Formation of clinohumite ± spinel in dolomitic marbles from the Makrohar Granulite Belt, Central India: Evidence for Ti mobility during regional metamorphism

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Abstract

The mobility of Ti, a member of high field strength elements, in metamorphic fluids is crucial to understand the recycling of commonly perceived nominally soluble elements and for mass-flux calculations during crustal processes. In this study, we present evidence for large-scale Ti mobility from a suite of clinohumite±spinel-bearing dolomitic marbles from the Makrohar area in central India. The studied rocks mostly contain dolomite and calcite (in subequal proportions) and a subordinate amount of forsterite. It commonly develops 1–5 cm thick, laterally continuous, mostly parallel, sometimes anastomosing, brown-colored clinohumite rich bands with variable spinel. Clinohumite has moderate Ti and F (TiO₂ = 0.55-2.88 wt%; F=0.94-1.88 wt%; n=32). Textural and phase equilibria modeling indicate that clinohumite grew at the expense of forsterite + dolomite under static conditions due to infiltration of F- and Ti-bearing extremely H₂O-rich fluids ($X_{CO_2} < 0.03$), at ~5–6 kbar pressure and \sim 650–700 °C temperature. The Ti and F were most likely supplied by highly channelized aqueous fluids restricted within the centimeter-thick bands. The negative volume change of the reactions further facilitated fluid ingress. The lateral continuity of the bands over several meters across multiple outcrops indicates that Ti was mobile at the meter to kilometer scale. The results are in accordance with experimental studies that solubility of Ti increases in the presence of halides and imply that Ti may be much more mobile in metamorphic fluids during regional metamorphism than previously anticipated.

Keywords: Clinohumite, Ti mobility, forsterite marble, textural modeling, Makrohar, Central India

INTRODUCTION

Aqueous fluid flow is an integral part of prograde regional metamorphism (Ague 2003). Ti, the most abundant member of the high field strength elements (HFSE, along with Zr, Hf, Nb, Ta, Th, U, REEs), is generally considered immobile during regional crustal metamorphism due to the low solubility of rutile (TiO_2) in pure H₂O (Audétat and Keppler 2005; Tropper and Manning 2005). The conservativeness and abundance of HFSEs are, in turn, commonly used to classify tectonic settings of igneous rocks, identify protolith of altered rocks, and understand element cycling during metamorphic processes (Jiang et al. 2005 and references therein). However, there are examples from natural systems that Ti can be mobile under certain conditions and high enrichment up to even economic significance may occur (Tanis et al. 2016 and references therein). This makes it crucial to better understand conditions that affect the mobility of Ti (as a proxy for the HFSEs) during common metamorphic processes.

In this study, we document natural evidence of Ti mobility during crustal metamorphism that led to the formation of Tibearing clinohumite in a forsterite marble from the Makrohar Granulite Belt, Central India. The humite group of minerals has a limited paragenesis wherein Ti- and F-bearing clinohumite has been reported from very few contact or regionally metamorphosed limestones, dolomites, and skarns (Jones et al. 1969; Franz and Ackermand 1980; Rice 1980; Ehlers and Hoinkes

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1987; Gieré 1987; Young and Morrison 1992; Piazolo and Markl 1999; Tropper et al. 2007; Proyer et al. 2008, 2014; Fernandes and Chaves 2014) with only a few reported occurrences in India (Muthuswami 1958; Bhattacharyya 1974; Satish-Kumar and Niimi 1998; Pradeepkumar and Krishnanath 2000; Chattopadhyay et al. 2009). Rarely, Ti-rich but F-poor members have been reported from mantle-derived ultramafic rocks where they form due to high to ultrahigh-pressure metamorphism (Trommsdorff and Evans 1980; Evans and Trommsdorff 1983; Dymek et al. 1988; Scambelluri et al. 1991; Gaspar 1992; Okay 1994; Rahn and Rahn 1998; Wunder 1998; Scambelluri and Rampone 1999; Stalder and Ulmer 2001; Sánchez-Vizcaíno et al. 2005; Groppo and Compagnoni 2007; Shen et al. 2015; González-Jiménez et al. 2017; Nishio et al. 2019). The humite group of minerals, having a general formula of $nM_2SiO_4 \cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$, is essentially a hydrous olivine, with n=1, 2, 3, 4 for norbergite, chondrodite, humite, and clinohumite, respectively, and M = Mg, Fe, Mn, Ca, Zn (Jones et al. 1969; Rice 1980). Ti thus plays a special role in the formation of humite minerals because the Ti content of olivines is generally quite low, whereas clinohumite may contain significantly higher amounts (Jones et al. 1969).

In the studied marbles from the Makrohar Granulite Belt, Central India, the formation of clinohumite, the only hydrous Tiand F-bearing phase, in an otherwise Ti- and F-free assemblage of forsterite-calcite-dolomite, along parallel continuous bands of uniform thickness, indicate its formation due to infiltration of external fluids. Textural and thermodynamic modeling in the CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂ (CMASV) system indicate that

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the presence of Ti and F in H₂O-rich fluids facilitated the formation of clinohumite, which in turn indicates that the presence of F in the H₂O-rich fluids must have enhanced Ti mobility, as the solubility of Ti (or TiO₂) in pure water is very low (Audétat and Keppler 2005; Tropper and Manning 2005). The results are in agreement with experimental studies indicating that Ti is increasingly more mobile in halogen-bearing aqueous fluids, particularly F, by forming soluble complexes with the F⁻ and Cl⁻ ions (Ryzhenko et al. 2006; Antignano and Manning 2008; Purtov and Kotel'nikova 2010; Rapp et al. 2010; Hayden and Manning 2011; Tanis et al. 2016).

REGIONAL GEOLOGY

The study area is a part of the Makrohar granulite belt (MGB) that belongs to the northeastern part of the Central Indian Tectonic Zone (CITZ) (Fig. 1). The CITZ is a ~1500 km long E-W to ENE-WSW trending Proterozoic orogenic belt that results from a complex collision between the Archean Southern and Northern Indian Blocks (Acharyya 2003; Roy and Prasad 2003; Bhowmik 2019) The CITZ contains several Proterozoic supracrustal belts of varied metamorphic grade, which are set in largely undifferentiated migmatitic gneisses and intruded by syn- to post-tectonic granitoids and mafic rocks (Acharyya 2003; Bhowmik 2019). The Mahakoshal supracrustal belt occurs along the northern fringe of the CITZ, and the MGB occurs near the southern margin of the Mahakoshal supracrustal belt (Fig. 1).

The MGB dominantly comprises a suite of ~1.73 Ga granite

FIGURE 1. (a) Generalized geological map of part of the Central Indian Tectonic Zone (CITZ) after Roy and Prasad (2003) showing the studied area. (b) Map of the studied area showing the major lithological distributions and sample locations of the studied banded marbles. (Color online.) gneisses containing slivers of charnockites (Sarkar et al. 1998; Acharyya 2003; Deshmukh et al. 2017). This whole package is intruded by a suite of mafic rocks (apatite–ilmenite-bearing olivine norite) and late pegmatites and overlain by a supracrustal package comprising the studied banded marbles and some metapelites (Fig. 1). The banded marbles occur as kilometer-scale bands (up to a few meters thick) that are folded with northwest-southeast oriented axial planes (Fig. 1). The centimeter-scale internal banding of the marbles is parallel to their length.

FIELD FEATURES AND PETROGRAPHY

The studied marbles are off-white to grayish-white in color and show a saccharoidal appearance due to a high degree of recrystallization (Figs. 2a–2c). Microscopic study reveals that they mostly comprise polygonal grains of dolomite and calcite (in subequal proportions) and a subordinate amount of forsterite, showing a granoblastic fabric (Figs. 2d and 2e).

The marbles commonly develop 1–5 cm thick brown to brownish-gray colored layers rich in clinohumite and spinel (Figs. 2a–2c). The layers are mostly parallel and laterally continuous within a single outcrop, a few meters in size (Fig. 2a). Small patches of white marble are occasionally preserved within the thick layers, and the layers anastomose around the patches (Fig. 2a). Microscopically, the brown layers comprise almost entirely of recrystallized grains of clinohumite (80–90 vol%) with minor calcite (10–15 vol%) and rounded relict grains of forsterite (Fig. 2f). The contact between the host marbles and the





FIGURE 2. (a) Field photograph and (b and c) hand-specimen photographs showing the off-white to grayish white colored saccharoidal marbles with brown colored clinohumite and gray colored spinel-rich layers. (d and e) Backscattered electron (BSE) microscopic images of the unaltered host marbles showing a granoblastic texture defined by polygonal grains of dolomite and calcite (in subequal proportions) and subordinate amount of forsterite. (f) Photomicrograph of brown band (as in b) showing recrystallized polygonal clinohumite grains, with rounded forsterite relicts, and minor calcite. (g) Photomicrograph of gray band (as in a or c) showing recrystallized spinel and clinohumite grains. (h and i) Photomicrograph and BSE image showing recrystallized spinel grains with magnetite at the core. (Color online.)

brown clinohumite layers is quite sharp (Figs. 2a-2c).

The brownish-gray layers comprise recrystallized grains of clinohumite, spinel, and calcite. They are commonly zoned, with dark gray spinel-rich domains in the center usually grading into brownish-gray spinel-poor fringes (Figs. 2a and 2c). The gray spinel-rich central domains (Fig. 2g) are comprised of spinel (10–20 vol%) in addition to clinohumite (60–70 vol%) and calcite (10–20 vol%). The spinel grains commonly contain magnetite at their cores (Figs. 2h and 2i). The brownish-gray spinel-poor fringes (Fig. 2g) comprise spinel (5–15 vol%) in addition to clinohumite (50–60 vol%) and calcite (20–30 vol%). The internal zonation has variable thickness with no discernible boundary between the spinel rich and poor domains (Fig. 2c). The brownish-gray layers as a whole have almost uniform thickness, and their contact with the host marbles is also quite sharp, as marked by the abrupt absence of clinohumite. But due to the gradual decrease in spinel content and the presence of 20–30 vol% calcite in the fringes, the contact with the host marbles may appear gradational (Fig. 2c).

MINERAL COMPOSITIONS

Chemical compositions of the minerals were determined with a CAMECA SX5 microprobe with 5 WD spectrometers at the Central Research Facility of the Indian School of Mines, Dhanbad, India. The instrument was operated at 15 kV accelerating voltage, 2-3 µm beam diameter, and 15 nA current. Natural standards were used for most major elements (Si, Al, Cr, Fe, Mg, Ca, Na, K, Zn, Cl, and F) except for Mn and Ti, for which synthetic standards were used. The raw data were corrected by PAP procedure (Pouchou and Pichoir 1984). Mineral abbreviations in figures and tables have been used after Whitney and Evans (2010). Representative mineral compositions are presented in Online Materials1 Table OM1. Most minerals show fairly uniform composition across the different outcrops/samples (Fig. 1). So, the total numbers of analyses, the average values, and the 2σ standard deviation for each oxide and cation are also indicated in Online Materials1 Table OM1. In the following section salient compositional features of the minerals in the studied rocks are described.

The calcite and dolomite have virtually end-member compositions. X_{Mg} in dolomite ranges between 0.98–0.99 (n=42; average = 0.99±0.01). The forsterite is extremely magnesian with $X_{Mg} = 0.96\pm0.01$ and negligible TiO₂ (<0.04 wt%; n=32; Online Materials¹ Table OM1).

The spinel is fairly magnesian with $X_{Mg} = 0.89 \pm 0.03$ and has insignificant Ti, Cr, Zn, and Mn with recalculated Fe³⁺ < 0.05 apfu (n=15; Online Materials Table OM1). The magnetite virtually has the end-member composition with Fe³⁺/Fe²⁺ = 2.14±0.12, 0.36±0.28 wt% TiO₂, and insignificant Cr and Al [n=10; Online Materials¹ Table OM1; Fe³⁺ is recalculated after the scheme of Grew (2013)].

The clinohumite structural formulas were calculated based on 13 cations following the scheme of Jones et al. (1969). In spite of the slightly low-analytical totals, the ratio of 2Si:[M_{Ti}·2n/ (2n+1)] = 1.00±0.07 indicates that the measured compositions are stoichiometric (Jones et al. 1969) (Online Materials¹ Table OM1). There are three possible exchange vectors in humite minerals: FeMg₋₁, OHF₋₁, and TiO₂Mg₋₁(F, OH)₋₂ (Jones et al. 1969; Rice 1980). Both FeMg₋₁ and OHF₋₁ are observed with X_{Mg} = 0.97 ± 0.02 , and the fluorine content ranging from 0.94-1.88 wt% with $X_F = 0.25 \pm 0.11$ (Online Materials¹ Table OM1). Clinohumite contains 1.14-2.88 wt% TiO₂ with $M_{Ti}/Si=2.25\pm0.16$ (ideal=2.25; Online Materials¹ Table OM1). Ti vs. (OH+F) data presented in Figure 3a shows the efficiency of the exchange vector $TiO_2Mg_{-1}(F, OH)_{-2}$ [or (OH+F) = $-2Ti + \frac{2}{3}M_{Ti}$] (Jones et al. 1969). A plot of TiO₂ vs. [MgO/(MgO+MnO+FeO)] after Ríos et al. (2015) shows that clinohumite compositions from this study are similar to those from other marbles (Fig. 3b).

TEXTURAL MODELING

Textural modeling is a powerful tool to identify if a given mineral assemblage developed in an open or closed system and helps to identify the mass balanced reactions among a set of minerals (Fisher 1989; Lang et al. 2004; Sengupta and Dasgupta



FIGURE 3. (a) Plot of OH+F vs. Ti (apfu × 10⁴) after Jones et al. (1969) showing the efficiency of the exchange vector TiO₂Mg₋₁(F,OH)₋₂ in clinohumite. The data fall along the straight line whose equation matches well with the theoretical equation (OH+F) = $-2\text{Ti}+\frac{3}{3}M_{\text{Ti}}$ (**b**) Plot of TiO₂ vs. MgO/(MgO+MnO+FeO) after Rios et al. (2015) showing that the composition of clinohumite of the studied marbles are similar to those from other marbles. (**c**) Chemographic relations of the phases in the CaO-(MgO+FeO)-Al₂O₃-SiO₂ volume tetrahedron. CO₂ and H₂O are considered excess. All the phases lie on the bounding surfaces of the tetrahedron.

2009). Details of the textural modeling process can be found in Karmakar et al. (2017) and Chowdhury et al. (2013), and the computer program C-Space of Torres-Roldan et al. (2000) has been used for the same.

Observed textural features like recrystallized granoblastic texture and forsterite relicts within clinohumite demonstrate that clinohumite and spinel both crystallized under static conditions and also that clinohumite preferentially replaced forsterite. However, compositionally, forsterite in host rock is anhydrous and Ti-free, whereas clinohumite is not only a hydrous mineral but also the sole phase that contains significant amounts of Ti and F. Therefore, it seems that clinohumite formation requires the presence of Ti- and F-bearing hydrous fluids. This then requires that the balanced chemical reaction that links the reactant and product phases must involve several mobile chemical species. However, although spinel is the sole aluminous phase in the system, dolomitic limestones usually contain minor to moderate amounts of clinochlore or Mg-chlorite (Rice 1977; Bucher-Nurminen 1981; Sharp and Buseck 1988; Bucher and Frey 1994, 2002) and the two Al-rich minerals chlorite and spinel commonly form at each other's expense during metamorphism (Novak and Houzar 1996; Buick et al. 1997; Tropper et al. 2003; Castelli et al. 2007; Groppo et al. 2007; Proyer et al. 2008, 2014; Rapa et al. 2017). So, clinochlore is the likely precursor of spinel in the studied rocks, which was completely consumed.

Through textural modeling, the following mass balanced reactions are obtained using the representative mineral compositions marked in Online Materials¹ Table OM1 (Fig. 3c: dashed lines):

28.41 Dol + 40.0 Fo + 7.00 H₂O + 2.40 SiO₂^(aqueous) + 6.72 Ca²⁺ + 1.00 Ti⁴⁺ + 6.00 F¹⁻ = 16.74 Cal + 10.00 Chu + 16.41 CO₂
$$(\Delta V_{\text{SOLID}} = -37.6\%; V_{\text{CHU}}: V_{\text{CAL}} = 5.8:1)$$
 (1)

The mass balanced reaction for spinel formation is obtained using an end-member clinochlore composition with only slight Fe such that $X_{Mg} = 0.98$ (Fig. 3c: solid lines):

98.94 Dol + 8.42 Chl + 4.71 Fe²⁺ + 1.00 Ti⁴⁺ + 6.00 F¹⁻ = 39.57 Cal + 26.57 Spl + 10.00 Chu + 60.34 H₂O + 70.24 CO₂ + 6.25 Mg^{2+}

$$(\Delta V_{\text{SOLID}} = -39.5\%; V_{\text{CHU}}: V_{\text{CAL}}: V_{\text{SPL}} = -2:1.5:1)$$
(2a)

 $\begin{array}{l} 85.40 \ Dol + 8.42 \ Chl + 4.71 \ Fe^{+2} + 1.00 \ Ti^{+4} + 6.00 \ F^{-1} = \\ 30.95 \ Cal + 26.57 \ Spl + 10.00 \ Chu + 60.34 \ H_2O + 62.89 \ CO_2 \\ + 4.02 \ Ca^{+2} \end{array}$

$$(\Delta V_{\text{SOLID}} = -30.7\%; V_{\text{CHU}}: V_{\text{CAL}}: V_{\text{SPL}} = -2:1.2:1.1)$$
 (2b)

The predicted volume ratio of the product phases roughly matches observed proportions.

PHASE RELATIONS IN THE CMASV SYSTEM

Clinohumite being the sole hydrous phase in the rock, it not only formed from externally derived fluids, but its stability is also likely to be highly dependent on the fluid compositions (Rice 1980). As such, isothermal or isobaric phase diagram projections as a function of the fluid composition are useful tools for interpreting the genetic history of such fluid-influenced assemblages (Connolly and Trommsdorff 1991). Thus topology of the clinohumite-bearing assemblages has been computed and discussed qualitatively in isothermal pressure vs. X_{CO2} (*iT-P-X*_{CO2}) and isobaric temperature vs. X_{CO2} (*iP-T-X*_{CO2}) spaces using the computer program PER-PLEX_6.8.0 (Connolly 2005; 2009). The *iT-P-X*_{CO2} diagram (Figs. 4a–4b) has been calculated at T=600 °C, and the *iP-T-X*_{CO2} (Figs. 4c–4d) diagram was calculated separately at P=5 kbar and P=6 kbar, but since no significant change in topology is observed, only one figure has been presented. The reasons for selecting the *iT=600* °C and *iP=5–6* kbar values have discussed later. However, as the influence of the key metamorphic variables P and T may get obscured in isothermal or isobaric phase diagram projections, a petrogenetic grid was also computed in mixed fluid-P-T space (Figs. 4e–4f) at fixed $X_{CO2}=0.13$, based on the Ip *iT-P-X*_{CO2} and the *iP-T-X*_{CO2} diagrams.

The reaction topologies were computed using the internally consistent thermodynamic data set and equation of state for H₂O-CO₂ fluid of Holland and Powell (2004), updated in 2004. Calculations were done in the simplified six-component system CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂ (CMASV) (Fig. 4). The following solid end-members were considered: calcite, dolomite, forsterite, spinel, clinohumite [Mg-OH: Mg₉Si₄O₁₆(OH)₂], clinochlore, brucite, periclase, antigorite, diopside, tremolite; along with binary H₂O-CO₂ fluid (Connolly and Trommsdorff 1991). The presence of non-CMASH components (e.g., Fe2+ in forsterite, spinel) expands the stability fields of the minerals that accommodate these elements by reducing the activity of the CMASH-end-members. Specifically, OH-clinohumite is metastable in natural assemblages, and the presence of small amounts of F and Ti renders it stable in H₂O-rich fluids (Rice 1980; Grützner et al. 2017). So, to account for the effects of non-CMASH components, computations are done after reducing the activity of the CMASH end-members using the measured compositions of the solid-solution phases (marked with * in Fig. 4; aSpl=0.83, aFo=0.94, Online Materials¹ Table OM1). The activities of spinel and forsterite were obtained using the computer program AX (Holland and Powell 2015). However, for the humite group of minerals, while Duffy and Greenwood (Duffy and Greenwood 1979) have shown that they exhibit non-ideal OH-F solution behavior, activity-composition relationships for the remaining two substitutions [FeMg-1 and $TiO_2Mg_{-1}(F,OH)_{-2}$] are not completely defined. Also, in the internally consistent database, thermodynamic data are available only for the Mg₉Si₄O₁₆(OH)₂ end-member [derived from the experiments of Duffy and Greenwood (1979) and discussed in Pawley (2000)]. So, following Sánchez-Vizcaíno et al. (2005) and the structural refinement scheme of Jones et al. (1969), the activity of the Mg₉Si₄O₁₆(OH)₂ end-member was estimated assuming ideal mixing on all the sites (aChu=0.1, Online Materials¹ Table 1). But since reaction topologies essentially depend on the absolute activity value of the phases (independent of the activity-composition relations), additional calculations were also made for aChu=0.3 and aClc=0.7 (Figs. 4b, 4d, and 4f) to investigate the extent to which the phase stability limits are dependent on the activities. The activities of the phases that are absent in the studied rocks are considered unity (minimum stability). Similar petrological modeling in simplified systems, using activity-constrained end-members to discuss the effects of non-system components, is a useful tool to qualitatively discuss mineral evolution in many natural systems, particularly in fluid-saturated metacarbonate rocks, where all necessary thermodynamic data and solid-solution models are not

FIGURE 4. Phase topology in the fluid saturated CMASV (CaO-MgO-Al2O3-SiO2-H2O-CO₂) system calculated in (a and b) isothermal Pressure vs. X_{CO2} space at 600 °C; (c and d) isobaric T vs. X_{CO_2} space at 5 kbar (similar topology at both pressures); and (e and f) mixed volatile P vs. T space at fixed $X_{CO_2} = 0.13$. (g) Change in the relative modal abundance of the different phases along the texturally modeled reactions 1 and 2. * indicates phases whose activities were reduced based on their measured compositions: (a, c, and e) aSpl=0.83, aFo=0.94, aChu=0.1, and pure Clc; (b, d, and f) red dashed lines for aChu=0.3 and green dashed lines for aClc=0.7. The calculated topologies constrain the stability of the assemblage clinohumite + calcite + dolomite + spinel (±forsterite) in the studied marbles at ~5-6 kbar pressures, at ~650-700 °C in the presence of hydrous fluids with $X_{CO_2} < 0.03$. (Color online.)



available (Connolly and Trommsdorff 1991; Castelli et al. 2007; Groppo et al. 2007, 2017; Dey et al. 2019).

Figure 4g demonstrates the relative volume changes of the reactant and product phases along the texturally modeled reactions 1 and 2, respectively. The calculated topologies constrain the stability of the assemblage clinohumite + calcite + dolomite + forsterite \pm spinel in the studied marbles at ~5–6 kbar pressures, at ~650–700 °C in the presence of hydrous fluids. The results are similar to published studies constraining clinohumite formation in regionally metamorphosed marbles from other localities worldwide (Franz and Ackermand 1980; Rice 1980; Ríos et al. 2015).

DISCUSSION

Mineral evolution in an open system

Petrographic observations and textural modeling indicate that clinohumite + spinel formed from a pre-existing assemblage most likely comprising calcite + dolomite + forsterite + chlorite. Whereas calcite + dolomite + forsterite was ubiquitously present in the whole rock, chlorite possibly occurred only in restricted domains. The clinohumite and spinel forming reactions (1 and 2) require the presence of free fluids, and Putnis (2002) suggested that due to the high-molar volume of free fluids compared to the solid hydrous phases (e.g., chlorite, clinohumite), hydration reactions tend to have negative volume change (ΔV_{SOLID}), which in turn enhances the porosity of the rock, facilitating further fluid influx. The centimeter thick brown to brownish-gray colored clinohumite and spinel bearing layers thus indicate the fluid flow channels. Compositionally, the host rock is devoid of any Ti-bearing accessory phase (like rutile, titanite, ilmenite, etc.). The major minerals of the host rock forsterite + dolomite are also devoid of Ti, F, and OH (H2O), all of which are present in clinohumite. Even chlorite, although a hydrous phase, is not known to contain significant F or Ti (Rice 1980). So, Ti and F were most likely transported by the H2O-rich fluids from outside the system. Hence, the infiltration of free fluids transporting new components into the system indicates that the clinohumite and spinel forming reactions (1 and 2) occurred in an open system. Spinel formation is restricted only to the previously chlorite-bearing domains (gray bands). Because of the ubiquitous presence of forsterite + dolomite in the whole rock, clinohumite forms only where the infiltrated fluids affected this assemblage (brown layers). Forsterite remains preserved elsewhere (the white to gravish-white host rock) and is not replaced by any hydrous phase like serpentine, tremolite, or brucite, which in turn indicates that fluid flow was not pervasive. The morphological features of the clinohumite \pm spinel bands, like uniform thickness, fairly sharp boundaries, lateral continuity, and mostly parallel sometimes anastomosing nature, indicate that the fluid infiltration was highly channelized and restricted within the centimeter thick bands.

Formation of spinel and source of Al

Corundum solubility experiments indicate that the combined effects of pressure, temperature, and the presence of dissolved alkalis, SiO₂ (albite), and halides (F and Cl) in aqueous fluids significantly increases Al solubility by the formation of Na/K-Al-Si-O clusters and/or polymers (Manning 2006, 2007; Tropper and Manning 2007; Newton and Manning 2008; Lucassen et al. 2010). In accordance with the experimental studies, the reported geological manifestations of fluid-mediated Al mobility are also in the form of quartz veins containing Al_2SiO_5 polymorphs \pm biotite (in the wall rock) in regional metamorphic terrains (Kerrick 1988; Ague 1995; Whitney 2000; McLelland et al. 2002; Sepahi et al. 2004). Hence, the mineralogy of the studied rocks, particularly the absence of quartz, sillimanite, and any Na/K-bearing phase with spinel, does not support that Al was mobile in the present case.

If Al remained conserved, then, from Figure 4g, to form ~12 vol% spinel in a layer, it had to contain ~40-45 vol% clinochlore/Mg-chlorite initially. Such chlorite-rich layers are indeed common in dolomitic limestones, and they represent clay layers of primary sedimentary origin (Bucher and Frey 2002). During regional metamorphism of the impure marbles, the clay layers form chlorite and then spinel during prograde metamorphism, whereas chlorite can form during retrogression (Rice 1977; Bucher-Nurminen 1981; Sharp and Buseck 1988; Bucher and Frey 1994, 2002; Novak and Houzar 1996; Buick et al. 1997; Tropper et al. 2003; Castelli et al. 2007; Groppo et al. 2007; Proyer et al. 2008, 2014; Rapa et al. 2017). Moreover, in the studied marbles, spinel does not always occur with clinohumite, but only in some of the layers (gray bands). So, while it is possible that the F- and Ti-bearing hydrous fluids might have carried minor Al form outside, the predominant source of Al for spinel is more likely to be pre-existing chlorite/clinochlore. Because of the schistose habit of chlorite, the chlorite rich bands possibly provided easier pathways for the fluids, and hence chlorite is no longer preserved.

P-T-fluid regime of clinohumite formation

During regional metamorphism, although forsterite marbles are usually diagnostic of granulite-facies conditions (5-8 kbar, 700-800 °C), forsterite can be produced at slightly lower temperatures through interaction with an externally derived H2O-rich fluid (Bucher and Frey 2002). However, chlorite remains stable at all metamorphic grades below the granulite-facies (Bucher and Frey 2002). Hence, prior to fluid infiltration and the formation of clinohumite + spinel, the initial assemblage calcite + dolomite + forsterite + chlorite was stabilized possibly during amphibolitefacies metamorphism. So, the iT-P-X_{CO2} diagram was calculated at 600 °C (Fig. 4a), and the iP-T-X_{CO2} diagram was calculated at 5-6 kbar to examine the domains of the forsterite-in and spinel-in reactions (Fig. 4c). Rice (1980) has shown that that for X_F-clinohumite <0.4, the clinohumite forming reaction 1 in the CMASV system is restricted to extremely low-X_{CO2} values (<0.1). With this knowledge in mind, the P-T-X topologies were calculated for H₂O-rich fluids having $X_{CO_2} < 0.03$; Also, based on the iT-P- X_{CO_2} and the iP-T- X_{CO_2} diagrams, the mixed fluid-*P-T* diagram was constructed at fixed $X_{CO_2} = 0.13$ (Fig. 4e). The figures indicate that:

(1) The reaction 1 (Dol+Fo \rightarrow Cal+Chu) is the primary clinohumite forming reaction in the CMASV system.

(2) The assemblage clinohumite + calcite + dolomite + spinel is not only highly dependent on pressure, with a decrease of the stability field as the pressure increases becoming extremely restricted above ~6–7 kbar pressure, but is also restricted to very H₂O-rich fluid compositions ($X_{CO_7} < 0.02$; Fig. 4a).

(3) At \sim 5–6 kbar pressures, clinohumite + spinel is present

above ~600 °C temperature (Figs. 4c and 4e).

Additional calculations with reduced activity of clinochlore (aClc=0.7; green dashed lines in Figs. 4b, 4d, and 4f) show that there is no significant shift in the spinel forming reaction 2 in *P*-*T*-X space. Calculations with increased activity of clinohumite (aChu=0.3; red dashed lines in Figs. 4b, 4d, and 4f) demonstrate that:

(1) There is a significant shift in reaction 1 to even more H_2O -rich fluid compositions ($X_{CO_2} < 0.01$; Fig. 4b) and higher temperatures >700 °C (Figs. 4d and 4f).

(2) For aChu > 0.1, reaction 2 (Dol+Clc \rightarrow Cal+Chu+Spl) is no longer stable, and the reaction on the opposite side of the invariant point 9 becomes the stable spinel-forming reaction (Dol+Clc \rightarrow Cal+Fo+Spl) (Figs. 4b and 4d).

(3) For aChu > 0.3, the assemblage calcite + brucite becomes stable prior to calcite + clinohumite (Figs. 4b, 4d, and 4f). But the absence of brucite in the studied rocks indicates that the absolute value of activity of clinohumite was indeed <0.3, which is independent of the activity-composition relationships that govern how the non-CMASH components are incorporated.

(4) The low-activity values of clinohumite also mean that the presence of F and Ti is the primary cause for stabilizing clinohumite in the studied rocks.

The absence of brucite in the studied rocks brackets the stability of the assemblage clinohumite + calcite + dolomite + spinel to below 700 $^{\circ}$ C (Figs. 4d and 4f).

In summary, the calculated topologies thus indicate that clinohumite grew in the studied forsterite marbles at ~5–6 kbar pressures and ~650–700 °C in the presence of F-bearing hydrous fluids having $X_{CO_2} < 0.03$ (the field of clinohumite + spinel in Fig. 4). Forsterite remains stable in the host rocks unaffected by the infiltrating fluids. The fugacity of HF in equilibrium with the assemblage clinohumite-bearing assemblage with $X_F < 0.4$ over the temperature range of 600–700 °C is extremely low, ranging from 0.002 to 0.008 bars (Rice 1980). But such small amounts of HF in the fluid are not likely to have a measurable effect on the properties of the dominant CO₂-H₂O mixture. The stability of clinohumite was further facilitated by the presence of Ti in the fluids.

Ti mobility during regional metamorphism

The foregoing discussion clearly demonstrates that clinohumite formed in the rock due to infiltration of Ti- and F-bearing H2O-rich fluids. The results are in accordance with experimental studies that the solubility of Ti significantly increases in the presence of halides in aqueous fluids, especially F, by forming soluble complexes with the F- and Cl-ions (Ryzhenko et al. 2006; Antignano and Manning 2008; Purtov and Kotel'nikova 2010; Rapp et al. 2010; Hayden and Manning 2011; Tanis et al. 2016). Although Ti can be mobile in alkali-Si-bearing hydrous fluids, like Al (Antignano and Manning 2008; Lucassen et al. 2010; Hayden and Manning 2011), Ti content in the hydrous fluids is dominantly influenced the content of halides, with solubilities greater in fluoride than in chloride solutions, and in acid than in neutral or alkaline solutions (Purtov and Kotel'nikova 2010). The Ti-bearing fluids also affected the spinel-magnetite compositions as magnetite occurring at the core of the spinel grains also contain 0.6–0.9 wt% TiO₂. The presence of the clinohumite \pm spinel bands over several kilometers across multiple outcrops indicates that Ti and F were mobile at least at kilometer scale.

The source of the Ti-F-H₂O-fluids is, however, not absolutely clear. As already mentioned, the studied area contains abundant intrusions of a suite of mafic rocks (Fig. 1). These mafic rocks dominantly comprise recrystallized amphibole + plagioclase, but relicts of the primary magmatic minerals (F-apatite, ilmenite, olivine) are still present. So, the most likely scenario seems to be that, during infiltration-driven regional metamorphism, the aqueous fluids hydrated and altered the mafic rocks, thereby becoming enriched in F and dissolving Ti (ilmenite). This Ti-Frich fluid then led to alteration of the nearby marbles, forming clinohumite.

IMPLICATIONS

Ti is essentially considered immobile in common metamorphic systems due to its retention in rutile, ilmenite, and titanite at the source and low-TiO₂ solubility in common metamorphic fluids (Audétat and Keppler 2005; Tropper and Manning 2005). As a consequence, the constant-Ti frame of reference is widely used in most mass-flux calculations in fluid transport and to evaluate open-system behavior during metasomatism. Also, the low mobility of Ti and other HFSEs is one of the suggested sources of the HFSE depletion observed in all arc magmas. However, natural examples and experimental studies have shown that Ti can be significantly mobile in F-bearing aqueous fluids. This compositional dependence of Ti solubility not only questions a fundamental premise of most mass-flux calculations but also has implications for HFSE mobility during metamorphic processes, and consequently, in the understanding of trace element recycling during crustal processes. Therefore, the assumption of Ti immobility and the use of Ti as a chemical frame of reference is not universally valid and should be used with caution.

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Endnote:

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