99.24	98.78	97.21	97.52	97.64	97.39	97.34	
Si	4.999	5.004	5.991	4.988	4.992	4.975	4.007	3.992	4.002	4.025	3.988	3.996	
Ti	0.070	0.078	0.087	0.070	0.089	0.221	0.185	0.195	0.255	0.194	0.254	0.129	
Mg	10.752	10.712	12.726	10.781	10.744	10.691	8.714	8.668	8.563	8.616	8.563	8.708	
Fe <sup>2+</sup>	0.127	0.158	0.166	0.125	0.136	0.085	0.072	0.145	0.167	0.166	0.195	0.167	
Mn					0.036	0.020	0.020						
Ca	0.052	0.048	0.031	0.035	0.005	0.008	0.002		0.014				
Total	16.000	16.000	19.000	16.000	16.000	16.000	13.000	13.000	13.000	13.000	13.000	13.000	
F					0.963	0.507	0.755						
OH†					0.860	1.051	0.874						
M <sub>n</sub> /Si	2.200	2.197	2.172	2.208	2.205	2.216	2.245	2.256	2.249	2.230	2.260	2.253	

	R										
	3R (2)	4C (2)	4R (2)	5C <sub>1</sub> (10)	5C <sub>2</sub> (2)	5R (4)	6C (2)	6R (2)	7C (2)	7R (2)	
SiO <sub>2</sub>	38.10	38.40	38.10	38.70	38.50	38.52	38.40	38.55	38.50	37.85	
TiO <sub>2</sub>	2.45	1.67	2.36	2.50	2.59	3.32	2.52	3.37	1.79	2.41	
MgO	54.90	55.30	55.40	54.90	55.60	54.22	54.90	53.65	54.55	53.20	
FeO*	1.95	1.86	1.81	1.65	1.64	1.77	1.63	1.66	2.01	1.68	
MnO				0.22	0.30	0.09	0.25	0.32	0.18	0.26	
CaO				0.02	0.01	0.01	0.01	0.02	0.00	0.03	
F	nd	nd	nd	2.27	1.88	1.24	1.47	1.20	1.49	1.56	
H <sub>2</sub> O**				0.69	1.38	0.99	1.58	0.97	1.20	1.00	
Total	97.40	97.23	97.67	100.95	101.92	100.17	100.75	99.75	99.73	97.99	
O = F				0.95	0.79	0.52	0.62	0.51	0.63	0.66	
Total	97.40	97.23	97.67	99.99	101.13	99.65	100.13	99.24	99.10	97.33	
Si	4.013	4.969	3.995	4.993	4.005	4.994	4.035	5.025	5.008	5.020	
Ti	0.194	0.163	0.186	0.243	0.203	0.323	0.199	0.330	0.175	0.240	
Mg	8.621	10.667	8.660	10.559	8.621	10.479	8.600	10.425	10.577	10.519	
Fe <sup>2+</sup>	0.172	0.201	0.159	0.178	0.143	0.192	0.143	0.181	0.219	0.186	
Mn				0.024	0.027	0.010	0.022	0.035	0.020	0.029	
Ca				0.003	0.002	0.002	0.001	0.003	0.001	0.004	
Total	13.000	16.000	13.000	16.000	13.000	16.000	13.000	16.000	16.000	16.000	

TABLE 1—Continued

	R									
	3R (2)	4C (2)	4R (2)	5C <sub>1</sub> (10)	5C <sub>2</sub> (2)	5R (4)	6C (2)	6R (2)	7C (2)	7R (2)
F				0.926	0.621	0.508	0.488	0.496	0.620	0.656
OH†				0.588	0.973	0.845	1.115	0.843	1.030	0.863
M <sub>Ti</sub> /Si	2.239	2.220	2.254	2.205	2.246	2.204	2.222	2.184	2.195	2.187

Note: C1, C3, C4 = carbonatites; R = reaction rock; (n) = number of analyses; nd = not determined (EDS); XC = core composition; XR = rim composition.

\* Total Fe as FeO.

\*\* Calculated.

† Calculated by OH = 2 - 2Ti - F.

nism in the Jacupiranga TiCl as well as in other occurrences (Jones et al., 1969). Cl could not be detected with the microprobe.

Despite the scatter of data in Figure 2, a roughly inverse variation of TiO<sub>2</sub> with MgO/(MgO + FeO + MnO) may be observed. This is caused by the substitution of both Ti and Fe for Mg. The analysis of a Jacupiranga TiCl presented by Mitchell (1978) is also plotted in Figure 2. According to Mitchell's description, it is a C1 TiCl. The TiO<sub>2</sub> content of this TiCl is similar to that from the C1 carbonatite, but it has more FeO than any of the C1 TiCl presented in this work. Observe that TiCl from each carbonatite and from the reaction rock has characteristic compositions that separate fields for each group. As observed in Figure 2, zoning is another feature of this TiCl. TiCl from carbonatites presents random variations, whereas that from the reaction rock shows a consistent increase of Ti toward the margins. Crystal averages were always made for TiCl from carbonatites except when M<sub>Ti</sub>/

Si changed throughout the crystal. In these cases, similar M<sub>Ti</sub>/Si analyses were averaged separately. Two cases of the zoning pattern present in these minerals will be examined in detail below but only after some discussion of M<sub>Ti</sub>/Si.

**The M<sub>Ti</sub>/Si ratio**

Jones et al. (1969) showed that the general formula for the Ti-bearing humite minerals is n[M<sub>2</sub>SiO<sub>4</sub>]·[M<sub>1-x</sub>Ti<sub>x</sub>(OH,F)<sub>2-2x</sub>O<sub>2x</sub>] where M includes the octahedrally coordinated cations Mg, Fe, Mn, Ca, Zn, etc., x < 1, and n is an integer that varies from 1 to 4, representing respectively the mineral species norbergite, chondrodite, humite, and clinohumite. Ribbe (1979) observed that x never appears to exceed approximately 0.5 Ti atoms per formula unit as a result of charge imbalances. Following the general formula above and using M<sub>Ti</sub> as the sum of all octahedral cations including Ti (to follow the Jones et al., 1969, nomenclature), M<sub>Ti</sub>/Si for each member of the group is different. These values are, for n from 1 to 4, 3.0, 2.5, 2.3, and 2.25, respectively.

Analyses of the Jacupiranga TiCl showed variable M<sub>Ti</sub>/Si. Table 1 shows M<sub>Ti</sub>/Si for the averages, and Figure 3

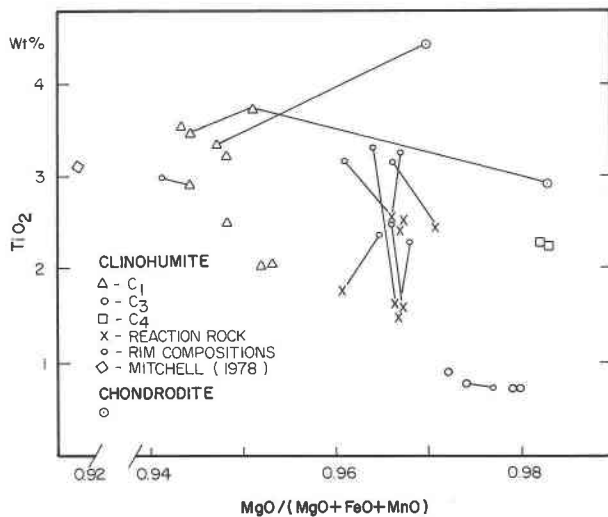


Fig. 2. Analyses of cores, rims, and coexisting TiCl and TiCh. Observe the constant TiO<sub>2</sub> enrichment toward the rims of TiCl from the reaction rock. Analysis from Mitchell (1978) is a TiCl from the C1 carbonatite. TiCl from the same origin tend to plot next to each other, delimiting a separate compositional field for each carbonatite and for the reaction rock.

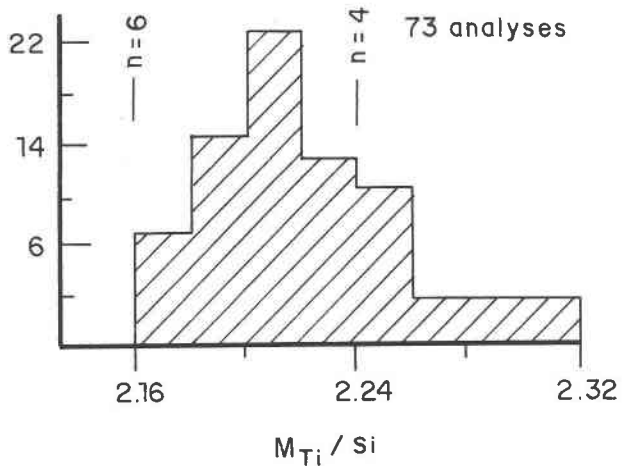


Fig. 3. Histogram representing 51 individual WDS analyses and 22 averages of two EDS analyses each. TiCh analyses are not included.

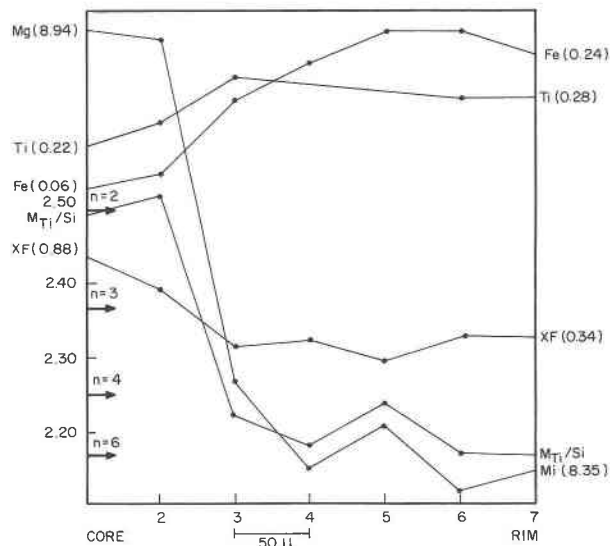


Fig. 4. Electron microprobe profile for a crystal from the C1 carbonatite where no olivine relict is present. The scale presented for  $M_{Ti}/Si$  is the same for the other elements (but the absolute numbers are different) except for  $X_F$ , which is half that scale. Different values of  $n$  corresponding to  $M_{Ti}/Si$  are shown. All analyses were normalized to 13 cations for the sake of comparison, except  $X_F$  that was calculated according to assigned  $n$  values.

is a histogram of all the data except the TiCh. It is clear from these data that a kind of nonstoichiometry must be present in the TiCl. Most of the data fall below the expected value of 2.25 that would be the minimum for the humite group, i.e., the clinohumite  $M_{Ti}/Si$ . Theoretically, it indicates that  $n > 4$  is present in these minerals.

Thompson (1978) considers the humite minerals as members of a polysomatic series where norbergite is taken as the limit of the series and the other members as an interlayering of olivine and norbergite modules. Muller and Wenk (1978) found in a preliminary electron microscopy study that structural faults in two samples of clinohumite corresponded to humite and chondrodite layers. White and Hyde (1982) carried out a study of synthetic and natural humite minerals using electron microscopy with the purpose of looking for upper members ( $n > 4$ ) in the group and coherent intergrowths between them. They found that clinohumite is a phase likely to contain lamellae parallel to (001) composed of  $n > 4$ , where  $n = \text{odd}$  is almost nonexistent. No perfectly ordered superstructures were found, but "some crystals gave lattice images with almost regular groups of faults corresponding to higher members of the series" (White and Hyde, 1982, p. 60). These crystals correspond, according to their figures, to clinohumite samples where the stacking sequence is mainly made up of  $n = 4$  and  $n = 6$  in different proportions for each superstructure. Highly disordered regions may present lamellae with  $n$  up to 24. If electron microprobe analyses were carried out on the clinohumite samples of White and Hyde (1982), there is no

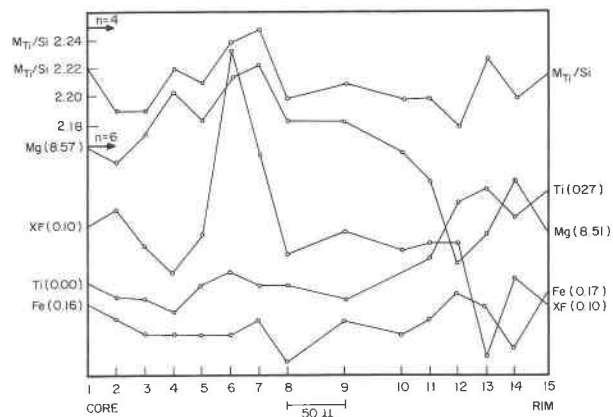


Fig. 5. Electron microprobe profile for a TiCl from the reaction rock. Scales and normalizations as in Figure 4.

doubt that a large range of  $M_{Ti}/Si$  would be found, mainly from 2.25 (the clinohumite ratio) to lower values (for  $n = 6$   $M_{Ti}/Si$  is 2.167 and for  $n = 8$   $M_{Ti}/Si$  is 2.125). The lower possible limit is 2.00, corresponding to the value for olivine, or  $n = \infty$ .

The great majority of the TiCl analyses from Jacupiranga are in the range of  $M_{Ti}/Si$  from 2.17 to 2.26 (Table 1 and Fig. 3). The first interpretation of these data indicates that these TiCl are composed of a mixture of  $n = 4$  ( $M_{Ti}/Si = 2.25$ ) and  $n = 6$  ( $M_{Ti}/Si = 2.167$ ), similar to those described by White and Hyde (1982). We have seen above that TiCh also occurs in the Jacupiranga TiCl. This kind of intergrowth results in larger areas of  $n = 2$  in the TiCl as few analyses seem to indicate a mixture of the two phases ( $M_{Ti}/Si > 2.25$ ) (Fig. 3). Intergrowths of TiCl and TiCh were also reported by White and Hyde (1982) in synthetic crystals, in natural crystals from the kimberlitic diatremes of the Colorado Plateau (Aoki et al., 1976), and from the Isua dunite (Dymek et al., 1988). Based on X-ray observations, Aoki et al. (1976) determined that their intergrowth was parallel to (001).

#### Interpretation of chemical profiles

The interpretation of the profiles is not simple because four variables may contribute to the observed variations. The first variable is the already-discussed superstructures and disordered faults inferred to be present, and the others are the chemical substitutions inherent to these minerals. The three principal mechanisms of substitution, modified from Evans and Trommsdorff (1983), are (1) Mg by Fe (and Mn, Ca), (2) OH by F, and (3)  $Mg(OH)_2$  by  $TiO_2$ .

Figure 4 shows a profile across a coarse-grained TiCl from the C1 carbonatite where no relict olivine is present. Analyses 1 and 2 correspond to TiCh, whereas the others correspond to intergrowths of TiCl and higher  $n$  members. Accordingly, the large variation observed between analyses 3 and 2 is a reflection of a change in the relative proportion of the elements present or, in other words, the

result of a change in the proportions of olivine and norbergite modules in the structures. In Figure 5 (a TiCl from the reaction rock), it is also possible to see that for the inner part of the crystal the observed variation in Mg is also a reflection of the change in the relative proportion of olivine and norbergite modules that is easily observed by the similar variations of Mg and  $M_{Ti}/Si$ . However, at point 9, Mg begins to diverge from  $M_{Ti}/Si$  and at the margin has an opposite behavior in relation to it. Such behavior is caused by the substitution of Mg by Fe and Ti, which can be seen in the profile (Fig. 5).

The H-H repulsion in the humite minerals plays a very important role in their stability (Fujino and Takéuchi, 1978), and this repulsion becomes stronger with decreasing  $n$  (Ribbe, 1979). Jones et al. (1969) found that  $X_F$  decreases from norbergite to clinohumite, i.e., with increasing  $n$ , which is in agreement with Ribbe's (1979) observation. The traverses in the TiCl from Jacupiranga (Figs. 4 and 5) show a similar behavior, which is evidenced by the same general variation of  $X_F$  and  $M_{Ti}/Si$ . This fact is more evident in the larger variations of  $M_{Ti}/Si$ , from TiCh to TiCl as in Figure 4 and from TiCl to TiCl intergrown with higher  $n$  members as in Figure 5. In detail, the substitution of  $MgF_2$  by  $TiO_2$  causes deviations in this behavior of  $X_F$ , as in analysis 13 of Figure 5.

#### $M_{Ti}/Si$ and $n$ values

As seen from Figures 4 and 5, the variation of  $M_{Ti}/Si$  inside each crystal is significant and the normalization of the analyses based on a unique number of cations for all the TiCl (as 13 for example) would result in cation numbers with little meaning. The normalization based on a fixed number of Si atoms would not solve the problem because the Si cation number per formula unit is equal to  $n$  and  $M_{Ti}/Si$  is a function of  $n$ . It does not matter what normalization number is used,  $M_{Ti}/Si$  is always the same for the same analysis. So, a first normalization was made based on 13 cations, and  $M_{Ti}/Si$  was calculated. New  $n$  values were then assigned to different analyses or averages according to  $M_{Ti}/Si$ , even if  $n$  needed to be an odd number. The final cation normalization was made based on the corresponding stoichiometric formula of the assigned  $n$  values (see Appendix 1). The results are presented in Table 1, where for each analysis Si (as an integer) is equal to the  $n$  value used and Total is the cation number used in the normalization. When we use  $n = 5$  or 6, it does not mean that a new mineral of the humite group exists corresponding to such  $n$  values, but it certainly represents intergrowths of the kind reported by White and Hyde (1982). Only TEM studies are able to reveal the real structures that are related to these numbers.

A nonstoichiometric humite mineral has been reported by Ehlers and Hoikens (1987). It occurs as lamellae in Ti-free clinohumite that is adjacent to olivine in marbles. The published analysis has a  $M_{Ti}/Si = 2.155$ , which is not far from the value of 2.167 that corresponds to  $n = 6$ . Cimmino et al. (1979) presented two analyses of a

"titaniferous mineral" that occurs associated with the TiCl and olivine in a metamorphosed peridotite from the Voltri Massif, Italy. The  $M_{Ti}/Si$  values in their analyses are low (2.065 and 2.005) and would represent very high  $n$  numbers, chiefly for the lowest value that is close to that of olivine. However, the high content of Ti in their analyses (3.95 and 3.93 wt%) suggests that these phases do not belong to the humite group. For very high  $n$  values, the number of the  $M(F,OH)O$  layers, where Ti enters the structure of the humite minerals (Ribbe, 1979), will be so small that such a high  $TiO_2$  content is not allowed, unless Ti enters the olivine layers, which seems unlikely.

#### PETROGENETIC CONSIDERATIONS ABOUT THE JACUPIRANGA TiCl

Clinohumite is reported to contain the same Mg-Fe ratio as coexisting olivine (Cimmino et al., 1979; Trommsdorff and Evans, 1980; Dymek et al., 1988). Evans and Trommsdorff (1983) found that the  $K_d$  for Fe-Mg partitioning between TiCl and olivine from an Alpine recrystallized garnet peridotite is a function of the Ti content and  $X_F$  in the TiCl. In Figure 10 of Dymek et al. (1988), two cases do not fall near the line representing a  $K_d = 1$  for coexisting clinohumite and olivine. One is the analysis of the Jacupiranga TiCl and olivine reported by Mitchell (1978). This pair gives  $K_d = 0.64$ . Our data give  $K_d = 0.62$  for a C1 sample,  $K_d = 0.49$  for a C3 sample, and  $K_d = 0.22$  for a C4 sample. Note that Mitchell's sample is also from the C1 carbonatite and is in good agreement with our data. The equations relating  $K_d$  and Ti or F from Evans and Trommsdorff (1983) do not apply to the Jacupiranga pairs, and we were not able to find any correlation between the observed values of  $K_d$  and other chemical variables in the TiCl or the olivine. It is apparent from these calculated coefficients that the Jacupiranga TiCl is enriched in Mg in relation to coexisting olivine.

As already mentioned, TiCl in the Jacupiranga carbonatites occurs as reaction rims or patches in the olivine crystals. It is obvious from the compositions of the two minerals that the replacement of olivine by TiCl implies the entry of Ti, F, and OH in the olivine crystals. The above calculated Fe-Mg partition coefficients point to a replacement mechanism that includes also a loss of Fe, a gain of Mg, or both. The observed differences in  $K_d$  for the pairs from the three carbonatites show that the final compositions of the TiCl are not a function of the initial Fe-Mg ratio of the olivines. This fact, combined with the marked chemical differences of the TiCl from the three carbonatites (Fig. 2), is evidence that the major control on their composition is external variables like temperature, pressure, and the chemical composition of the reacting fluids. The chaotic zoning and the variability in the patterns of structural faults in each crystal (Figs. 4 and 5) are certainly a reflection of a rapidly changing environment and probably a reflection of variations in fluid compositions. The previously mentioned unexpected relation of the Ti-Si ratios of coexisting TiCl and TiCh is certainly also the result of rapidly changing conditions

of crystallization where equilibrium was not always attained.

TiCl that occurs in the reaction rocks is associated with brown phlogopite, calcite, serpentine, magnetite, and ilmenite. The serpentine forms pseudomorphs after olivine. Alkali amphibole, which is a common phase in these rocks, has not been found so far in association with TiCl. The textures present in these parageneses show that TiCl may be the alteration product of preexisting olivine grains, but in many others the TiCl seems to have no relation at all with olivine, as is the case when TiCl is present as subhedral to euhedral prismatic crystals reaching up to 20% of a silicate band and no olivine or pseudomorphs of it are present. Despite a similar variability in stacking faults as in the TiCl from the carbonatites (Figs. 4 and 5), the TiCl in the reaction rocks presents a constant zoning trend of increasing TiO<sub>2</sub> toward the margins (Table 1 and Fig. 2), indicating a relatively more constant crystallization environment.

Analyses were obtained on coexisting TiCl and phlogopite in two samples of the reaction rock. The values of  $K_d$  for F-OH gave 7.6 and 12.8, which is much higher than the partition coefficient of 4 for F-OH between clinohumite and phlogopite in marbles (Rice, 1980). Despite this high fractionation of F into TiCl relative to phlogopite, the F contents in clinohumite should not be used as an indication of high F environments, as in Lapin (1982); the half percent of F normally present in the much more abundant phlogopite is actually more significant.

#### HUMITE MINERALS FROM OTHER CARBONATITES

The humite minerals are classified by Heinrich (1963) as of very rare occurrence in carbonatites. Chondrodite is reported in the Glenover and Nooitgedacht carbonatites in South Africa (Verwoerd, 1966) and from Palabora (Verwoerd, 1966; Palabora staff, 1976). Minerals of the humite group occur sporadically in the Cargill Lake carbonatite, Canada, according to Gasparrini et al. (1971); the crystal structure of one TiCl from this carbonatite was determined by Kocman and Rucklidge (1973). In the Sokli carbonatite, the first minerals that form as alteration products of olivinites are clinohumite and ferri-phlogopite (Vartiainen, 1980). A similar type of occurrence of clinohumite is found in the Catalão I carbonatite, Brazil, where carbonate-rich veins intruding the dunites cause the transformation of olivine to clinohumite (Gaspar and Adusumilli, 1976). These last two occurrences of clinohumite together with the above description of the TiCl and TiCh in the Jacupiranga Complex point to a common metasomatic origin for these minerals in carbonatites, a conclusion also expressed by Mitchell (1978) and by Lapin (1982).

Nielsen and Johnsen (1978) described veins intruded in dunite that contain TiCl-rich centers in the Gardiner Plateau Complex (a complex where carbonatite is present) as well as the occurrence of TiCl in joints of this dunite. The other minerals in the veins are phlogopite, apatite, antigorite, and minor diopside. This kind of oc-

currence is not very different from those of Sokli and Catalão I and probably also has a metasomatic origin. Nielsen and Johnsen (1978) regard the Gardiner TiCl to be a magmatic occurrence as in "certain kimberlites and carbonatites." J. Gittins (personal communication) found a sympathetic range of composition of TiCl with amphiboles and micas in some Cargill carbonatites, which may represent the first actual evidence of a possible magmatic crystallization of TiCl.

#### COMPARISON OF CLINOHUMITE COMPOSITIONS FROM DIFFERENT ENVIRONMENTS

Clinohumite occurs in five different environments: carbonatites, kimberlites, Alpine peridotites, Archean ultramafics, and marbles. Their mode of occurrence and origin in carbonatite complexes have been discussed above. TiCl is reported from the Moses Rock, Green Knobs, and Buell Park kimberlitic diatremes of the Colorado Plateau (McGetchin et al., 1970; Aoki et al., 1976; Smith, 1977, 1979) and from the Ruslovaya kimberlite, Siberia (Voskresenskaya et al., 1965, in Deer et al., 1982). Menzies et al. (1987) described the diatremes from the Colorado Plateau as composed of serpentized microbreccias that for the case of Green Knobs and Buell Park are closely associated with minette magmatism. According to the detailed study of Smith (1979), the TiCl from the Green Knobs and Buell Park diatremes (and the associated hydrous assemblage amphibole, chlorite, magnesite, and antigorite) is the product of hydration of upper mantle peridotite before the onset of the magmatic activity. TiCl crystals dispersed in the rock resulted from the comminution of the peridotite inclusions during transport to the surface (Smith, 1977, 1979).

In Alpine peridotites, TiCl occurs in different grades of metamorphism depending on its F content (Evans and Trommsdorff, 1978, 1983; Trommsdorff and Evans, 1980; Cimmino et al., 1979), where its breakdown with increasing metamorphism results in an intergrowth of olivine and geikielite (Trommsdorff and Evans, 1980). In Archean ultramafics, TiCl may occur as lamellae in TiCh in stratiform ultramafic rocks in the volcano-sedimentary sequences of the Isua belt, western Greenland (Dymek et al., 1988) or as discrete crystals in the ultramafic bodies of Wolf Creek and Ruby Range, Montana (Heinrich, 1963; Desmarais, 1981).

TiCl occurs both in contact and regionally metamorphosed limestones, where it can form in the higher grades (Rice, 1980). In the marbles of the Ötztal crystalline basement, Ti-rich clinohumite and chondrodite often break down to a symplectite of Ti-poor clinohumite (or olivine) and magnesium ilmenite, whereas F-rich clinohumite remains stable.

The compositions of the clinohumite from the above geological environments are compared in Figure 6. This shows a plot of MgO/(MgO + FeO + MnO) against TiO<sub>2</sub>. These two variables take into account the two most effective substitution processes in clinohumite: Mg by Fe (and Mn) and Mg(FOH)<sub>2</sub> by TiO<sub>2</sub>. As a general behavior,



we may say that F has an inverse correlation with Ti and that, as a consequence, F decreases from the top to the bottom of Figure 6.

Clinohumite from marbles delimits a well-defined composition field (except for one analysis) representing the most Mg-rich clinohumite of all types of occurrence. Marbles contain, as well, some of the most TiO<sub>2</sub>-poor clinohumite samples. The compositional field of TiCl from the Jacupiranga carbonatites (Mitchell, 1978; this study) falls inside that of clinohumite from marbles and presents the same trend of increasing TiO<sub>2</sub> with decreasing MgO/(MgO + FeO + MnO). Clinohumite from veins in dunites from the Gardiner Plateau is at the limit of the marble field. However, TiCl from the Cargill Lake carbonatite is by far the most Fe-rich clinohumite so far analyzed.

Clinohumite from the Colorado Plateau has lower MgO/(MgO + FeO + MnO) and higher TiO<sub>2</sub> than those from marbles and from Jacupiranga. The TiCl richest in TiO<sub>2</sub> comes from the Moses Rock diatreme (Fig. 6) and is represented by a unique occurrence as inclusions with olivine and geikielite in garnet (McGetchin et al., 1970). This TiCl contains 0.55 Ti per formula unit, which is slightly above the upper Ti limit, approximately 0.5, as reported by Ribbe (1979). The humite mineral from Siberia has lower TiO<sub>2</sub> but similar MgO/(MgO + FeO + MnO) to those from the American diatremes. The TiCl from the Colorado Plateau is similar in composition to that from the Alpine peridotites, except the sample of TiCl from the recrystallized garnet peridotite (RGP) reported by Evans and Trommsdorff (1983). However, TiCl from the RGP defines a particular composition field and is not, itself, coincident with other Alpine TiCl. The RGP TiCl contains the highest F contents of all reported clinohumite samples associated with ultramafic rocks of any environment. The only two analyses from Archean ultramafics have very different compositions from each other for all chemical variables considered (Fig. 6). TiCl from a metadunite of the Isua belt has a particular composition characterized by high TiO<sub>2</sub> and high MgO/(MgO + FeO + MnO).

In the RGP, Evans and Trommsdorff (1983) found a large variation in the chemical composition of TiCl crystals not only as a whole (Fig. 6) but also on a very small scale as, for example, in the same thin section. This feature shows that chemical variations on a millimeter scale may cause a significant shift in the final composition of clinohumite. Such characteristics and the above-mentioned large difference in composition of two TiCl from the same environment, those from Archean ultramafics, are an indication that TiCl compositions are not a reflection of the macrogeological environment from which they crystallize. It is important, however, to remember that this statement is entirely based on major elements and that there are no data available regarding the trace elements or the isotope compositions of TiCl from the different geological environments. TiCl from the Jacupiranga carbonatites and TiCl from marbles have coincident

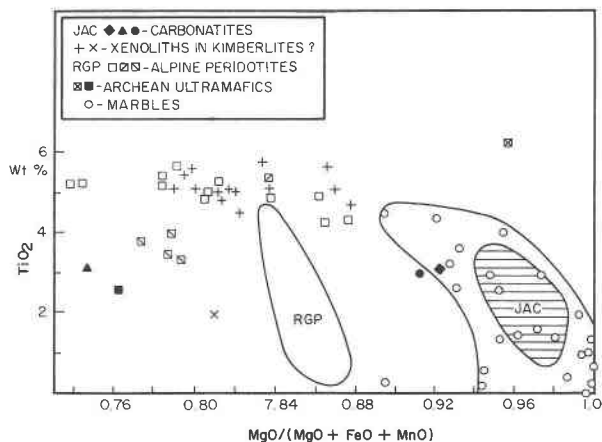


Fig. 6. Comparison of TiCl compositions from different geological environments. Data references follow. Carbonatites: JAC, Jacupiranga from this work; filled diamond, Jacupiranga from Mitchell (1978); filled triangle, Cargill Lake from Kocman and Rucklidge (1973); filled circles, Gardiner Complex from Nielsen and Johnsen (1978). Xenoliths in kimberlites?: crosses, Green Knobs, Buell Park, and Moses Rock (Colorado Plateau) from Smith (1977), McGetchin et al. (1970), Aoki et al. (1976), and Fujino and Takéuchi (1978); ×, Ruslovaya kimberlite from Voskresenskaya et al. (1965, in Deer et al., 1982). Alpine peridotites: RGP, recrystallized garnet peridotite (Cima di Gagnone) from Evans and Trommsdorff (1983); square with diagonal at right top, Cima di Gagnone from Evans and Trommsdorff (1978); squares, Val Malenco from Trommsdorff and Evans (1980) and Jones et al. (1969) in Robinson et al. (1973); squares with diagonal at left top, Voltri Massif from Cimmino et al. (1979). Archean ultramafics: square with ×, metadunite from the Isua belt, western Greenland, from Dymek et al. (1988); filled square, Ruby Range, Montana, from Desmarais (1981). Marbles: circles, Ross Lake, Alta aureola, western Tauern, Otztal basement, and Hameenkyla (Finland) from Rice (1980), Moore and Kerrick (1976), Franz and Ackermann (1980), and Ehlers and Hoikens (1987), and from Jones et al. (1969) in Robinson et al. (1973), respectively.

compositional fields (Fig. 6). Such similarity in composition is certainly a reflection of the similarity of the paragenesis in both rocks represented by the abundance of carbonate and the presence of at least some of the following minerals: olivine, phlogopite, serpentine, magnetite, and Mg-rich ilmenite. The similarity in composition of TiCl in marbles and the Jacupiranga carbonatites cannot be extrapolated to carbonatites in general, as illustrated by the composition of the TiCl from the Cargill Lake carbonatite (Fig. 6). TiCl from the Colorado Plateau and TiCl from the Alpine peridotites have similar compositions (Fig. 6). The two types crystallized in similar environments (peridotites with the presence of a fluid phase).

#### TiCl AND TiCh IN THE UPPER MANTLE?

Using the topological analysis of the reactions in the ternary subsystem forsterite-geikielite-H<sub>2</sub>O and the experimental work of Engi and Lindsley (1980) and Duffy and Greenwood (1979), Dymek et al. (1988) suggested



that TiCh is a mantle mineral. They suggested that the intergrowths of TiCh and TiCl, such as those from the xenoliths of the Colorado Plateau and from the Isua metadunite, "may represent an arrested decompression reaction." Despite the fact that the observed intergrowths of TiCh in the Jacupiranga TiCl do not seem to be candidates for such a process, there follows a discussion about the existence of these humite minerals in the upper mantle.

Because McGetchin et al. (1970), Aoki et al. (1976), and Aoki (1977) observed TiCl and TiCh in the xenoliths from the diatremes of the Colorado Plateau (regarded by them as kimberlites), they supported the idea that clinohumite (and chondrodite) may be components of the upper mantle, being consequently a site for H<sub>2</sub>O. Aoki et al. (1976), based on the experimental work of Yamamoto and Akimoto (1977), proposed that TiCl and TiCh crystallized directly from the kimberlite magma. Smith (1977, 1979) demonstrated that the TiCl-bearing xenoliths from the Colorado diatremes were the result of hydration of upper-mantle peridotites "in a range of water fugacities at temperatures below 700 °C and depths from 45 to 60 plus km," eliminating the possibility of a direct crystallization of TiCl from a kimberlitic magma. Mitchell (1978), after observing the metasomatic origin of TiCl in the Jacupiranga carbonatites, questioned the suggestion that TiCl is ever a liquidus phase in kimberlites or is important in the mantle. Engi and Lindsley (1980) carried out reversed hydrothermal experiments on a natural hydroxyl-TiCl [previous experiments by Merrill et al. (1972) and Yamamoto and Akimoto (1977) were not able to reverse the reactions] and found that it breaks down at 475 °C (3.5 kbar), 6209 °C (14 kbar), and 625 °C (21 kbar) to the assemblage olivine + ilmenite + vapor. Trommsdorff and Evans (1980) described the breakdown of hydroxyl-TiCl to olivine + magnesian ilmenite + magnetite in the Malenco serpentinite at approximately 520 °C and 3 kbar. Considering that the TiCl from the xenoliths of the Colorado diatremes is also hydroxyl-TiCl, it is possible that the experimental data and the conditions of stability of the hydroxyl-TiCl deduced from natural assemblages are consistent.

The entry of Ti in the structure of humite minerals has a destabilizing effect that limits the Ti content of the natural minerals to approximately 0.5 cations per formula unit (Ribbe, 1979). It is the substitution of OH by F that increases the stability of these minerals because it reduces the number of neighboring H atoms, diminishing the amount of proton-proton repulsion (Ribbe, 1979). Engi and Lindsley (1980) calculated the shifts caused in the upper stability limit of TiCl containing different mole fractions of F and found significant displacements toward higher temperatures. The breakdown reaction (TiCl = olivine + geikielite) for a clinohumite sample containing  $X_F = 0.6$ , according to Figure 1 from Engi and Lindsley (1980), would occur at about 1000 °C for a pressure of 3.5 kbar. These calculated curves seem to be in reasonable agreement with the unreversed reactions of Merrill

et al. (1972). Evans and Trommsdorff (1983) reported on the occurrence of fluorine-hydroxyl-TiCl in an Alpine re-crystallized garnet peridotite from Cima di Gagnone, Switzerland. The  $X_F$  content of these clinohumite samples varies from a little above 0.1 to approximately 0.45 and the number of Ti cations per formula unit from a little above zero to approximately 0.4 (from their Fig. 4).  $X_F$  and Ti show inverse correlation. The paragenesis includes olivine, chlorite, tremolite, cummingtonite, orthopyroxene, and magnesite, and the estimated conditions for the Central Alpine garnet lherzolite (800 °C and 25 kbar) represent the conditions through which the clinohumite samples were stable. The  $X_F$  present is large enough for these conditions if the calculated curves from Engi and Lindsley (1980) are taken into account.

Cimmino et al. (1979), after studying the TiCl-bearing serpentinites from the Voltri Massif, Italy, questioned whether the H<sub>2</sub>O liberated by the subsiding oceanic lithosphere would produce clinohumite and chondrodite after olivine in the overlain peridotite edge, a suggestion already made by Aoki et al. (1976). Smith (1979) also suggested this as a hypothesis to explain the source of the H<sub>2</sub>O that caused the hydration of the TiCl-bearing xenoliths from the Colorado Plateau diatremes. Helmstaedt and Schulze (1979), based on the similarity of the ultramafic xenolith suite from the Colorado Plateau "kimberlites" to metamorphosed ophiolite complexes of high-pressure metamorphic belts, stated that a shallow slab of subducted oceanic lithosphere existed under the Colorado Plateau at the time of the eruptions from which the xenoliths were derived; this theory is more in agreement with recent analysis of the geotectonic implications of xenoliths in the southwestern area of the U.S.A. (Menzies et al., 1987).

Disregarding the suggestion that clinohumite and chondrodite may crystallize from a kimberlite magma, we are essentially left with two possibilities for the existence of clinohumite and chondrodite in the upper mantle. The first is that these minerals crystallize in the hydrous oceanic lithosphere and are carried down with the slab, and the second is that H<sub>2</sub>O released from dehydration reactions in the descending oceanic slab produces the alteration of olivine to clinohumite or chondrodite in the peridotite wedge above it.

The suggestion of crystallization of TiCl or TiCh in the oceanic lithosphere in subduction zones is consistent with the occurrence of these minerals in ophiolites. The problem is the survival of the humite minerals as the slab sinks. We have seen that most of the TiCl that occurs in the ultramafic rocks is Ti rich and F poor, and this type of clinohumite breaks down at temperatures below that of the upper mantle. As noted by Trommsdorff and Evans (1980), the typical product of the breakdown of TiCl, the olivine-ilmenite intergrowths, has never been observed in xenoliths or as megacrysts. The only exception is the occurrence of olivine, ilmenite, and TiCl as inclusions in garnet from the Moses Rock diatreme (McGetchin et al., 1970). No textural detail is given, but this olivine and

ilmeneite could have originated by the breakdown of TiCl because of pressure release caused by the ascent of the xenolith. Despite the fact that most of the TiCl in ultramafic rocks is F poor, F-bearing TiCl has been found in the Alpine peridotites (Evans and Trommsdorff, 1983) and was stable under 800 °C and 25 kbar. Another possible exception would be the clinohumite sample from the Ruslovaya kimberlite (Voskresenkaya et al., 1965, in Deer et al., 1982) (see Fig. 6) that contains 1.8 wt% F, but it is not possible to know from their description if this TiCl comes from comminuted xenoliths or is the alteration product of olivine from the kimberlite. The fact is that F-bearing clinohumite seems to be stable under upper mantle conditions (Engi and Lindsley, 1980). The suggestion regarding the alteration of olivine to TiCl or TiCh in the peridotite wedge above the subduction zone seems theoretically possible, but no direct or indirect evidence of it exists.

To the question of whether TiCl or TiCh exists in the upper mantle, the answer is probably yes; but to the question of whether they are important to the upper mantle petrology, the answer is certainly no. The rarity of clinohumite as a whole in ultramafic rocks combined with the fact that fluorine clinohumite (which is the stable phase under typical upper mantle conditions) is even rarer in these rocks and the practical absence of these minerals from world-wide collected xenoliths make their importance to mantle geology negligible. Engi and Lindsley (1980) observed that if 1% of the upper mantle consisted of fluorine clinohumite, the calculations of the abundance of F in the Earth would be significantly different. This observation is relevant, but to define the actual abundance of a certainly very rare mineral in the upper mantle is not a simple task.

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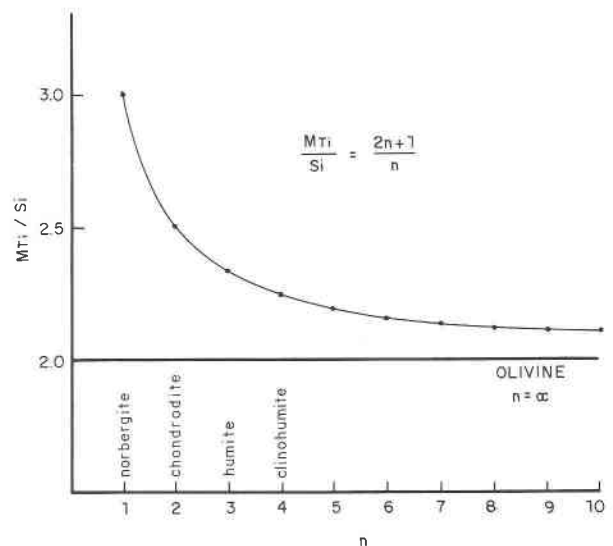
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### APPENDIX 1. THE USAGE OF $M_{Ti}/Si$ TO ASSIGN $n$ VALUES TO HUMITE MINERALS

From the stoichiometry of the humite minerals, the relation of  $M_{Ti}/Si$  with  $n$  is

$$\frac{M_{Ti}}{Si} = \frac{2n + 1}{n}$$

where  $M_{Ti}$  is the sum of all octahedrally coordinated cations including Ti, as defined by Jones et al. (1969). Appendix Figure 1 shows the curve of this function that is limited by  $n = 1$  and by  $M_{Ti}/Si = 2$ , which is the olivine ratio ( $n = \infty$ ). It is obvious from the curve that the assignment of  $n$  by  $M_{Ti}/Si$  gets progressively more difficult and inaccurate as  $n$  increases and that for high  $n$  values this procedure will give meaningless results, particularly if analytical errors are taken into account. However, for the most abundant cases, which are represented by low  $n$  phases,  $M_{Ti}/Si$  is useful.



Appendix Fig. 1. Curve representing the variation of  $M_{Ti}/Si$  with  $n$ .