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Fluorine-rich clinohumite from Ambasamudram marbles, Southern India: mineralogical and preliminary FTIR spectroscopic characterization

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ABSTRACT

Humite group minerals occur in the marbles of granulite grade at Ambasamudram, southern India. Detailed mineralogical and mineral chemical characterization indicate the mineral is a flourine-rich titanian-poor variety of clinohumite. Average M_{Ti}/Si values of 2.22 with typical XRD pattern indicate the mineral to be clinohumite. Petrological constraints on the clinohumite formation shows a high temperature (>700°C) and low a_{CO_2} during its formation. The fluorine content of these clinohumites is the highest reported in any environment, with F/(F+OH) ratio reaching a value of 0.70. The high fluorine content reflect the high $P-T$ condition of formation. The OH content of the clinohumites is around 0.59 mole fraction. Preliminary FTIR spectra of the clinohumites show eight sharp absorption peaks between wave numbers 3700 and 3400 cm^{-1} and a broad absorption band with a peak at 3840 cm^{-1}. The sharp peaks are due to OH in the clinohumite. The high fluorine content of the Ambasamudram clinohumites possibly resulted from the isochemical reactions involving (OH-F) silicates such as amphiboles or phlogopites. The internal fluid buffering is also supported by the stable isotope as well as the petrological studies of the marble assemblages.

KEYWORDS: fluorine, clinohumite, mineralogy, FTIR, India, humite.

Introduction

THE humite-group consists of four minerals, norbergite, chondrodite, humite and clinohumite. The group is defined by the general formula

$$n\mathrm{Mg_2SiO_4.Mg}_{1-x}\mathrm{Ti}_x(\mathrm{OH,F})_{2-2x}\mathrm{O}_{2x}$$

where $n = 1$ for norbergite, $n = 2$ for chondrodite, $n = 3$ for humite and $n = 4$ for clinohumite. The minerals of the humite-group have a limited paragenesis and occurrence. Metamorphosed and metasomatised limestones and dolomites adjacent to acid plutonic rocks have humite minerals typically poor in titanium and rich in fluorine (Fujino and Takeuchi, 1978). Contrary to this, the humite-group minerals in rocks of ultrabasic compositions, including carbonatites and kimberlites (McGetchin *et al.*, 1970; Aoki *et al.*, 1976) and serpentinites (Trommsdorff and Evans, 1980) are enriched in titanium and generally contain less fluorine. Ti usually substitutes for Mg in clinohumite and titanium rich variety is commonly described as titanoclinohumite. Contrasting views have been proposed as to the possibility of clinohumites acting as H_2O reservoirs in the upper mantle (Aoki *et al.*, 1976; Trommsdorff and Evans, 1980).

Humite-group minerals were reported from the marbles of southern Indian granulite facies regional metamorphic terrain by Krishnanath (1981). In this study we present results of mineralogical and mineral chemical features of clinohumite. Preliminary FTIR spectroscopic characterization of clinohumite is also presented. Based on the evidences presented here, we evaluate the possible source and movement of volatiles in marble of the present study area.

Regional geological situation

The Kerala Khondalite Belt which forms the southern part of the granulite facies segment of southern India is a vast metasupracrustal terrain. This belt is bounded to the north by the Achankovil Shear Zone and to the south by the Nagercoil massif charnockites (Fig. 1A). A recent classification of this region identifies the south of the Achankovil shear zone as the Trivandrum block (formerly the Kerala Khondalite Belt), which consists of the Achankovil metasediments south of the shear zone (having younger Nd model ages of about 1.3–1.4 Ga), the Kerala Khondalite Belt (with older Nd model ages between 3.0 and 2.0 Ga) and the Nagercoil massif (possibly of igneous origin) in the extreme south (Bartlett *et al.*, 1995; Bartlett, 1995; Brandon and Meen, 1995; Harris *et al.*, 1996). The marble horizon in which clinohumite occurs forms part of the Achankovil metasediment zone.

The Kerala Khondalite Belt predominantly consists of metapelitic lithologies which include garnet + biotite ± graphite gneisses, garnet + sillimanite + graphite ± cordierite gneisses and othopyroxene-bearing anhydrous granulites. Subordinate lithologies include mafic granulites, quartzites and calc-silicates. These lithologies have been metamorphosed to upper amphibolite and to granulite facies conditions. Estimates of metamorphic P–T conditions reported account for a peak of 750 ± 50°C and 5 ± 1 kbar (Chacko *et al.*, 1987; Santosh *et al.*, 1993).

The Achankovil metasediments (cf. Bartlett, 1995) comprise a narrow belt of young (*c.* 1.3–1.4 Ga) sediments metamorphosed to granulite grade. The main lithologies in this zone are cordierite-bearing assemblages, calc-silicates and marbles. The cordierite-bearing assemblages (cf. Santosh, 1987) occur as elongate patches in this zone and exhibit reaction histories indicative of partial replacement of a higher pressure garnet-bearing assemblage by lower pressure one, a feature that is also well supported by fluid inclusion studies (Santosh, 1987). A well defined Sm–Nd isochron age of 539 ± 20 Ma from the cordierite assemblages has been reported (Santosh *et al.*, 1992). This zone is also characterized by diopside-rich calc-silicate bands (Satish-Kumar *et al.*, 1996). Further towards the eastern extension of the Achankovil shear zone, calcite-rich marble and metapelitic gneisses predominate (cf. Satish-Kumar *et al.*, 1996)

An extensive band of marbles and associated calc-silicate rocks occurs in the northeastern part of Ambasamudram in southern Tamil Nadu (Fig. 1B). This band can be traced for about 10 km along strike and varies in thickness from 25 m to 300 m. It is structurally concordant with the

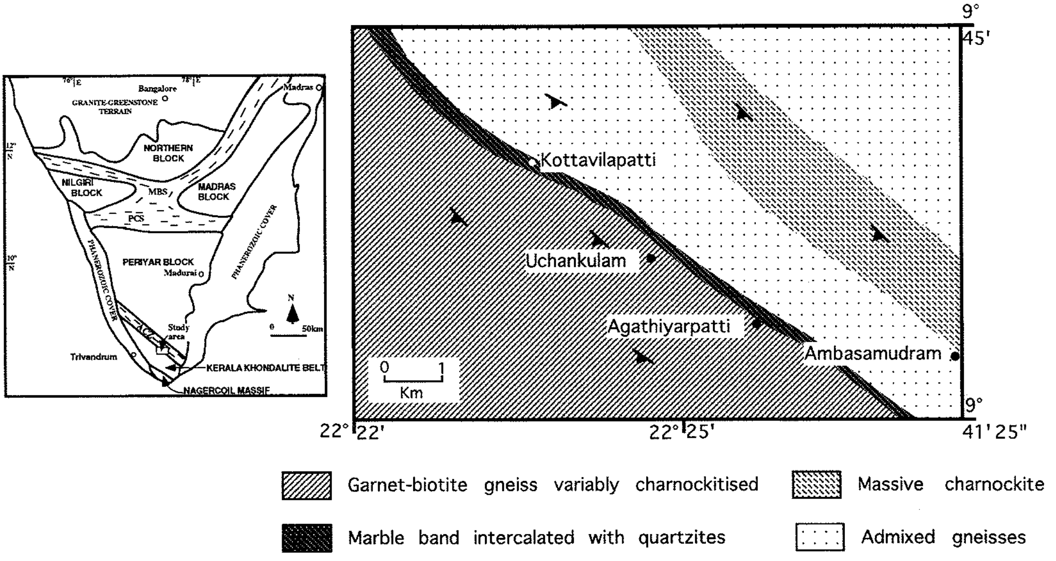

FIG. 1. A. Regional geological setup of southern Indian Granulite terrain. B. Generalised geological map of Ambasamudram area showing the marble horizon of the present study (after Satish-Kumar *et al.*, 1997*a*).

adjacent lithologies, striking parallel to the NW–SE trending Achankovil shear. Within the marble horizon, the calcite-rich marbles show great variations in grain size from coarse grained (>5 mm) to fine grained (<1 mm). The marble band is intercalated with quartzite bands of varying thickness and is often graphite bearing. A humite + chondrodite + spinel + magnesian calcite assemblage has been reported in a marble from this locality (Krishnanath, 1981; Satish-Kumar *et al.*, 1996; Pradeepkumar *et al.*, 1996; Rosen *et al.*, 1996).

Petrological features

Calcite-rich marbles dominate the lithologies within the marble horizon at Ambasamudram. Different layers paralleling the regional trend of the band have varying mineral assemblages. The marble is chiefly composed of more than half the mode of calcite/magnesian calcite and the variations in mineralogy are controlled by the Mg-rich phases. The characteristic mineral assemblages include (i) calcite + scapolite + phlogopite + K-feldspar + titanite ± quartz ± graphite; (ii) calcite + clinopyroxene + scapolite + wollastonite ± grossular ± titanite ± quartz ± graphite; (iii) calcite + clinohumite + chondrodite + spinel + phlogopite + clinopyroxene ± titanite ± graphite; (iv) calcite + forsterite + spinel ± dolomite ± diopside; (v) calcite + K-feldspar + phlogopite ± quartz ± graphite; (vi) calcite + graphite.

The equilibrium mineral assemblage in marble layers might have resulted in prograde reactions from an impure dolomitic limestone. Prograde mineral reactions in the calcite-rich marble can be modeled in the system K_2O–CaO–MgO–Al_2O_3–SiO_2–H_2O–CO_2 (KCMAS). The T–X_{CO_2} reaction grid in this system was constructed (Fig. 2) using THERMOCALC (Powell and Holland, 1988) with the internally consistent data set of Holland and Powell (1990). A confining fluid pressure of 6 kbar was assumed for the peak metamorphic assemblages. End-member mineral activities were used for the solid solution series in the computation of the grid.

One of the main problems in deducing the P–T conditions of the metacarbonates is the lack of appropriate mineral geothermobarometric pairs.

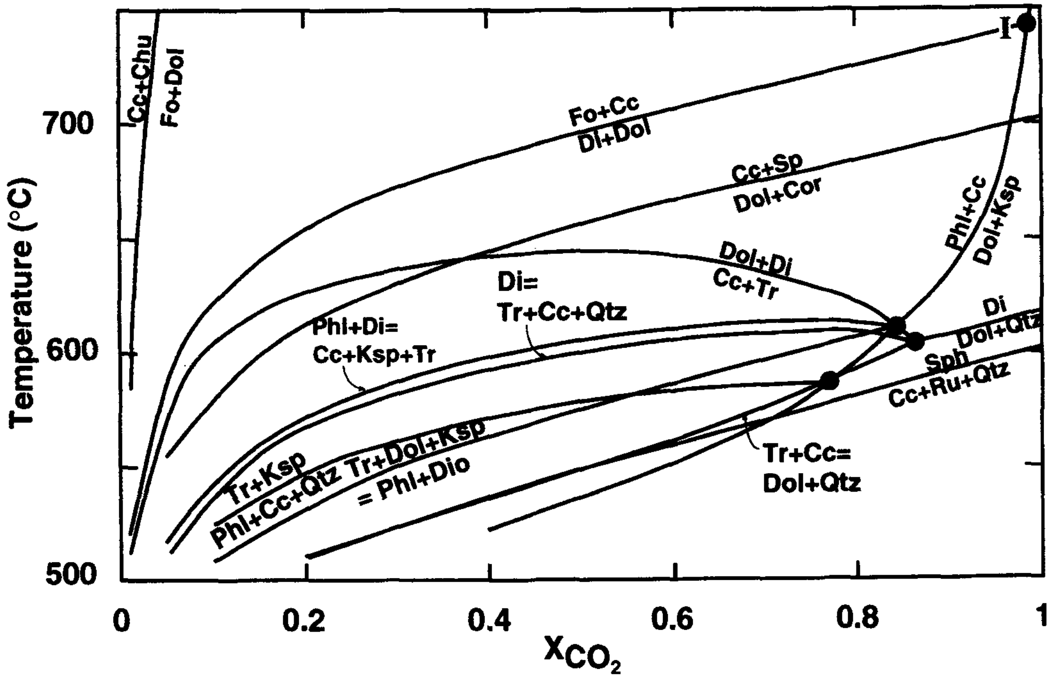

FIG. 2. Isobaric T–X_{CO_2} grid constructed for marble assemblages in the system K_2O–CaO–MgO–Al_2O_3–SiO_2–H_2O–CO_2 (KCMAS) at 6 kbar. Mineral abbreviations are Cc – calcite; Chu – clinohumite; Dol – dolomite; Di – diopside; Fo – forsterite; Ksp – K-feldspar; Phl – phlogopite; Qtz – quartz; Sp – spinel; Sph – sphene; Tr – tremolite.

Only an approximation of the conditions can be deduced from the assemblages. Since the mineral assemblages are controlled by the fluid compositions in the $P-T$ space, one way is to approach the given assemblages through the $T-X_{CO_2}$ space. As mentioned above, the grid was constructed with end-member compositions for the marble assemblages (Fig. 2). The assemblage forsterite + diopside + K-feldspar + phlogopite + calcite + dolomite is stable at the invariant point marked **I** in the grid. This indicates that the fluid composition was nearly equal to unit X_{CO_2} and the temperature conditions to be around 700°C. On the other hand, stability of humite-bearing assemblages in other layers indicate that the fluid conditions should be nearly equal to unit X_{H_2O}. As can be seen below, the stable isotopes of calcites coexisting with humite do not show any imprint of infiltration of water-rich fluids to buffer the system, and hence it can be assumed that the fluid composition in this assemblage was also internally buffered. Again, the local occurrence of grossular-bearing assemblage indicates a fluid-absent or low-fluid activity. The grossular-bearing assemblages formed during cooling from higher temperatures. Taken altogether, it can be concluded that the prograde metamorphism of the marble band occurred with layer by layer internally controlled fluid compositions. Satish-Kumar *et al.* (1997*a*) reported the carbon isotope thermometric results which yields temperatures in the range of about 720°C.

Analytical techniques

The present study concentrated on the mineralogical, chemical and spectroscopic characterization of clinohumite. A marble sample containing pure humite group minerals was crushed and sieved to a fraction between 0.5 to 1 mm. Pure crystals were separated under a binocular microscope, powdered and analysed at room temperature using a RIGAKU XRD with analytical condition of 30 kV and 10 mA. Doubly polished sections (~300 μm) were prepared from the same hand specimen. Micro FTIR measurements were carried out using a SHIMADZU FTIR-4200 spectrometer. The spectrometer is an interference type which is based on the principle of the Michelson interferometer. Analyses were carried out at room temperature with an unpolarised incident beam. The analysis targets were carefully selected in order to avoid microcracks or inclusions. The same polished wafers were later mounted on glass plates and used for mineral chemical analyses. Care was taken to analyse the exact point at which FTIR spectra were taken. EPMA analysis were done using JEOL JXA 8600 housed at Kochi University, Japan. The analyses were done with an accelerating voltage of 15 kV, a beam diameter of 2–3 μm and a beam current of 18 mA. Both natural and synthetic standards were used, and oxide ZAF correction was performed throughout. Quantitative analyses of fluorine were obtained using a JEOL JXA 8800 at the National Institute of Polar Research in Tokyo. The analytical conditions were 15 kV accelerating voltage, 15 mA beam current and a minimum beam diameter (~1 μm). Bence and Albee (1968) correction was used.

Results and discussion

The Ambasamudram clinohumite occurs as granular crystals set in a matrix of coarse calcite exhibiting a granoblastic texture (Fig. 3). It shows honey-yellow to orange-yellow colour and displays a light yellow to colourless pleochroism in thin section. No optical discontinuity was observed.

An XRD pattern of the pure mineral separate is shown in Fig. 4. Twenty four peaks corresponding exactly with the standard of clinohumite were observed. The typical absence of the peak at 8.4° which is prominent for humite and the presence of peaks at 20° amd 17.6°, which should be absent for chondrodite, confirms that the present sample consists only of clinohumite, although other members of the group have been reported (Krishnanath, 1981; Pradeepkumar *et al.*, 1996; Rosen *et al.*, 1996).

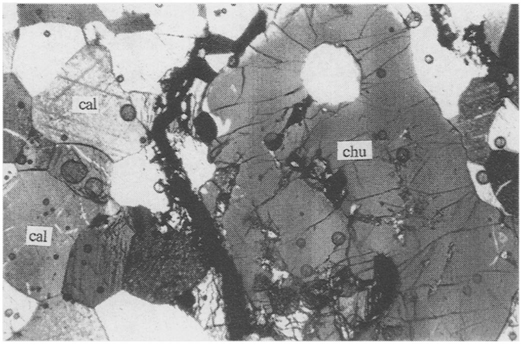

FIG. 3. Photomicrograph of clinohumite set in a granoblastic texture with calcite. Width of the photograph is 3 mm.

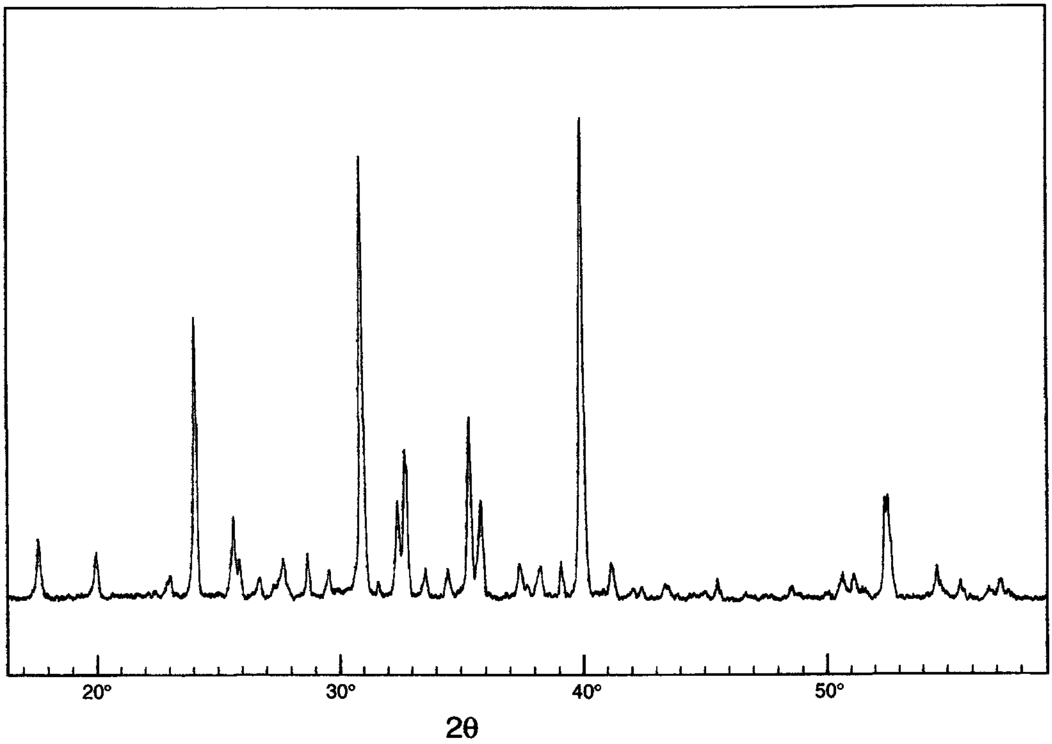

FIG. 4. X-ray diffractogram of clinohumite.

The microprobe analytical results of Ambasamudram clinohumite are given in Table 1. From the EPMA results, cations were calculated on the basis of 18 (O). Several points were analysed to find out any compositional variations within and between the grains. There is only minor compositional variation between grains of clinohumite. TiO_2 content is very low (<0.49 wt.%) and with low FeO content. Only negligible quantities of other cations are present in the clinohumite. These general characters indicates the Ambasamudram clinohumites as titanium free fluorine rich type, which is typical for marbles.

OH content

The OH content of the clinohumites were calculated from the mineral chemical analysis using the method given by Jones *et al.* (1969). OH is calculated using the relation (OH) = 2 − 2Ti − F. The calculations show that Ambasamudram clinohumite contain OH from 0.51 to 0.61 in mole fraction, with an average of OH content of 0.58.

M_{Ti}/Si

Gaspar (1992) introduced a new mineralogical criteria to identify the humite group minerals using the ratio of total octahedral cations including Ti to the Si. This (M_{Ti}/Si, M_{Ti} = Mg+Fe+Mn+Ti+Ca) is found to be 3.0, 2.5, 2.33 and 2.25 respectively for the minerals with n from 1 to 4. The Ambasamudram samples gave an average M_{Ti}/Si value of 2.27 (ranging from 2.21 to 2.38). The range of the values show a bimodal distribution (Fig. 5). This suggests the possibility of an intergrowth of humite with clinohumite. But neither petrographic observatons nor XRD pattern points to such an intergrowth. It is possible that very thin lamellae which could not be identified by normal optical observation might be present.

Fluorine content

The humite group minerals in contact with regionally metamorphosed impure dolomitic limestone are generally titanian-poor and fluorine-rich. The fluorine content of

TABLE 1. EPMA analytical results of clinohumites from Ambasamudram

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2	38.94	38.47	38.51	38.37	38.34	38.28	38.81	38.52	38.39	38.36	37.98	37.48	38.08	38.24	37.54	38.90
TiO_2	0.30	0.17	0.29	0.29	0.24	0.39	0.26	0.11	0.29	0.10	0.31	0.22	0.22	0.29	0.27	0.12
Al_2O_3	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.00	0.01	0.02	0.01	0.01	0.00	0.02	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
FeO	0.95	0.89	0.93	0.90	0.97	0.93	0.94	0.91	0.91	0.93	0.90	0.92	1.05	1.14	1.03	1.07
MnO	0.08	0.04	0.09	0.11	0.09	0.08	0.10	0.10	0.07	0.08	0.14	0.07	0.06	0.12	0.07	0.14
MgO	56.90	56.30	56.71	56.65	56.18	56.55	57.17	57.11	58.79	59.17	57.72	59.23	58.20	58.42	58.86	59.80
CaO	0.02	0.03	0.01	0.02	0.01	0.01	0.04	0.03	0.03	0.05	0.01	0.04	0.00	0.03	0.04	0.02
Na_2O	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.02	0.04	0.03	0.00	0.00	0.00	0.00
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.39	4.36	4.43	4.33	4.22	4.20	4.39	4.42
	97.21	95.91	96.56	96.34	95.85	96.26	97.33	96.79	102.89	103.10	101.55	102.32	101.83	102.44	102.19	104.48
O=F	–	–	–	–	–	–	–	–	1.85	1.83	1.86	1.82	1.78	1.77	1.85	1.86
Total	97.21	95.91	96.56	96.34	95.85	96.26	97.33	96.79	101.04	101.27	99.68	100.50	100.05	100.67	100.34	102.62
Si	4.054	4.055	4.033	4.026	4.046	4.022	4.031	4.019	3.927	3.909	3.943	3.841	3.932	3.927	3.861	3.916
Ti	0.024	0.013	0.023	0.023	0.019	0.031	0.021	0.009	0.022	0.008	0.024	0.017	0.017	0.022	0.021	0.009
Al	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.001	0.002	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Fe	0.083	0.079	0.081	0.079	0.085	0.082	0.081	0.079	0.077	0.079	0.078	0.079	0.090	0.098	0.088	0.090
Mn	0.007	0.003	0.008	0.009	0.008	0.007	0.009	0.009	0.006	0.006	0.013	0.006	0.005	0.010	0.006	0.012
Mg	8.829	8.845	8.851	8.859	8.838	8.855	8.851	8.879	8.962	8.985	8.931	9.047	8.956	8.940	9.020	8.971
Ca	0.002	0.003	0.001	0.002	0.001	0.001	0.004	0.004	0.004	0.005	0.001	0.005	0.000	0.003	0.004	0.002
Na	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.004	0.008	0.005	0.000	0.000	0.000	0.000
K	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
F	–	–	–	–	–	–	–	–	1.420	1.404	1.453	1.402	1.379	1.365	1.427	1.406
Total cation	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13
M_{Ti}*	8.944	8.944	8.964	8.972	8.951	8.975	8.966	8.979	9.071	9.083	9.047	9.154	9.068	9.073	9.139	9.084
Mg/Mg+Fe	0.991	0.991	0.991	0.991	0.990	0.991	0.991	0.991	0.991	0.991	0.991	0.991	0.990	0.989	0.990	0.990
M_{Ti}/Si	2.207	2.206	2.223	2.229	2.212	2.232	2.224	2.234	2.310	2.324	2.294	2.383	2.307	2.311	2.367	2.320
OH**	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.552	0.599	0.509	0.597	0.603	0.607	0.562	0.594
F/(F+OH)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.720	0.701	0.741	0.701	0.696	0.692	0.717	0.703

n.a.=not analysed; * M_{Ti} = Mg+Fe+Mn+Ti+Ca; ** calculated

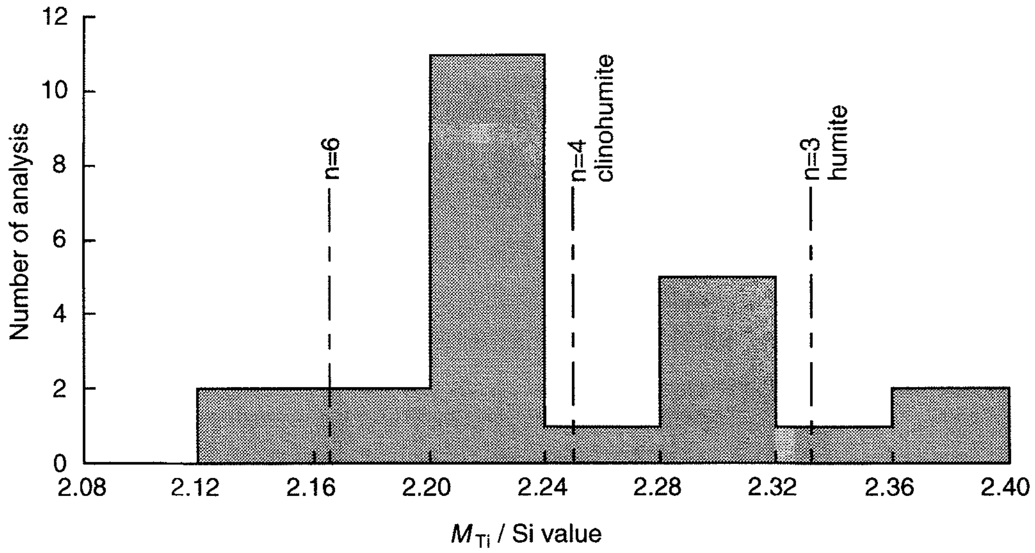

FIG. 5. Histogram representing the M_{Ti}/Si values of different analysis of clinohumite grains. Total 24 analyses of 8 clinohumite grains gave results indicative of clinohumite as the prominent phase.

Ambasamudram clinohumites varies from 4.20 to 4.43 wt.% with an average of 4.3 wt.% and are listed in Table 1. The F/(F+OH) values of the clinohumites range from 0.692 to 0.741, with an average of 0.709 (Table 1). This value is higher than that previously reported for clinohumites. Rice (1980) demonstrated that the increase in stoichiometric amount of (OH, F) in the humite series from clinohumite to norbergite is accompanied by an increase in the mole fraction of fluorine F/(F+OH). The most fluorine-rich natural clinohumite reported contains 63 mole% F. The F/(F+OH) values for the clinohumite previously reported in different geological environments were calculated. These clinohumites occur in carbonatites (Gaspar, 1992), metamorphosed impure dolomitic limestone recrystallized near 5 kbar pressure (Rice, 1980), serpentinite (Dymek *et al.*, 1988), dolomitic marbles of the upper amphibolite-facies (Hiroi and Kojima, 1988), garnet ortho-pyroxenite (Okay, 1994), in limestone (Sahama, 1953), marble (Muthuswami, 1958) and in vein in ultramafic alkaline complex (Nielsen and Johnsen, 1978). Fig. 6 shows the F/(F+OH) values where almost all clinohumite in calcitic and dolomitic rocks (open symbols) reported are between 0.3 to 0.6 in spite of variation of titanium contents. On the other hand, the F/(F+OH) values of clinohumite in basic rocks are very low.

It would be expected that fluorine contents correlate inversely with titanium according to the substitution (Mg,Fe) + 2(OH,F) = Ti + 2(O) (Evans and Trommsdorff, 1983; Dymek *et al.*, 1988). The substitution is thought to have the effect of stabilizing the structure under high-grade *P–T* condition. Fujino and Takenouchi (1978) determined hydrogen atom positions and inferred that strong repulsion in the Mg(O,OH) layers would occur. This results in a replacement of OH by fluorine or by oxygen to stabilize the structure. Therefore, we can consider that the very high F/(F+OH) values of the Ambasamudram clinohumite reflect the condition under which they were formed. In this case, the clinohumite of Ambasamudram occurs in the Achankovil metasediments (cf. Bartlett, 1995) metamorphosed to granulite grade. Estimates of metamorphic *P–T* conditions reported account for a peak of 750±50°C and 5±1 kbar (Chacko *et al.*, 1987; Santosh *et al.*, 1993). Rice (1980) has reported that clinohumite+calcite stability increases with higher fluorine content and decreasing pressure. The Ambasamudram clinohumites are fluorine-rich, which agrees well with the calculated stability.

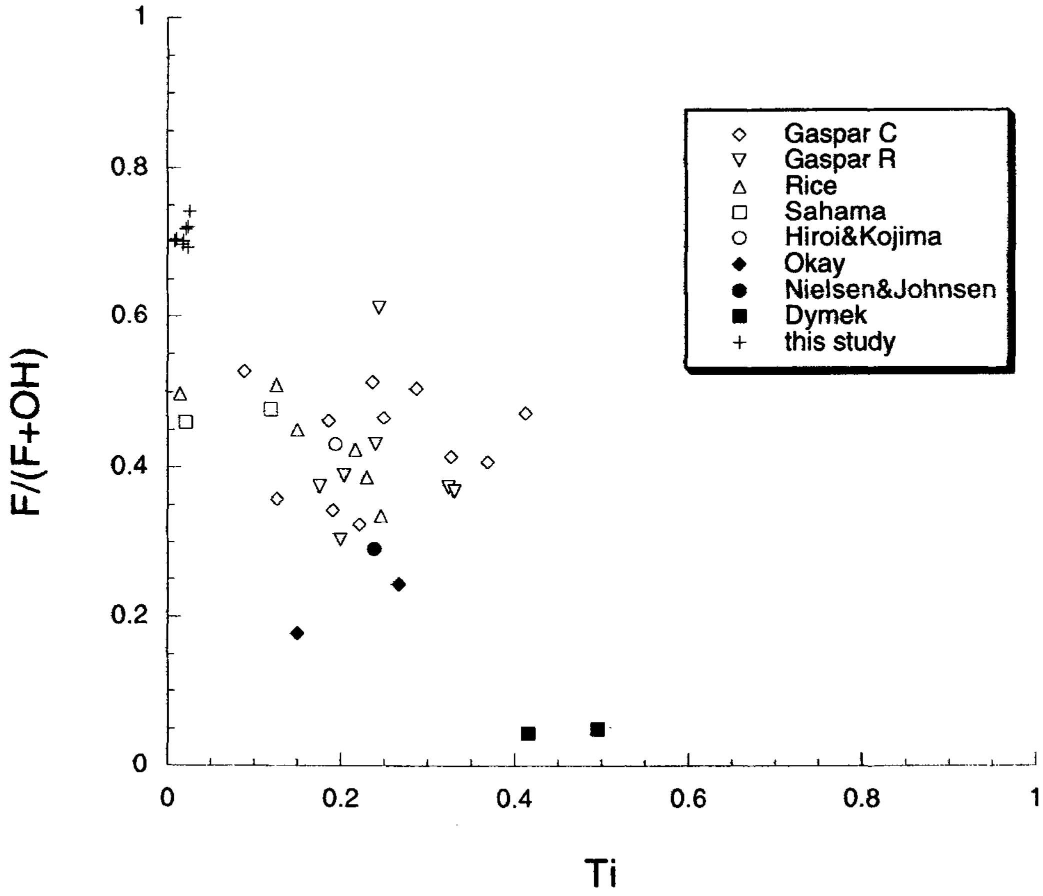

FIG. 6. F/(F+OH) *vs* titanium plot for clinohumites in carbonatites (Gaspar, 1992), in reaction rock (carbonatite with magnetite pyroxenite; Gaspar, 1992), in dolomitic limestone (Rice, 1980), in serpentinite (Dymek *et al.*, 1988), in dolomitic marble (Hiroi and Kojima, 1988), in garnet pyroxenite (Okay, 1994), in plateau basalt (Nielsen and Johnsen, 1978), in limestone (Sahama, 1953) and in marbles (this study).

Spectroscopic characterization of volatile phase

Absorption in the 3800–3000 cm^{-1} wave number infrared region is typical of the O-H stretching vibration, its presence is the first indication that a mineral contains hydrogen (Aines and Rossman, 1984). FTIR spectroscopy is a useful tool to study the hydrous components in minerals. Humite group minerals contain hydrous components of OH in their structure. Eight crystals were analysed for Micro-FTIR spectrum and a typical spectrum of clinohumite is shown in Fig. 7. Eight absorption bands are observed with the major three showing sharp narrow bands. Distinguishable relatively narrow sharp absorption bands are observed at 3693, 3675, 3647, 3572, 3563, 3534, 3410 and 3394 cm^{-1}. Although the sharp narrow bands in three major bands change in intensity relatively, their peak positions are fixed for all samples analysed. If no cracks or fluid inclusions or grain boundaries were included in the measured area, then these absorption bands can be attributed to the OH which is incorporated in brucite layers in the clinohumite. Moreover, a weak broad peak at 3840 cm^{-1} is also observed. In general, the absorption band due to molecular water is broad and ranges from 3700 to 2800 cm^{-1} centered at 3400 cm^{-1}, which is a symmetric absorption band. Surficial hydrogen species like silanol groups give rise to a relatively

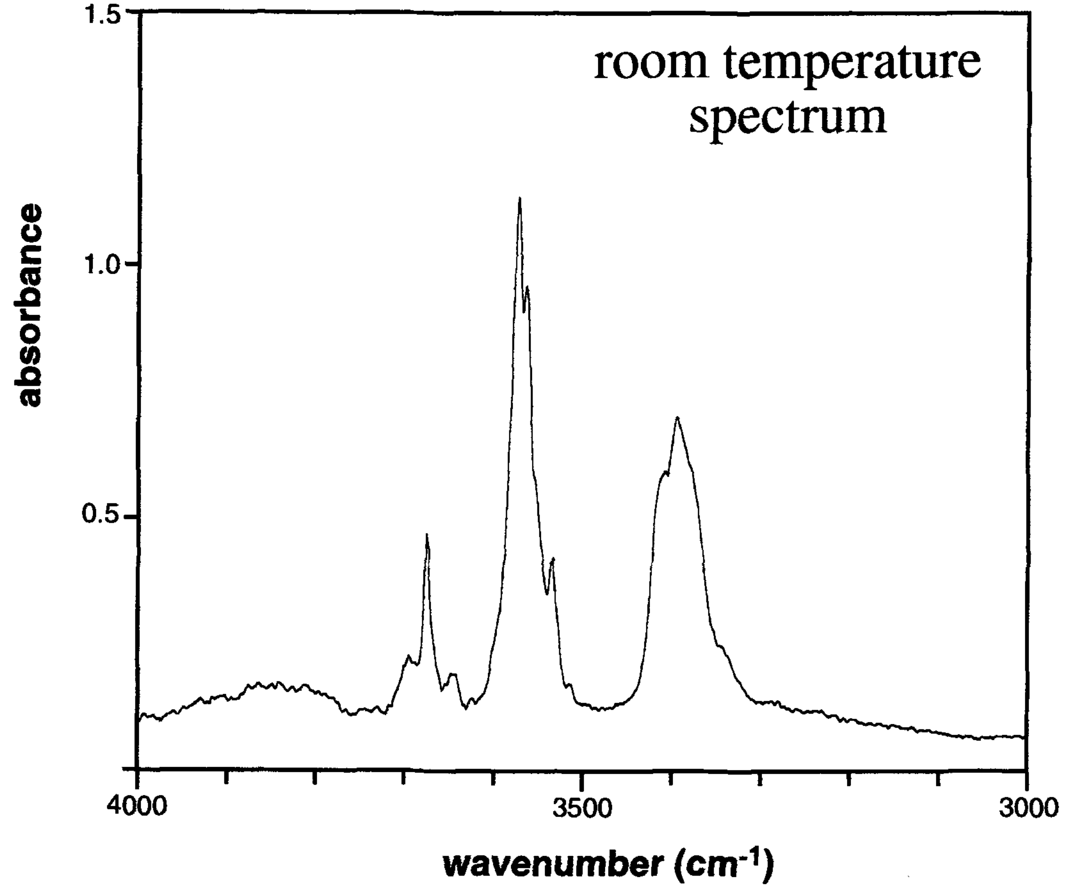

FIG. 7. Room temperature infrared spectrum of the Ambasamudram clinohumite in the 3 μm infrared region. Vertical axis shows absorbance. Sample thickness is about 0.3 mm.

sharp absorption band in the same region. However, the broad band observed is not due to both these cases because of its shape and peak wave-number. Further detailed spectroscopic analysis is necessary to characterise this.

Origin of fluorine-rich clinohumite, metasomatic or metamorphic?

The origin of fluorine-rich clinohumites can be attributed to one of the two processes, viz. a metasomatic process resulting from the external influx of fluorinated fluids or to internal buffering during metamorphism. The former is normally the case in the contact aureoles, where granitic and granodioritic intrusions inject fluids into the impure limestones causing the formation of fluorine-rich clinohumites (e.g. Moore and Kerrick, 1976). Pradeepkumar *et al.* (1996), based on the geochemical studies of mineral and rock samples of Ambasamudram marbles, suggested an extraneous origin for the fluids, which they attributed to the granitic gneiss, which expelled aqueous fluorinated fluids. Our views contradict this. The EPMA results show that clinohumite in Ambasamudram marbles is fluorine rich. Rice (1980) stated that it is possible that all marbles which contain fluorine-rich clinohumite have not resulted from metasomatic introduction of fluorine and that concentration of fluorine can result from strong 'partitioning' of fluorine into hydrous minerals. The primary evidence is from the stable isotopes of calcite in association with the clinohumite. The $\delta^{13}C$ and $\delta^{18}O$ of calcite are +2‰ and +21‰ respectively (Satish Kumar *et al.*, 1997*a*). If the marbles were infiltrated by aqueous fluorinated fluids from extraneous granitic sources, then the oxygen isotopes should preserve the isotopic signatures. The present values correspond with the primary Proterozoic sedimentary carbonate values. Also, Satish-Kumar *et al.* (1997*b*) suggested, from detailed petrological and stable isotopic studies, during the prograde and peak metamorphic conditions, that fluid compositions of the Ambasamudram marbles were internally controlled. In addition, both the marbles and the granitic gneisses have been affected by regional metamorphism during which the formation of clinohumites occurred, and there is lack of synmetamorphic granitic activity. This also suggests an internal fluid buffering rather than an external fluid influx. Calcite-rich marbles are usually impermeable to fluids, except for fracture-controlled fluid infiltration (Holness and Graham, 1991). The clinohumite-bearing assemblages at Ambasamudram are calcite-rich and hence supports our view that they were not affected by the external influx.

The origin of fluorine in the Ambasamudram clinohumites can be attributed to the isochemical reactions involving (OH-F) silicates such as amphiboles or phlogopite, which are abundant in the marble. Rice (1980) attributed to the partitioning of fluorine into hydrous silicates relative to H_2O-CO_2 fluids. We, in our case, also attribute the source for the high concentration of fluorine in clinohumite to this internal buffering mechanism of fluorine concentration.

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