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Origin of cl	inopyroxene-ilmenite symplectites in mafic granulites from eastern parts of the
	Chotanagpur granite gneissic complex, East Indian shield.
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#### ABSTRACT

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In this manuscript, we report a rare occurrence of rod-like intergrowths of clinopyroxene-23 24 ilmenite that variably replace titanite in a suite of high pressure mafic granulites from the Chotanagpur Granite Gneissic Complex, Eastern Indian Shield. Garnet proximal to the 25 clinopyroxene-ilmenite intergrowth is invariably replaced with symplectic clinopyroxene-26 plagioclase or a rind of plagioclase. Textural modeling of the reaction textures and mineral 27 compositions suggests that the garnet-titanite became unstable and the ilmenite-clinopyroxene 28 preferentially develop after titanite. The presence and texture of halogen rich apatite within the 29 30 ilmenite-clinopyroxene are consistent with a fluid mediated process. Thermodynamic modeling in the NCFMAST (+H<sub>2</sub>O) system, demonstrates that the clinopyroxene-ilmenite symplectite was 31 32 formed along a steeply decompressive retrograde P-T path (from  $\sim 13$  kbar to  $\sim 7$  kbar, at  $\sim$ 800°C), in the presence of partial melts. The study demonstrates that relative to Fe, Mg, and Ca, 33 Ti was less mobile and that the mobility of Ti was restricted within the confines of titanite being 34 replaced by the clinopyroxene-ilmenite symplectite. This study implies that besides the ligand 35 activity, the fluid/rock ratio exerts a strong control on the length scale of Ti transport in natural 36 37 rocks.

38 Keywords:

## Clinopyroxene-ilmenite symplectite; High pressure metamorphisim; CGGC; Textural modeling; CSpace; XMapTools; Ti mobility.

41

#### INTRODUCTION

42 Symplectic intergrowths of clinopyroxene and ilmenite are quite rare in metamorphic rocks.

43 Clinopyroxene-ilmenite symplectites have been reported from mantle xenolith of deep origin,

44 kimberlites, and other alkaline rocks (Nixon and Boyd 1979; Garrison and Taylor 1981; Litasov

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et al. 2003; Ashchepkov et al. 2014 and the references therein), where, their origin is explained 45 either by exsolution from high pressure garnet (Ringwood and Lovering 1970) or clinopyroxene 46 (Dawson and Reid 1970), or by cotectic or eutectic co-precipitation from a protokimberlite melt 47 (Nixon and Boyd 1979; Garrison and Taylor 1981; Litasov et al. 2003). But in metamorphic 48 49 rocks formation of clinopyroxene-ilmenite symplectites is even rarer, and its occurrence is 50 mainly restricted to high pressure metamorphic rocks such as HP basic granulites and retrogressed eclogites (O'Brien and Rötzler 2003; Zhang et al. 2003; Faryad et al. 2006; Marsh 51 52 and Kelly 2017). Depending upon bulk rock compositions and the ambient physiochemical conditions, metabasic rocks contain one or more of the accessory phases, like titanite, rutile, and 53 ilmenite that chiefly contribute to the Ti-budget of the metabasic rocks. Experimental studies 54 have shown that the solubility of Ti in pure H<sub>2</sub>O is very low over a range of pressure and 55 temperature (nominally soluble, Purtov and Kotel'nikova 1993; Ryzhenko et al. 2006; Antignano 56 and Manning 2008; Rapp et al. 2010; Hayden and Manning 2011; Tanis et al. 2016; Karmakar 57 2021). However, the solubility of Ti is dramatically enhanced in presence of halogen-rich, 58 particularlyF-rich fluid (Rapp et al.2010). The experimental data suggest, therefore, different 59 60 length scale of transport of Ti in crustal rocks depending on the physical conditions and the composition of the transporting media (Antignano and Manning 2008; Rapp et al. 2010; Hayden 61 and Manning 2011). Furthermore, rutile, titanite, and ilmenite, the main Ti-sink of metabasic 62 63 rocks, An understanding of the relative stability of the three Ti-rich phases put important constraints on the behavior of Tiduring the evolution of the metabasic rocks. Ti (and other 64 HFSEs) is commonly used as a fixed reference frame for mass-balance calculations and 65 geochemical interpretations in metamorphic and metasomatic processes (Ague 2011). This 66 approach may be seriously affected if Ti becomes significantly mobile. 67

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68 In this communication, we document an occurrence of clinopyroxene-ilmenite symplectite that grew after titanite in a suite of high pressure high temperature mafic granulites 69 70 from the Chotanagpur Granite Gneissic Complex (CGGC), Eastern Indian Shield (Fig. 1a). Our 71 study demonstrates that the clinopyroxene-ilmenite symplectite was formed due to the instability of garnet and titanite when the rock evolved along a steeply decompressive P-T path. Despite 72 73 the presence of halogen-bearing fluid, the length scale of movement of Ti is restricted to a few tens of microns in length. The likely mechanism of formation of the clinopyroxene-ilmenite 74 75 symplectite vis-à-vis the significance of the limited transport of Ti in the metamorphic regime is 76 discussed. **BACKGROUND GEOLOGY AND FIELD OBSERVATIONS** 77 78 The CGGC comprises the northern part of the East Indian shield along with the southern 79 Archean Singhbhum Craton, separated by the Proterozoic North Singhbhum Fold Belt (Fig. 1a). To the west of CGGC, occurs the Paleo to Neoproterozoic rocks of the Central Indian Tectonic 80

81 Zone but its contact with CGGC is concealed by Gondwana sediments (Fig.1a). The northern

82 and eastern boundaries of the CGGC are covered by sediments from Gangetic alluvium. On the

basis of lithological, petrological, and geochronological data, CGGC is divided into three 83

domains (Domain I, Domain II, and Domain III) by Mukherjee et al. (2019). These domains (Fig. 1a), trend approximately E-W. The southernmost Domain I records the most thorough 85

86 geological history. Domain I is dominated by felsic orthogneiss, which contains a variety of

87 mafic, metapelitic, and meta-calcareous enclaves.

84

Geological and geochronological data of Domain I reveal three distinct phases of 88 89 deformation and metamorphism. These three metamorphic events were punctuated by several

90	mafic (Mukherjee et al. 2018b; Dey et al. 2019), felsic (Mukherjee et al. 2017, 2018a),
91	anorthosite(Chatterjee et al. 2008), and alkaline (Das et al. 2018) magmatic events.
92	The earliest distinct metamorphic event (D <sub>1</sub> -M <sub>1</sub> ) reached high to ultra-high temperature
93	metamorphism between 1680-1580 Ma (Sanyal and Sengupta 2012; Dey et al. 2020). The most
94	ubiquitous tectonothermal event (D <sub>2</sub> -M <sub>2</sub> ), present throughout Domain I, is characterized by HP
95	metamorphism with a decompressive retrograde P-T path (~12-9 kbar, 780-800°C) during the
96	early Neoproterozoic (1000 - 950 Ma) time in an inferred continent-continent collisional setting
97	(Chatterjee et al. 2008; Chatterjee and Ghose 2011; Karmakar et al. 2011; Rekha et al. 2011;
98	Mukherjee et al. 2017; Dey et al. 2019, 2020). Between D <sub>1</sub> -M <sub>1</sub> and D <sub>2</sub> -M <sub>2</sub> there was a
99	pronounced period of felsic(1450 Ma) (Mukherjee et al. 2018a) and anorthosite (1550
100	Ma)(Chatterjee et al. 2008) magmatism. The subsequent D <sub>3</sub> -M <sub>3</sub> event at 900-880 Ma deformed
101	and metamorphosed the rocks at amphibole facies (Das et al. 2018; Mukherjee et al. 2018b)
102	condition. These two metamorphic events were interrupted by some mafic (950-900 Ma)
103	(Mukherjee et al. 2018b) and alkaline (Das et al. 2018) magmatism in CGGC.
104	The studied area belongs to the eastern margin of the CGGC, located to the northeast of
105	the Masanjore dam site near Asanbani within Domain I. Like the rest of the CGGC Domain I,
106	the country rock of the area comprises a variety of felsic orthogneiss, within which, the studied
107	mafic granulites occur as subcrops along a NE-SW trend (Fig. 1b).
108	The mafic granulites are medium to coarse-grained, showing a distinct bimodal variation
109	in grain size, and hence the mineralogy is quite evident from the outcrops scale. The medium-
110	grained rock comprises garnet, clinopyroxene, plagioclase, and amphibole(Fig. 1c). The uniform
111	distribution of garnet porphyroblasts (≤1cm diameter) imparts a spotted appearance to the rock
112	(Fig. 1c). The coarse-grained part of the rock occur mostly as amoeboid patches or segregations

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comprising plagioclase, garnet, amphibole, quartz, ± clinopyroxene(Fig. 1d). The patches have a
rim of amphibole around them, separating them from the medium-grained host rock, the
boundary between the two being gradational (Fig. 1d). These patches possibly represent
segregated partial melts or leucosomes.

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#### PETROGRAPHY

118 The studied rocks display plethora of textures that presumably formed in response to the 119 changing physicochemical conditions the rock traversed. In the following section, the textures that help understand the formation of the ilmenite-clinopyroxene intergrowth are discussed. 120 121 Based on overprinting relations, textures and mineralogy of the studied rock can be divided into 122 primary and secondary. The primary textures are defined by the granoblastic aggregates of 123 garnet, clinopyroxene (Cpx<sub>1</sub>), plagioclase (Pl<sub>1</sub>), and rare quartz (Fig.2a-b). Titanite and rutile 124 (Fig. 2f-g; 3a-b) that occur as accessory phases are scattered in the granoblastic mosaic. Garnet grains of variable size (1 mm to  $\leq 10$  mm) and shape contain one or more of the inclusions 125 quartz, plagioclase (Pl<sub>0</sub>), and amphibole (Amp<sub>0</sub>) (Fig. 2c), rutile, and ilmenite. Rarely, garnet 126 contains ilmenite inclusion that is successively rimmed by rutile and plagioclase (Fig. 2e). 127 Although the inclusion of titanite is not seen in garnet, locally inclusion of titanite is seen within 128 the granoblastic clinopyroxene ( $Cpx_1$ ) getting replaced by amphibole ( $Amp_2$ ) (Fig. 2g). This 129 130 raises the possibility that titanite and rutile were stabilized during and/or prior to the stabilization 131 of the granoblastic assemblage. Locally inclusion of amphibole  $(Amp_0)$  and plagioclase  $(Pl_0)$ occur within Cpx<sub>1</sub> (Fig. 2d). The secondary textures are formed after the primary granoblastic 132 133 assemblage. The most conspicuous secondary texture is a fine symplectic intergrowth of ilmenite 134 and clinopyroxene ( $Cpx_2$ ) (<2 $\mu$ m to 55 $\mu$ m lamellar width). The Ilm-Cpx<sub>2</sub> symplectite variably replaces titanite (Fig. 3a-f, 4d-h). The Ilm-Cpx<sub>2</sub> symplectite has a bulbous/wavy front that 135

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protrudes into the titanite (Fig. 3a-b). Locally the Ilm-Cpx<sub>2</sub> symplectite completely replaces 136 titanite preserving the original boundary of the titanite it replaces (Fig. 3c-d). Ilmenite in the 137 138 central part of the Ilm-Cpx<sub>2</sub> symplectite form fine rod-shaped lamellae with small inter lamellar space (~2µm, Fig.3d). Marginal part of the symplectite show distinctly coarse and irregular 139 ilmenite lamellae in the matrix of clinopyroxene (Cpx<sub>2</sub>) (Fig. 3d). The Ilm-Cpx<sub>2</sub> symplectite 140 141 contains fine grains of apatite (mostly visible in the Ca- X-ray intensity maps as the fine red dots within the symplectic domain) (Fig. 4g; 5g). Rarely, small volume of orthopyroxene lamellae are 142 seen in ilmenite-clinopyroxene (Cpx<sub>2</sub>) symplectite (Fig. 4d). The Ilm-Cpx<sub>2</sub> symplectite is 143 144 separated from garnet by a rind of plagioclase (Pl<sub>2</sub>) (Fig.3c) or a symplectic intergrowth of 145 plagioclase (Pl<sub>2</sub>) and clinopyroxene (Cpx<sub>2</sub>) that protrudes into garnet (Fig. 3d-e). Proximal to titanite, Ilm-Cpx<sub>2</sub> symplectite (Fig. 3a-b;e) develops that commonly replaces the titanite 146 147 completely (Fig.3c-d). Nowhere in the rock does Ilm-Cpx<sub>2</sub> symplectite show physical contact with garnet. Plagioclase rind or Pl<sub>2</sub>-Cpx<sub>2</sub> symplectite is always proximal to the garnet grain 148 149 boundary. So, the secondary clinopyroxene (Cpx<sub>2</sub>) is forming symplectic intergrowth with both plagioclase and ilmenite, from here on they are denoted as Cpx<sub>2</sub><sup>PL</sup> and Cpx<sub>2</sub><sup>ILM</sup> respectively. 150 151 Secondary amphibole (Amp<sub>2</sub>) variably replaces the primary granoblastic garnet, clinopyroxene 152 (Fig. 2c; g-i). Amp<sub>2</sub> also replaces the secondary clinopyroxene (Cpx<sub>2</sub>) (Fig.3e). This feature 153 suggests that  $Amp_2$  formed after the development of the secondary clinopyroxene (Cpx<sub>2</sub>). Secondary amphibole (Amp<sub>2</sub>) preserves the initial shape of the clinopyroxene when replacing 154 155 Cpx<sub>1</sub> and Cpx<sub>2</sub> (pseudomorphic replacement) (Fig. 2i; 3e-f). During this replacement of Cpx<sub>1</sub>, titanite inclusion appears to be stranded within the secondary phase (Amp<sub>2</sub>) (Fig. 2g). 156 157

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#### PHASE COMPOSITION

#### 159 Analytical techniques

- 160 Major elemental analyses were performed using a Cameca SX100 Electron Probe Micro
- 161 Analyser equipped with four wavelength-dispersive spectrometers (WDS) from the Department
- 162 of Geology and Geophysics, Indian Institute of Technology, Kharagpur. All points were
- analyzed with 15 kV acceleration voltage, 20 nA beam current, and a beam size of 1  $\mu$ m. The
- 164 dwell time for the measured elements was set at 10 s for the peak and 5 s for the background.
- 165 Natural minerals and synthetic compounds were used as standards.
- 166 Representative mineral compositions are presented in Tables 1 to 4. Mineral abbreviations in

167 figures and tables have been used after (Whitney and Evans 2010). Cation recalculation for the

estimation of  $Fe^{3+}$  is done following the scheme of Droop (1987). In the following section,

salient compositional features of the minerals are described.

#### 170 Mineral compositions

171 Garnet. The garnets are dominantly solid solutions of almandine, pyrope, and grossular, with a

minor amount of spessartine (Table-1): almandine (43- 57mol %) contents are highest with a

lesser amount of grossular (19- 33 mol%) and pyrope (16- 26%) and minor spessartine (1- 4

174 mol%). The porphyroblasts show internal core-rim zonation with the core compositions being

less ferroan and grossular rich ( $Grt_C$ :  $Alm_{43-47}Grs_{28-33}Prp_{21-26}Sps_{1-2}$ ;  $X_{Mg}$ =0.31-0.37) than rims

176 (Grt<sub>R</sub>: Alm<sub>49-57</sub>Grs<sub>20-26</sub>Prp<sub>16-20</sub>Sps<sub>2-4</sub>;  $X_{Mg}$ =0.23-0.29). TiO<sub>2</sub> content of garnet is negligible, below

- 177 0.25 wt%. Garnet core composition is flat and homogenous, extended up to the thin rim.
- 178 **Pyroxene.** Representative data of the pyroxenes are presented in Table 2. Both matrix
- 179 clinopyroxenes ( $Cpx_1$ ) and symplectic clinopyroxenes ( $Cpx_2^{PL}$  and  $Cpx_2^{ILM}$ ) represent diopside-
- hedenbergite solid solutions with  $X_{Mg}=0.72-0.83$  (Fig 3a). Cpx<sub>1</sub> has slightly higher Al (0.12-0.24)

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- 181 a.p.f.u) and Na (0.03-0.05 a.p.f.u) content than  $Cpx_2^{PL}$  and  $Cpx_2^{ILM}$  (Al=0.05-0.10 a.p.f.u;
- 182 Na=0.02-0.03 a.p.f.u). TiO<sub>2</sub> content of Cpx<sub>1</sub> (0.137-0.628 wt%), as well as Cpx2 (0.069-0.536
- 183 wt%), is negligible. The orthopyroxenes in the symplectic intergrowths are magnesian with
- 184  $(X_{Mg}=0.55-0.58, Fig 4i.).$
- 185 Plagioclase. Representative plagioclase compositions are given in Table 3. There is a
- 186 considerable variation in plagioclase compositions depending on the textural types with  $X_{OR} < 1$ .
- 187 The matrix plagioclase (Pl<sub>1</sub>)shows a prominent increase in anorthite content from the core
- 188  $(X_{An}=0.43-0.60)$  to the rim  $(X_{An}=0.75-0.86)$  (Fig 3b). Symplectic plagioclase (Pl<sub>2</sub>) is similar to
- 189 the rim of  $Pl_1$  (X<sub>An</sub>=0.72-0.86).
- 190 Amphibole. Representative compositions of the amphiboles are presented in Table 4. According
- to the (Leake et al. 1997) and (Leake et al. 2004) classification scheme, all the amphiboles are
- 192 calcic. The amphibole inclusions in garnets (Amp<sub>0</sub>) are mostly pargasitic in nature with
- 193  $X_{Mg}=0.62-0.70$ . The matrix amphibole (Amp<sub>1</sub>) composition ranges between tschermakite and

194 magnesio-hornblende with  $X_{Mg}=0.59-0.72$ .

- Accessory minerals. Representative chemical compositions of the accessory phases are in Table
  5. Ilmenite present in the clinopyroxene + plagioclase symplectite is nearly pure FeTiO<sub>3</sub>. Rutile
- is present as a pure phase. Titanite is slightly aluminous (1.1-1.4 wt% Al<sub>2</sub>O<sub>3</sub>) with no F. Apatite
  has 1.657 wt% of F and 0.25 wt% of Cl.
- 199

# 200 MODELING THE FORMATION OF CPX<sub>2</sub> + ILM SYMPLECTITES USING CSPACE 201 AND XMAPTOOLS

202 Textural modeling of Ilm-Cpx<sub>2</sub>(±Opx) symplectite: a mass balance approach

203	The textural features, described above, suggest that the symplectic intergrowth of $IIm$ -Cpx <sub>2</sub> (with
204	rare Opx) develops preferentially over the titanite. Rutile was present prior to the formation of
205	the symplectite. It is also possible that the rutile might have been involved in some symplectite
206	forming process. However, textural features support involvement of titanite in the formation of
207	Ilm-Cpx <sub>2</sub> symplectite, while such features on account of rutile (e.g. presence of rutile in the
208	vicinity of or in contact with Ilm-Cpx <sub>2</sub> symplectite) are absent. Accordingly, the textural
209	modeling study was carried out using titanite as the only Ti-bearing reactant phase that was
210	replaced by the Ilm-Cpx <sub>2</sub> ( $\pm$ Opx).
211	Mass balance calculations with the measured mineral compositions are a powerful technique to
212	explain the observed mineralogy and the textural relations (Fisher 1989; Lang et al. 2004;
213	Sengupta et al. 2004; Chowdhury et al. 2013). This approach returns stoichiometrically balanced
214	chemical reactions involving the reactant and product phases and hence, provides vital clues
215	about the mobility of the different chemical species in a given compositional space (Lang and
216	Rice 1985; Fisher 1989; Lang et al. 2004; Sengupta et al. 2004, 2009; Sengupta and Dasgupta
217	2009; Chowdhury et al. 2013; Karmakar et al. 2017). The computer program CSpace (Torres-
218	Roldan et al. 2000) has been employed for identifying stoichiometrically balanced chemical
219	reaction(s) involving the measured compositions of the reactant and product phases. This
220	algebraic analysis with Cspaceinvolves the singular value decomposition (SVD) of a
221	compositional matrix <b>M</b> of <b>m</b> mineral phases in terms of <b>n</b> components ( <b>M=m x n</b> ) (Lang et al.
222	2004).The chemical species that are suspected to show mobility (e.g FeO, MgO, CaO, Na <sub>2</sub> O,
223	TiO <sub>2,</sub> etc in this study) are considered as 'phases' in the computational matrix (Sengupta and
224	Dasgupta 2009). A detailed discussion on the SVD method is presented in several studies (Lang
225	et al. 2004; Sengupta et al. 2004; Sengupta and Dasgupta 2009; Chowdhury et al. 2013). In the

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226	multi-component system with a number of mobile species, the CSpace programs can return
227	several stoichiometrically balanced reactions for a set of reactant and product phases. Of these
228	probable reactions, if more than one reaction is returned by the CSpace, the likely reaction will
229	be chosen based on the following criteria:
230	1. The observed reactant and the product phases must lie on the opposite side of the reaction
231	2. The calculated and observed volume ratio of the $IIm-Cpx_2$ in the symplectite must match
232	Calculation of volume ratio of Ilm-Cpx2 symplectite obtained from reactions: The
233	coefficients in the obtained balanced reactions are the molar proportions of the phases and the
234	volumes of the necessary solid phases are calculated by multiplying the molar proportions by the
235	molar volume of that phase. The molar volume of the phase is obtained using the computer
236	program PERPLE_X (ver. 6.9.1) (Connolly 2005, 2009) with the thermodynamic data of
237	Holland and Powell (2011). For a particular solid solution phase, the molar volume of the
238	different end-members are calculated, at an average P-T condition of 800°C, 9 kbar, based on the
239	constrained physical conditions of metamorphism (presented in the following section). The
240	molar volume of the solid-solution phases, $(V^{SS})$ is then calculated using the following relation:
241	$\mathbf{V_N}^{\mathbf{SS}} = (X_{\mathrm{A}} \times V_{\mathrm{A}}) + (X_{\mathrm{B}} \times V_{\mathrm{B}})$
242	where A and B are the two end members of the solid-solution phase N, V is the molar volume of

that end member, and X is the mole fraction of the corresponding end member.

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244	Estimation of volume ratio of Ilm-Cpx2 symplectite using XMapTools: The volume
245	proportion of Cpx and Ilm only from the Cpx <sub>2</sub> -Ilm symplectic domain is estimated to check how
246	well the modeled reaction product is correlating with the observed textures. We have taken this
247	as a parameter as other phases such as Grt, Pl are formed or consumed in other concurrent
248	reactions, and texturally they can't be attributed solely to the titanite breakdown reaction.Owing
249	to the fine-grained nature of the Cpx2-Ilm symplectites, estimation of observed volume
250	proportion is difficult. For accurate estimation of the phase proportions of Cpx and Ilm in the
251	symplectites, the software XMapTools (ver. 3.4.3) (Lanari et al. 2014, 2019) is used. In this
252	process X-ray intensity maps of the elements, Si, Ti, Al, Fe <sup>TOTAL+2</sup> , Mg, Na, Ca (Fig 5a-g) of the
253	selected microdomains, produced using EPMA, are used to classify all the different phases
254	accurately with the help of XMapTools and phase proportions of Cpx and Ilm are calculated only
255	from the symplectic domain (Fig. 5h), omitting all other phases present.
256	The choice of domains for the textural modeling study
257	Two micro-domains viz. Domain I and Domain II are chosen for detailed textural analyses. In
258	Domain I (Fig.3c), Ilm-Cpx <sub>2</sub> symplectite is separated from the porphyroblastic garnet by a rind
259	of Pl <sub>2</sub> . In Domain II, Ilm-Cpx <sub>2</sub> symplectite is separated from garnet by a symplectic intergrowth
260	of Cpx <sub>2</sub> -Pl <sub>2</sub> (Fig 3d). Proximal to garnet, the fine symplectite of clinopyroxene (Cpx $_2^{PL}$ ) and
261	plagioclase ( $Pl_2^{CPX}$ ) develops on and variably replaces the garnet. Away from garnet, lamellar
262	intergrowth of Cpx <sub>2</sub> -Ilm develops after titanite.
263	In both of the domains, the core and rim of garnet are respectively treated as reactant and product
264	phases. The mineral compositions that are used for textural modeling from both of these micro-
265	domains (Domain I and II) are marked with the superscript 'MDI' and 'MDII' in the data tables

266 (Table 1-5) respectively.

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Modeled reactions in Domain I: If all the product phases between titanite and garnet are 267 considered, the CSpace program returns the net reaction: 268  $3.61 \text{ Ttn} + 7.28 \text{ Grt}_{\text{C}} + 5.21 \text{ Oz} + 1.20 \text{ [Na<sub>2</sub>O]}$ 269  $= 3.56 \text{ Ilm} + 4.07 \text{ Cpx}_{2}^{\text{ILM}} + 5.08 \text{ Pl}_{2} + 1.00[\text{CaO}] + 3.33 \text{ Grt}_{R}$ 270 (1)  $\Delta V_{\text{SOLID}} = V_{\text{PRODUCTS}} - V_{\text{REACTANTS}} = +7.5\%$ ; Cpx/Ilm =2.4 (observed Cpx/Ilm: 2.2) 271 This net reaction has two parts. 272 At the titanite end, the likely reaction is, 273 274 3.61 Ttn + 4.50 Oz + 4.60 [FeO] + 3.0 [MgO] + 0.1 [CaO] + 0.05 [Na<sub>2</sub>O]  $= 3.56 \text{ Ilm} + 4.07 \text{ Cpx}_2^{\text{ILM}}$ 275 (1.a)At the garnet end, the likely reaction is, 276 277 7.28  $Grt_{C}$  + 0.72 Oz + 1.15 [Na<sub>2</sub>O] = 3.33  $\text{Grt}_{\text{R}}$  + 5.08  $\text{Pl}_{2}^{\text{CPX}}$  + 4.60 [FeO] + 3.0 [MgO] + 1.1 [CaO] 278 (1.b)Modeled reactions in domain II: If all the products are considered CSpace program produces 279 the following net reaction, 280  $3.25 \text{ Ttn} + 14.44 \text{ Grt}_{C} + 7.10 \text{ Qz} + 0.60 \text{ [Na<sub>2</sub>O]} + 1.00 \text{ [CaO]}$ 281  $= 3.19 \text{ Ilm} + 6.80 \text{ Cpx}_2(\text{Cpx}_2^{\text{PL}} + \text{Cpx}_2^{\text{ILM}}) + 6.75 \text{ Pl}_2 + 8.40 \text{ Grt}_{\text{R}}$ (2) 282  $\Delta V_{\text{SOLID}} = V_{\text{PRODUCTS}} - V_{\text{REACTANTS}} = +6.6\%; Cpx(Cpx_2^{\text{PL}} + Cpx_2^{\text{ILM}})/\text{Ilm} = 4.5;$ 283 284 285 Similar to Domain I, the net reaction of Domain II can be divided into two sub-reactions. The following is the reaction at the titanite end, 286 3.25Ttn + 2.78Oz + 3.68 [FeO] + 2.40 [MgO] + 0.025 [Na<sub>2</sub>O] 287 = 3.19Ilm + 3.02Cpx<sup>ILM</sup> + 0.5[CaO] (2.a)288 Calculated volume ratio of  $Cpx_2/IIm$ , from reaction 2.a= 2.0;(Observed Cpx/IIm = 1.9) 289

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290 The reaction at the garnet end,

291 
$$14.44$$
Grt<sub>C</sub> +  $4.32$ Qz +  $1.5$  [CaO] +  $0.57$  [Na<sub>2</sub>O]

292 = 
$$8.40$$
Grt<sub>R</sub> +  $3.78$  Cpx<sub>2</sub><sup>PL</sup> + $6.57$  Pl<sub>2</sub> +  $3.68$  [FeO] +  $2.40$  [MgO] (2.b)

From the calculated volume change and volume ratios, Domain II is very similar to Domain I,

except for the addition of orthopyroxene as a product in it. The presence of minor amounts of

- orthopyroxene observed in the Cpx<sub>2</sub>-Ilm symplectic domains may be accounted for, by the
- 296 following mass-balanced reaction:

297 
$$3.29$$
Ttn + 14.44 Grt<sub>C</sub> + 7.10 Qz + 0.60 Na<sub>2</sub>O + 1.00 CaO

298 = 
$$3.26$$
Ilm +  $6.80$  Cpx +  $0.1$  Opx +  $6.75$  Pl +  $8.40$  Grt<sub>R</sub> (3)

299

#### 300 PHYSICAL CONDITIONS OF METAMORPHISM

#### 301 Detail study of the P-T evolution of the mafic rocks is beyond the purview of this study. In the

following sections emphasis will be given to the reconstruction of the change in the physical

303 conditions of metamorphism that led to the formation of the ilmenite-plagioclase-clinopyroxene

intergrowth after the primary granoblastic assemblages.

#### 305 Choice of phase compositions for the estimation of P-T condition of metamorphism

306 Ubiquitous presence of the assemblage garnet-clinopyroxene-plagioclase-quartz-titanite (±rutile)

307 suggests that the studied mafic granulites witnessed high pressure metamorphism(O'Brien and

308 Rötzler 2003; Pattison 2003). The high pressure assemblage was presumably in equilibrium with

a melt phase (represented by the garnet-bearing leucosome) at the thermal maxima. A number of

studies have shown that high pressure metamorphism of the rocks of diverse bulk compositions

develop garnet on the prograde path. These garnet grains may serve as a substrate over which

new garnet rims grow till the  $T_{max}$  (maximum temperature) is reached(Saxena and Ganguly

15

313 1987; Spear 1993). This leads to prograde growth zoning (rim-ward decrease in Fe and Mn and increase in Mg) in garnet (Harte and Henley 1966; Hollister 1966; Lopez Ruiz 1976; Tuccillo et 314 315 al. 1990; Ikeda 1993; Nyström and Kriegsman 2003; Kohn 2014; Dempster et al. 2020). Since garnet preferentially partitions Fe relative to the coexisting pyroxene, the highest temperature 316 will be obtained with rim compositions of garnet and coexisting pyroxene if the former shows 317 318 growth zoning. X-ray intensity maps and the measured composition of garnet show distinct 319 enrichment of Fe and Mn in the thin rim (30-80µm) relative to the core of garnet (Fig. 4a;4c). 320 The core part of garnet is compositionally homogeneous and is Mg-rich relative to the thin rim 321 (Fig.4d). The thin rim of garnet, therefore, is interpreted to have formed during the partial 322 exchange of elements with the coexisting ferromagnesian phases during retrogression (Spear 323 1993). Studies have demonstrated that at temperature >750°C and in presence of a melt phase, 324 volume diffusion in garnet and pyroxene are sufficiently fast to homogenize large garnet 325 porphyroblasts (>0.5 mm)over a range of cooling rates (Chakraborty and Ganguly 1991; Carlson and Schwarze 1997; Ganguly et al. 1998; Chakraborty 2008; Caddick et al. 2010). Several 326 327 studies in high temperature granulite metamorphic belts record that equilibrium among the mineral assemblages that developed during the T<sub>max</sub> occurs over a large area (several square km, 328 329 Kelsey and Hand 2015). This explains the rare preservation of growth zoning in garnet in high to 330 ultra-high temperature metamorphism. Rapid and short-lived heating at a high temperature can only develop the rare prograde zoning in high to ultra-high temperature granulites(Chen et al. 331 332 1998; Hollis et al. 2006). In view of all the observations, the compositionally homogeneous core compositions are chosen for the estimation of pressure and temperature during which the 333 334 primary(granoblastic) assemblages equilibrated. The compositions of the symplectic minerals

#### 16

and the rims of the porphyroblastic phases constrain the physical conditions during which thesymplectic assemblage equilibrated during retrogression.

337 Conventional thermobarometry

338 For estimation of temperature,  $Fe^{2+}$ - Mg exchange thermometer involving garnet and

clinopyroxene is used (Ellis and Green 1979). Metamorphic pressure has been computed from

340 the assemblage garnet-plagioclase-clinopyroxene-quartz (GCPS, Eckert et al. 1991). The core

341 compositions of the granoblastic assemblage of  $Grt_C+Pl_1+Cpx_1(\pm Qz)$ , yield a tight cluster of

temperature of 800-850°C (Table-6). The Fe-Mg exchange thermometer has a very steep slope in

the P-T field. This together with the accuracy of the geothermometer ( $\pm$  50°C) suggest that the

344 choice of reference pressure should not affect the estimated temperature values. At the reference

temperature of 850°C, the GCPS barometer yields 12-13 kbar pressure for the core compositions

of the granoblastic (primary) phases. The temperature of 850°C is, therefore, considered to be the

347 maximum temperature recorded by the primary assemblages at the estimated pressure of 13 kbar.

348 The rim compositions of garnet (Grt<sub>R</sub>) coupled with symplectic  $Pl_2+Cpx_2^{PL}$  yield distinctly lower

temperature (650-700°C) and pressure (6.5-8 kbar, Table-6). The estimated pressure and

temperature is considered as the recorded physical conditions when the symplectic intergrowth

 $of Cpx_2-Pl_2$  and  $Ilm-Cpx_2$  were formed.

#### 352 Isopleth intersection in pseudosection

353 Notwithstanding the following points:

1. The numerically computed phase diagram (pseudosection) is influenced by the input bulk

rock composition. The chosen bulk rock composition may or may not represent the

356 composition of the equilibrium.

17

2. Uncertainties associated with the internally consistent thermodynamic data and the

activities of the solid solutions

357

359	The isopleths intersection methods yield reasonably well constrained P-T estimate for
360	metamorphism and are widely used by petrologists (Evans 2004; Palin et al. 2016).
361	The P-T pseudosection has been computed using the program Perple_X (ver. 6.9.1;
362	Connolly 2005) with the internally consistent thermodynamic dataset of Holland and Powell
363	2011 (TC-DS633). The a-X relationships of the minerals chosen for the numerical calculations of
364	the phase diagram are the following: clinopyroxene (Holland et al. 2018), clino-amphibole
365	(Green et al. 2016), melt (Holland et al. 2018), garnet (Holland et al. 2018), orthopyroxene
366	(Holland et al. 2018), feldspars (Holland and Powell 2003). The numerically computed phase
367	diagram is presented in Figure 6a-c. In the computed P-T pseudosection, the primary
368	granoblastic assemblage ( $Grt_C$ -Pl <sub>1</sub> -Cpx <sub>1</sub> -Qz-Ttn-Rt) coexists with a melt phase at temperature
369	>800°C between 9-13 kbar (Fig.6a-b). The intersection of the isopleths of the garnet core ( $X_{ALM}$ ,
370	$X_{PRP}$ , $X_{GRS}$ ) and the plagioclase ( $X_{AN}$ ) define a narrow P-T domain of 800-900°C and 11-13 kbar
371	(Fig. 6b). Several experimental studies on a range of basaltic compositions showed that
372	dehydration melting of the basic rock produces high pressure assemblage
373	(garnet+clinopyroxene+plagioclase+q) at >800°C between ~10-13 kbar (Rötzler and Romer
374	2001; Vielzeuf and Schmidt 2001; O'Brien and Rötzler 2003; Pattison 2003). The presence of
375	abundant garnet-bearing leucosome, presumed to be a melt phase, with the primary granoblastic
376	assemblage and the results of the melting experiment on mafic protolith corroborate the P-T
377	values calculated of 800-900°C and 11-13 kbar from the isopleths intersection method. The
378	computed P-T pseudosection has a small P-T field (7-9 kbar and $\sim$ 750-800°C) in which the
379	symplectic intergrowth of Ilm+Cpx <sub>2</sub> ( $\pm$ Opx) and the plagioclase rind is stable with garnet. The

#### 18

380	isopleths of garnet rim $(X_{ALM}, X_{PRP}, X_{GRS})$ and the symplectic plagioclase $(Pl_2; X_{AN})$ converge
381	within this field at ~7.5-8 kbar and 750-780°C (Fig. 6b).

382

#### DISCUSSION

#### **Textural modeling of Cpx<sub>2</sub>-Ilm symplectite: an algebraic approach**

384 Textural features suggest that the garnet and titanite(±rutile)of the primary assemblages became 385 unstable and are separated by two types of symplectites. The symplectite of  $IIm-Cpx_2(\pm Opx)$ develops near and variably replaces the titanite. Whereas the symplectite of  $Cpx_2 + Plg_2$  replaces 386 387 garnet and forms away from the titanite (Fig. 3d-e). In another situation, a rind of plagioclase 388 having the same compositions as in Pl<sub>2</sub> develops at the contact of and replaces garnet porphyroblasts (Fig. 3c). Rutile is found to coexist with garnet but not in the symplectite 389 390 domains. This raises two possibilities. One likely scenario is that rutile might be consumed 391 during the formation of the Ilm-Cpx<sub>2</sub> symplectite and preserved only where the symplectite did not form. While there exists clinching textural evidence in support of Ilm-Cpx<sub>2</sub> symplectite 392 393 partially to completely replacing titanite, the role of rutile in the formation of this symplectite remains unclear. In the following section, we will focus on the process that promoted the growth 394 395 of the Ilm-Cpx<sub>2</sub> and Cpx<sub>2</sub>-Plg<sub>2</sub> symplectites after the primary titanite and garnet. 396 Formation of symplectites: Solution-reprecipitation vs volume diffusion: Two endmember 397 processes, commonly working in tandem, are invoked to explain mineral replacement textures. 398 These are (a) volume diffusion(Lasaga 1981; Ganguly 2002; Watson and Baxter 2007; Chakraborty 2008) and (b) solution reprecipitation(Putnis 2002, 2009; Hellmann et al. 2003; 399 Putnis and Putnis 2007; Ruiz-Agudo et al. 2014). Though both processes can be driven by 400 401 temperature, each process has its characteristic mechanism of mass transport during the mineral replacement. In the case of the diffusion-driven process, the framework of the mineral being 402

403	replace	ed remains essentially intact. Mass transport, through volume diffusion, occurs through the
404	frame	work during the replacement process (Ganguly 2002; Chakraborty 2008). In the case of a
405	fluid-a	ided solution and reprecipitation driven process, mineral replacement occurs through
406	compl	ete destruction of the reactant minerals, and the product phases are formed with new bonds
407	(Putni	s 2002, 2009). The replacement process can be isochemical or allochemical (common)
408	depen	ding on the composition of the fluid vis-à-vis the phases being replaced and the ambient
409	physic	al condition(Putnis and Putnis 2007; Putnis 2009). A number of features suggest that the
410	fluid-r	nediated solution-reprecipitation process dominated during the formation of $IIm$ -Cpx <sub>2</sub>
411	symple	ectite after titanite (with or without rutile). These are:
412	1.	Titanite has triclinic symmetry that is completely different from ilmenite (trigonal) and
413		clinopyroxene (monoclinic). This then follows that the growth of Ilm-Cpx <sub>2</sub> symplectite
414		requires complete breakdown of all the bonds in the titanite and redistribution of
415		elements including Ti. The replacement also involves a marked change in chemistry as
416		the reactant titanite contains insignificant FeO and MgO relative to Ilm-Cpx <sub>2</sub> . These
417		features are consistent with fluid aided solution-reprecipitation process (Putnis and Putnis
418		2007; Putnis 2009).
419	2.	The original outline of the reactant titanite is conserved during the variable replacement
420		of titanite by Ilm-Cpx <sub>2</sub> symplectite (pseudomorphic replacement, Fig.3c-d). Several
421		studies have demonstrated that pseudomorphic mineral replacement texture is the
422		consequence of the fluid-mediated solution reprecipitation process in which replacement
423		occurs in nano- to micrometer scale at nearly(Putnis 2009; Ruiz-Agudo et al. 2014). The
424		wavy/ bulbous outline of the protruding Ilm-Cpx <sub>2</sub> front into the titanite (Fig. 3a-b) also
425		supports the solution-reprecipitation process.

426	3.	The Ilm-Cpx <sub>2</sub> symplectite contains tiny apatite with significant F and Cl. Since the
427		primary assemblage does not have any sink of P or the halogens, only a fluid-mediated
428		process can explain the texture.
429	4.	The Ilm-Cpx <sub>2</sub> symplectite is commonly associated with Pl <sub>2</sub> -Cpx <sub>2</sub> symplectite that
430		preferentially replaces garnet porphyroblasts. Plagioclase in the symplectite contains a
431		significant albite molecule (Ab 15-25%). Since the garnet composition cannot account for
432		the Na in the symplectic plagioclase, Na must be supplied by the fluid.
433	Mobil	ity of chemical species during the formation of Ilm-Cpx2 symplectite: The mass-
434	balanc	ed reactions (Reaction 1-2) that are obtained from textural modeling studies suggest the
435	mobili	ity of a number of chemical species across the initial boundary between garnet and titanite.
436	In Do	main I wherein Cpx <sub>2</sub> did not develop with Pl <sub>2</sub> , the breakdown of garnet to plagioclase rind
437	release	es FeO, MgO, and CaO by the reaction (1.b)(Fig.7a). These chemical species moved to and
438	reacte	d with the titanite by a fluid-mediated process to produce $IIm-Cpx_2$ by reaction
439	(1.a)(H	Fig.7a). This feedback mechanism can explain the complete and partial decomposition of
440	titanite	e and garnet respectively in Domain I (Fig.7a). Both reactions (1.a-b) consumes Na <sub>2</sub> O.
441	Furthe	ermore, F, Cl-bearing apatite formed as a part of the Ilm-Cpx <sub>2</sub> symplectite. These
442	observ	vations require that the infiltrated fluid also supplied P <sub>2</sub> O <sub>5</sub> , Na <sub>2</sub> O, and halogens.
443	Simila	r feedback mechanism seems to have prevailed in Domain II as well where $Cpx_2$ -Pl <sub>2</sub>
444	sympl	ectite formed after garnet (Fig.7b). However, in contrast to Domain I, CaO in Domain II
445	moved	from the titanite end (now completely replaced with Ilm-Cpx <sub>2</sub> -Opx intergrowth) to the
446	garnet	end (Fig.7b). Since quartz is present in the rock, it is presumed that the symplectite
447	formir	ng reactions consumed the quartz in domains I and II.

448	X-ray intensity map of Ti (Fig.4h; 5c) and the modeled symplectite forming reactions in both
449	domains suggest that Ti was not mobile beyond the volume of the initial titanite grain. However,
450	the lamellar intergrowth of $IIm$ -Cpx <sub>2</sub> does support that Ti was locally mobile in the scale defined
451	by the interlamellar space(Abart et al. 2012; Remmert et al. 2018) between Ilm lamellae. The
452	interlamellar space between the lamellar ilmenite rods ranges from $\sim$ 2-55µm in Domains I and
453	II. Coarsening of the fine rods of ilmenite to bigger lamellae further attest to the view that Ti was
454	indeed mobile but its length scale of mobility was much smaller than the mobility of FeO, MgO,
455	and CaO (Fig.7a-b). The length scale of mobility of the latter species covered the whole width of
456	the product phases that develop between titanite and garnet (Fig.7a-b). Owing to the smaller size
457	of the titanite (than garnet) and the length scale of the transport of FeO, MgO, and CaO
458	completely replaced the titanite with the Ilm-Cpx <sub>2</sub> ( $\pm$ Opx) symplectite in both Domains I and II.
459	The solubility of TiO <sub>2</sub> is low in pure H <sub>2</sub> O or even in alkali, silica-bearing hydrous fluids (Audétat
460	and Keppler 2005; Tropper and Manning 2005; Antignano and Manning 2008; Lucassen et al.
461	2010; Hayden and Manning 2011), However, the presence of halogens can significantly enhance
462	the solubility of $TiO_2$ in the aqueous fluids (Purtov and Kotel'nikova 1993; Ryzhenko et al.
463	2006; Antignano and Manning 2008; Rapp et al. 2010; Hayden and Manning 2011; Tanis et al.
464	2016; Karmakar 2021). The presence of significant F and Cl in apatite granules in $IIm-Cpx_2$
465	symplectite support the view that segregations of ilmenite in the Ilm-Cpx <sub>2</sub> ( $\pm$ Opx) symplectites
466	were formed in presence of a halogen-bearing fluid. This fluid helped the migration of Ti in the
467	length scale of the interlamellar space of the Ilm rods (Abart et al. 2012; Remmert et al. 2018).
468	Very low concentrations of halogen in secondary amphibole that replaced the Ilm-Cpx <sub>2</sub>
469	symplectite can be explained by the greater affinity of halogens in apatite structure relative to
470	amphibole. The Ti content of amphibole is higher than the two minerals (Cpx and garnet) that it

- extensively replaces (Fig. 4h, 5c) and textural features (2f-g; 3e-f) suggest any one or all of the
  Ti-bearing accessory phases can be responsible.
- 473 Formation of Ilm-Cpx<sub>2</sub>: the control of metamorphic P-T path
- 474 The foregoing analyses (Physical condition of metamorphism) suggest that different methods of
- 475 P-T calculations suggest that the primary granoblastic assemblages (including both titanite and
- rutile) were formed in the realm of high pressure and high temperature (800-850°C and 12-14
- 477 kbar; Table-6, Fig. 6b) in the presence of partial melt. Studies have shown that melting and
- 478 accompanying thermal maxima  $(T_{max})$  in the high- to ultrahigh-pressure metamorphism can
- 479 occur at a pressure that is significantly lower than the  $P_{max}$  (maximum pressure). The
- 480 phenomenon of "decompression melting" has been documented from several areas (Groppo et al.
- 481 2012; Chen et al. 2017; Deng et al. 2018; Liu and Massonne 2022). It is, therefore, difficult to
- 482 identify if the pressure of 12-13 kbar represents the  $P_{max}$  or the primary granoblastic assemblage
- achieved this pressure during decompression and melting(Fig. 6b). High temperature
- 484 metamorphism in the studied area homogenized the primary porphyroblastic phases. However,
- 485 the presence of amphibole( $Amp_0$ ) and plagioclase ( $Pl_0$ ) as inclusion phases in garnet and
- 486 clinopyroxene ( $Cpx_1$ ) suggests the dehydration melting reaction,

$$487 \qquad Amp_1 + Pl_0 \rightarrow Grt_c + Cpx_1 \pm Qz + melt \qquad (4)$$

- This reaction has been inferred to explain the formation of mafic migmatites during high
  pressure and temperature metamorphism (Vielzeuf and Schmidt 2001; Pattison 2003; Watkins et
  al. 2007).
- 491 If the estimated P-T values of the primary granoblastic assemblage and the Ilm-Cpx<sub>2</sub> symplectite
  492 are joined, a steeply decompressive retrogressed P-T path results (Fig.6b). The volume increase
- 493 (6.5-7.5 %) that is predicted by the texturally modeled chemical reactions (Reaction 1-2) is

23

494	consistent with the view that the Ilm-Cpx $_2$ were formed on the steeply decompressive retrograde
495	P-T path. Though the textural modeling was done with titanite in the chosen microdomains,
496	rutile could also participate in other symplectic domains that are not studied here. The computed
497	pseudosection shows the presence of a melt phase even when the symplectites were formed
498	(Fig.6b). Based on textural evidence and the computed phase diagram, it seems likely that the
499	secondary amphibole formed after the formation of the clinopyroxene bearing symplectite
500	presumably during cooling. Incomplete hydration of the granulite facies assemblage could be
501	governed by several factors including ease of fluid movement and the abeyant physical
502	conditions.
503	IMPLICATIONS
504	Understanding the factors that control the stability of titanite over ilmenite and rutile is crucial
505	for the reconstruction of the tectonic history of the rocks in orogenic belts (cf.Angiboust and
506	Harlov 2017; Zhou et al. 2021). Experimental studies in rocks of mafic (Liou et al. 1998) and
507	felsic compositions (Angiboust and Harlov 2017) demonstrated that at higher pressure (>7 kbar)
508	
	ilmenite is unstable and is transformed into titanite and/or rutile. Liou et al (1998) demonstrated
509	ilmenite is unstable and is transformed into titanite and/or rutile. Liou et al (1998) demonstrated that in the basaltic system, titanite becomes unstable in favor of rutile at the pressure interval of
509 510	ilmenite is unstable and is transformed into titanite and/or rutile. Liou et al (1998) demonstrated that in the basaltic system, titanite becomes unstable in favor of rutile at the pressure interval of 14-16 kbar in the temperature range of 600°-1000°C. The observation of Liou et al.(1998) was
509 510 511	ilmenite is unstable and is transformed into titanite and/or rutile. Liou et al (1998) demonstrated that in the basaltic system, titanite becomes unstable in favor of rutile at the pressure interval of 14-16 kbar in the temperature range of 600°-1000°C. The observation of Liou et al.(1998) was also corroborated by Angiboust and Harlov (2017). Between 7-16 kbar the relative stability of

the most dominating factor (Liou et al. 1998; Frost et al. 2001; Angiboust and Harlov 2017). Our

study has demonstrated that titanite (with or without rutile) can be stable in mafic rocks beyond

515 17 kbar at a temperature  $\geq 1000^{\circ}$ C (Fig.6). This observation is consistent with the occurrence of

titanite in high-pressure mafic granulites where pressure exceeded 22 kbar (Romer and Rötzler

517	2003; Rötzler et al. 2004). Therefore, the presence of titanite, in exclusion of rutile, in mafic and
518	felsic granulites should not be taken as prima facie evidence for the absence of high-pressure
519	metamorphism or formation of titanite from rutile during exhumation of high-pressure rocks as
520	suggested in some studies (cf. Angiboust and Harlov 2017). The absence of zircon or baddyelite
521	often poses a constraint in fixing the timing of high pressure metamorphism in mafic rock (cf.
522	Timmerman 2004). U-Pb dating of titanite can be a useful technique for constraining the age of
523	high-pressure metamorphism if titanite develops at the peak metamorphic pressure as has been
524	documented here (Romer and Rötzler 2003; Timmerman 2004; Scibiorski et al. 2019; Zhou et al.
525	2021). A number of experimental investigations and studies in metasomatic rocks have
526	demonstrated that the solubility of Ti and other High Field Strength Elements (HFSE) can be
527	greatly enhanced in aqueous fluids due to the formation of ligands involving F, Cl, $PO_4^2$ , $SO_4^2$ ,
528	CO <sub>3</sub> <sup>2,-</sup> (Ryzhenko et al. 2006; Antignano and Manning 2008; Rapp et al. 2010; Hayden and
529	Manning 2011; Tanis et al. 2016; Borovikov et al. 2017; Liu et al. 2022). A reduction of ligand
530	activities, therefore, facilitates the deposition of the HFSE-bearing minerals (Gieré 1992). It is
531	likely that the formation of the tiny apatite grains rich F ( $\sim$ 1.66wt%) and Cl ( $\sim$ 0.25 wt%) in the
532	Ilm-Cpx <sub>2</sub> symplectite reduced the ligand activities and, therefore, facilitated the deposition of
533	ilmenite during decompression. Precipitation of Ti-bearing phases due to reduced ligand
534	activities have been reported (Gieré 1986, 1992; Gao et al. 2007; Rapp et al. 2010; Xiao et al.
535	2021). This study also demonstrates that both CaO and FeO activities, besides lowering of
536	pressure, play a critical role in the replacement of titanite with ilmenite. Precipitation of CaO-
537	bearing phases (e.g. clinopyroxene), reduced CaO activity whereas break down of garnet,
538	enhanced FeO activity in that helped titanite-ilmenite transition in the reaction domains. The
539	presence of hydrothermal veins rich in Ti-bearing minerals at different crustal depths requires

540	long transport of Ti by hydrothermal/metamorphic fluids in the scale of more than 1 meter to a
541	km or more (Gieré 1992; Gao et al. 2007; Rapp et al. 2010; Borovikov et al. 2017; Xiao et al.
542	2021). In the present study, fluid-aided mobility of Ti is shown to be restricted within a few tens
543	of microns of the reactant titanite (the length scale of ilmenite-clinopyroxene intergrowth). It is
544	also demonstrated that the activities of CaO and FeO in the ambient fluid phase were buffered by
545	local mineral reactions during the formation of the ilmenite-clinopyroxene symplectite. Two
546	major factors seem to be responsible for the smaller transport of Ti in the studied rocks. These
547	are (1) fluid flow was not pervasive (low fluid/rock ratio) enough to destroy the buffering
548	capacity of rocks and hence could not promote long transport of Ti as seen in Ti-bearing mineral
549	veins and (2) reduction of F, Cl and CaO in fluid due precipitation of F, Cl bearing apatite and
550	Cpx <sub>2</sub> further restricted the long transport of Ti. Restricted hydration of the granulite facies
551	assemblages during decompression and cooling is consistent with a low fluid-rock ratio. Our
552	study stresses the need for detailed petrological analyses before using Ti as a reference frame for
553	the estimation of element mobility of chemically altered rocks.
554	
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#### **FIGURE CAPTIONS**

- **Figure 1.(a)** Geological map representing different domains of CGGC (after Mukherjee et al.
- 2019). The boxed area represents the study area. (b) Lithological map of the study area showing
- Masanjore and the adjoining areas adapted and modified after the Geological and mineral map/

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885	district resource map of Dumka district, Jharkhand (Geological Survey of India, year 2009), also
886	showing the locations of the studied mafic granulites. (c) The studied mafic granulites showed a
887	medium-grained massive appearance, comprising garnet, clinopyroxene, plagioclase, and
888	amphibole. Garnet porphyroblasts ( $\leq$ 1cm diameter) are distributed uniformly in the rock. (d)
889	Coarse-grained amoeboid patches or segregations comprising plagioclase, garnet, amphibole,
890	quartz, and clinopyroxene. The coarse-grained patches are surrounded by amphibole, separating
891	it from the medium-grained host rock.
892	Figure 2. Photomicrographs and BSE images showing textural relations:(a) Garnet
893	porphyroblasts of variable size and, medium-grained clinopyroxene (Cpx1) and plagioclase (Pl1)
894	are forming the granoblastic mosaic matrix. Secondary amphibole (Amp <sub>2</sub> ) is replacing both Cpx <sub>1</sub>
895	and garnet. (b) Quartz present in the matrix is reacting with garnet porphyroblasts to form a
896	double corona of clinopyroxene (Cpx <sub>2</sub> ) and plagioclase (Pl <sub>2</sub> ). (c) Secondary amphibole(Amp <sub>2</sub> ) is
897	replacing garnet porphyroblasts along its boundary, while primary amphibole (Amp <sub>0</sub> ) is present
898	as inclusion within garnet. (d) Matrix clinopyroxene (Cpx1) hosts inclusions of plagioclase ( $Pl_0$ )
899	and amphibole (Amp <sub>0</sub> ). (e) Garnet contains ilmenite inclusion that is successively rimmed by
900	rutile and plagioclase. (f) Rutile is present in the rock matrix and also in contact with Amp <sub>2</sub> . (g)
901	Titanite appears to be stranded within $Amp_2$ which is replacing $Cpx_1$ . (h) Secondary amphibole
902	(Amp <sub>2</sub> ) is replacing garnet porphyroblasts both along its boundary and fracture planes. (i)
903	Amphibole (Amp <sub>2</sub> ) is replacing matrix clinopyroxene (Cpx <sub>1</sub> ) along its boundary and cleavage
904	planes.
905	Figure 3.Photomicrographs and BSE images showing textural relations:(a) Titanite is present in
906	the rock matrix in contact with $Cpx_1$ and is getting replaced by a symplectic intergrowth of Ilm

and clinopyroxene ( $Cpx_2$ ). (b) Titanite is almost completely replaced by the symplectic

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intergrowth of Ilm and Cpx<sub>2</sub>. (c) Clinopyroxene (Cpx<sub>2</sub><sup>ILM</sup>)-ilmenite intergrowth is separated from 908 porphyroblastic garnet by a rind of plagioclase (Pl<sub>2</sub>). Small rounded grain of titanite (relict) is 909 present within the plagioclase rind. (d) $Cpx_2^{ILM}$ -Ilm symplectic intergrowth is set apart from 910 porphyroblastic garnet by the symplectic intergrowth of clinopyroxene (Cpx<sub>2</sub><sup>PL</sup>) and plagioclase 911 (Pl<sub>2</sub>). The Cpx<sub>2</sub><sup>ILM</sup>-Ilm symplectite is extremely fine-grained (lamellar width  $\leq 2\mu$ m) towards the 912 913 inside of the symplectic intergrowth. Lamellar width of the symplectite increases towards the outer margin (~55  $\mu$ m) of the intergrowth. (e)Cpx<sub>2</sub><sup>ILM</sup>-IIm symplectite with relict titanite is 914 separated from garnet by the Cpx<sub>2</sub><sup>PL</sup>-Pl<sub>2</sub> symplectite. These two symplectites are adjacent to each 915 other but the Cpx<sub>2</sub><sup>ILM</sup>-Ilm symplectite is proximal to titanite and the Cpx<sub>2</sub><sup>PL</sup>-Pl<sub>2</sub> symplectite is 916 proximal to garnet. Amphibole (Amp<sub>2</sub>) is partially replacing clinopyroxene ( $Cpx_2^{PL}$ ) in the 917 symplectic intergrowth (f) Symplectic clinopyroxene  $(Cpx_2^{ILM})$  in association with ilmenite is 918 replaced by amphibole, such that amphibole appears to form symplectic intergrowths with 919 ilmenite. 920 921 Figure 4. (a-c) X-ray intensity maps of Mn (a), Ca (b), and Fe (c) of a porphyroblastic garnet. 922 All three maps show flat homogenous core composition extending up to the rim, which is thin. 923 The X-ray intensity map of Mn shows a drastic increase in intensity in the thin rim, while the map of Fe shows a slight increase in intensity. The X-ray intensity map of Ca shows a dip in 924 intensity in the rim. The area marked in the X-ray intensity map of Mn (a) is magnified in the X-925 926 ray intensity maps of figure d-h (same domainas Figure 3.d; Domain II). (d-h) These represent 927 X-ray intensity maps of Mg, Fe, Mn, Ca, and Ti respectively. X-ray intensity elemental map of

928 Mg (d) indicates restricted occurrences of orthopyroxene within this symplectic intergrowth of

929

930 porphyroblasts. Very fine grains of apatite are present in the Cpx<sub>2</sub><sup>ILM</sup>-Ilm symplectic intergrowth.

Cpx<sub>2</sub><sup>ILM</sup>-Ilm. The X-ray intensity map of Mg (d) also shows a dip in intensity in the rim of garnet

- 931 (i)Plots showing compositional variation (or similarity) in clinopyroxene and orthopyroxene
- 932 (Morimoto 1988) occurring in different textural settings.
- **Figure 5. (a-g)** Elemental X-ray intensity maps of Si, Al, Ti, Fe, Mg, Na, Ca from the same
- region of Fig. 3.c (Domain I). Fine-grained apatite is present within the Cpx<sub>2</sub>-Ilm symplectites
- 935 (red dots in the Ca map). (h) A Composite CaO map processed in the XMapTools software is
- used to calculate phase proportions of ilmenite and clinopyroxene in the  $Cpx_2^{ILM}$ -Ilm
- 937 symplectites in the textural modeling study.
- **Figure 6. (a)** P-T pseudosection corresponding to the EBC (obtained from Domain II (Fig. 3.d)
- by XMapTools) is calculated in the NCFMASHT (Na<sub>2</sub>O-CaO-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-TiO<sub>2</sub>)
- 940 system where amphibole, melt, plagioclase, garnet, sphene, ilmenite, clinopyroxene,
- 941 orthopyroxene "IN" lines are marked. (b) Compositional isopleths for garnet (X<sub>ALM</sub>, X<sub>PRP</sub>, X<sub>GRS</sub>)
- and plagioclase  $(X_{AN})$  plotted on the pseudosection in the appropriate assemblage fields,
- 943 constrain the P-T conditions of peak and retrogression. P-T conditions estimated using
- onventional thermobarometry are also plotted in the diagram with the "plus" signs with red
- 945 (peak) and green (retrogression) squares. P-T conditions estimate a steeply positive P-T path
- 946 (near isothermal). Dotted lines represent various possible prograde paths. (c) Volume isopleths of
- 947 Grt, rutile and titanite are plotted on the pseudosection. (d) Change in volume proportion of the
- 948 major phases (Grt, Cpx, Opx, melt, Pl) and (e) Change in the volume proportions of the Ti-
- bearing phases (Ilm, Spn, Rt ) during a pressure drop of 13 to 7 kbar at 850°C, i.e. along the
- 950 estimated P-T path, is shown.
- 951 Figure 7. (a-b) Textural modeling studies from Domain I-II suggest mobility of several chemical
- 952 species across the initial boundary between garnet and titanite. In both domains, FeO and MgO
- are moving from the garnet end toward the titanite end. In both domains  $P_2O_5$ ,  $Na_2O$ , F, and Cl

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are coming from external sources. The direction of CaO movement is reversed between Domain-

955 I and II. Domain II requires an external source of CaO while Domain I is releasing CaO outside.

Table 1: Representative	microprobe analy	ses and calculated	l cations of garnet	based on 12 oxygens
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Sample	SM128A1							
Sr. no.	G-1	G-2	G-3	G-4	G-5	G-6	G-7	G-8
Texture	Core	Rim	Core	Rim	Core	Rim	Core	Rim
SiO <sub>2</sub>	38.50	36.93	38.41	38.43	38.41	36.90	38.19	38.38
TiO <sub>2</sub>	0.21	0.11	0.18	0.02	0.18	0.03	0.16	0.10
$AI_2O_3$	21.51	20.88	21.64	21.12	21.64	20.81	21.44	21.35
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.07	bdl	0.08	bdl	0.04	0.06	0.14
$Fe_2O_3^*$	2.05	4.35	2.99	0.51	2.99	3.17	3.00	1.81
FeO*	20.33	23.49	20.28	26.07	20.28	24.08	19.76	23.81
MgO	5.70	4.13	5.84	4.73	5.84	4.18	5.99	4.18
CaO	0.82	9.06	0.59	7.67	11.36	8.26	0.74	10.11
MnO	11.33	1.67	11.36	1.50	0.59	1.80	11.29	1.55
Na₂O	0.05	0.01	0.05	0.01	0.05	0.02	0.01	
Total	100.50	100.71	101.34	100.13	101.34	99.29	100.65	101.43
Si	2.96	2.90	2.93	3.01	2.93	2.93	2.93	2.97
Ті	0.01	0.01	0.01		0.01		0.01	0.01
Al	1.95	1.93	1.95	1.95	1.95	1.95	1.94	1.95
Cr								0.01
Fe <sup>+3</sup> *	0.12	0.26	0.17	0.03	0.17	0.19	0.17	0.11
Fe <sup>+2</sup> *	1.31	1.54	1.30	1.71	1.30	1.60	1.27	1.54
Mg	0.65	0.48	0.67	0.55	0.67	0.50	0.69	0.48
Са	0.93	0.76	0.93	0.64	0.93	0.70	0.93	0.84
Mn	0.05	0.11	0.04	0.10	0.04	0.12	0.05	0.10
Na	0.01		0.01		0.01			
X <sub>ALM</sub>	0.44	0.53	0.44	0.57	0.44	0.55	0.43	0.52
X <sub>GRS</sub>	0.32	0.26	0.32	0.21	0.32	0.24	0.32	0.28
X <sub>PRP</sub>	0.22	0.17	0.23	0.18	0.23	0.17	0.23	0.16
X <sub>SPSS</sub>	0.02	0.04	0.01	0.03	0.01	0.04	0.02	0.03
X <sub>Mg</sub>	0.33	0.24	0.34	0.24	0.34	0.24	0.35	0.24

\*Fe<sub>2</sub>O<sub>3</sub> and Fe<sup>+3</sup> is recalculated after the scheme of Droop (1987)

SM128A5	SM128A1	SM128A1 <sup>DM2</sup>	SM128A <sup>DM1</sup>
G-9	G-10	G-11	G-12
Core	Rim	Core	Core
39.37	39.00	38.50	39.28
0.18	0.03	0.21	0.24
21.55	21.94	21.51	21.72
0.04	0.10	0.01	bdl
0.26	0.17	2.05	0.99
21.23	25.69	20.33	22.09
5.47	5.12	5.70	5.61
12.09	7.97	11.33	10.71
0.83	1.48	0.82	0.88
0.01	0.02	0.05	0.06
101.03	101.52	100.50	101.57
3.01	3.00	2.96	2.99
0.01		0.01	0.01
1.94	1.99	1.95	1.95
	0.01		
0.01	0.01	0.12	0.06
1.36	1.65	1.31	1.41
0.62	0.59	0.65	0.64
0.99	0.66	0.93	0.87
0.05	0.10	0.05	0.06
		0.01	0.01
0.45	0.55	0.44	0.47
0.33	0.22	0.32	0.29
0.21	0.20	0.22	0.21
0.02	0.03	0.02	0.02
0.31	0.26	0.33	0.31

Sample	SM128A1	SM128A1	SM128A1	SM128A1	SM128A1	SM128A1	SM128A1	SM128A1	SM128A5
Sr. No.	Px-1	Px-2	Px-3	Px-4	Px-5	Px-6	Px-7	Px-8	Px-9
Texture	Cpx1	Cpx <sub>2</sub> <sup>PL</sup>	Cpx1						
SiO <sub>2</sub>	50.32	51.61	51.00	52.43	48.68	52.25	51.15	52.00	50.67
TiO <sub>2</sub>	0.56	0.13	0.40	0.19	0.63	0.12	0.34	0.25	0.54
$AI_2O_3$	4.41	1.44	3.94	1.89	5.44	1.33	3.33	1.65	3.91
$Cr_2O_3$	0.06	0.23	0.00	0.36	0.06	0.36	0.11	0.00	0.00
$Fe_2O_3^*$	4.11	1.62	2.99	0.00	4.58	1.86	2.39	2.01	2.60
FeO*	7.15	7.31	7.31	9.68	6.71	7.78	7.16	8.09	7.89
MgO	13.49	13.15	12.82	12.96	12.48	13.36	13.04	13.26	12.30
CaO	20.20	22.93	22.27	22.07	20.71	22.97	22.63	22.66	22.42
MnO	0.07	0.12	0.27	0.21	0.17	0.24	0.26	0.11	0.29
Na <sub>2</sub> O	0.72	0.34	0.54	0.30	0.70	0.29	0.41	0.31	0.50
Total	101.10	98.88	101.54	100.10	100.15	100.55	100.82	100.35	101.13
Si	1.86	1.95	1.88	1.96	1.82	1.95	1.89	1.94	1.88
Ті	0.02	0.00	0.01	0.01	0.02	0.00	0.01	0.01	0.02
Al	0.19	0.06	0.17	0.08	0.24	0.06	0.15	0.07	0.17
Cr	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00
Fe <sup>+3</sup> *	0.11	0.05	0.08	0.00	0.13	0.05	0.07	0.06	0.07
Fe <sup>+2</sup> *	0.22	0.23	0.22	0.30	0.21	0.24	0.22	0.25	0.24
Mg	0.74	0.74	0.70	0.72	0.69	0.74	0.72	0.74	0.68
Ca	0.80	0.93	0.88	0.88	0.83	0.92	0.90	0.91	0.89
Mn	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01
Na	0.05	0.02	0.04	0.02	0.05	0.02	0.03	0.02	0.04
X <sub>Mg</sub>	0.77	0.76	0.76	0.70	0.77	0.75	0.76	0.74	0.74

Table 2: Representative microprobe analyses and calculated cations of pyroxene based on 6 oxygens

\*Fe<sub>2</sub>O<sub>3</sub> and Fe<sup>+3</sup> is recalculated after the scheme of Droop (1987)

 SM128A1	SM128A1 <sup>DM2</sup>	SM128A1	SM128A	SM128A <sup>DM1</sup>	SM128A1	SM128A1
Px-10	Px-11	Px-12	Px-13	Px-14	Px-15	Px-16
 Cpx2 <sup>PL</sup>	Cpx <sub>2</sub> <sup>ILM</sup>	Cpx <sub>2</sub> <sup>ILM</sup>	Cpx <sub>2</sub> <sup>ILM</sup>	Cpx2 <sup>ILM</sup>	Орх	Орх
 53.04	53.00	51.53	52.33	53.33	52.05	51.45
0.14	0.38	0.46	0.22	0.32	0.58	0.08
1.29	1.16	1.12	1.45	1.05	0.78	0.89
0.00	0.09	0.07	0.00	0.00	0.02	0.03
0.07	1.15	2.22	2.17	0.41	0.93	3.47
9.56	8.66	7.17	8.75	10.43	25.53	26.95
13.23	13.65	13.49	13.04	12.79	20.21	18.54
22.38	23.01	22.89	22.67	22.85	0.42	0.54
0.23	0.18	0.23	0.13	0.04	0.49	0.51
0.31	0.23	0.26	0.33	0.31	0.03	0.01
100.24	101.50	99.43	101.08	101.52	101.04	102.46
 1.98	1.96	1.94	1.94	1.97	1.95	1.93
0.00	0.01	0.01	0.01	0.01	0.02	0.00
0.06	0.05	0.05	0.06	0.05	0.03	0.04
0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.03	0.06	0.06	0.01	0.03	0.10
0.30	0.27	0.23	0.27	0.32	0.80	0.85
0.74	0.75	0.76	0.72	0.71	1.13	1.04
0.89	0.91	0.92	0.90	0.91	0.02	0.02
0.01	0.01	0.01	0.00	0.00	0.02	0.02
0.02	0.02	0.02	0.02	0.02	0.00	0.00
 0.71	0.74	0.77	0.73	0.69	0.59	0.55

Sample	SM128A1	SM128A1	SM128A1	SM128A1	SM128A1	SM128A1	SM128A1	SM128A1 <sup>DMII</sup>	SM128A5
Sr. no.	Pl-1	PI-2	PI-3	PI-4	PI-5	PI-6	PI-7	PI-8	PI-9
Texture	Pl <sub>1</sub>	$Pl_1$	$Pl_1$	$Pl_1$	$Pl_1$	Pl <sub>2</sub>	$Pl_1$	Pl <sub>2</sub>	Pl1
	Core	Rim	Core	Rim	Core	Sym	Core	Sym	Core
SiO <sub>2</sub>	56.96	47.66	56.74	47.28	57.07	47.43	56.41	48.05	57.90
$AI_2O_3$	27.78	33.32	27.31	34.32	26.98	33.16	27.80	33.59	27.54
FeO	0.07	0.14	0.00	0.53	0.07	0.57	0.00	0.18	0.00
MgO	0.01	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.01
CaO	10.02	17.05	9.88	17.75	9.48	16.78	10.24	17.05	9.71
Na <sub>2</sub> O	6.41	1.90	6.51	1.57	6.77	1.63	6.27	1.90	6.46
K <sub>2</sub> O	0.05	0.01	0.07	0.02	0.10	0.09	0.04	0.01	0.10
Total	101.44	100.14	100.67	101.48	100.64	99.90	100.89	100.95	101.87
Si	2.53	2.18	2.54	2.15	2.55	2.18	2.52	2.19	2.55
Al	1.45	1.80	1.44	1.84	1.42	1.80	1.46	1.80	1.43
Fe <sup>+2</sup>	0.00	0.01	0.00	0.02	0.00	0.02	0.00	0.01	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
Ca	0.48	0.84	0.47	0.86	0.45	0.83	0.49	0.83	0.46
Na	0.55	0.17	0.56	0.14	0.59	0.15	0.54	0.17	0.55
К	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01
XOr	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01
XAb	0.54	0.17	0.54	0.14	0.56	0.15	0.52	0.17	0.54
XAn	0.46	0.83	0.45	0.86	0.43	0.85	0.47	0.83	0.45

Table 3: Representative microprobe analyses and calculated cations of plagioclase based on 8 oxygens

SM128A1	SM128A <sup>DMI</sup>
PI-10	PI-13
$PI_2$	Pl <sub>2</sub>
Sym	rind
47.78	50.81
33.56	31.87
0.10	0.35
0.00	0.01
16.94	14.79
1.92	3.42
0.01	0.02
100.41	101.32
100.41 2.18	101.32 2.29
100.41 2.18 1.81	101.32 2.29 1.69
100.41 2.18 1.81 0.00	101.32 2.29 1.69 0.01
100.41 2.18 1.81 0.00 0.00	101.32 2.29 1.69 0.01 0.00
100.41 2.18 1.81 0.00 0.00 0.83	101.32 2.29 1.69 0.01 0.00 0.71
100.41 2.18 1.81 0.00 0.00 0.83 0.17	101.32 2.29 1.69 0.01 0.00 0.71 0.30
100.41 2.18 1.81 0.00 0.00 0.83 0.17 0.00	101.32 2.29 1.69 0.01 0.00 0.71 0.30 0.00
100.41 2.18 1.81 0.00 0.00 0.83 0.17 0.00 0.00	101.32 2.29 1.69 0.01 0.00 0.71 0.30 0.00 0.00
100.41 2.18 1.81 0.00 0.00 0.83 0.17 0.00 0.00 0.17	101.32 2.29 1.69 0.01 0.00 0.71 0.30 0.00 0.00 0.29

Sample	SM128A1	SM128A1	SM128A1	SM128A	SM128A	SM128A	SM128A1
Sr. no.	Am-1	Am-2	Am-3	Am-4	Am-5	Am-6	Am-7
Phase	Amp <sub>2</sub>	Amp <sub>0</sub>					
SiO <sub>2</sub>	45.11	46.02	45.78	45.28	45.26	46.03	44.76
TiO <sub>2</sub>	1.53	1.31	1.41	1.59	1.54	1.69	1.32
Al <sub>2</sub> O <sub>3</sub>	11.09	10.65	10.26	10.65	10.65	9.88	11.96
$Cr_2O_3$	0.31	0.23	0.17	0.01	0.07	0.04	0.00
FeO	15.14	13.90	14.68	15.90	16.30	16.34	14.66
MgO	11.55	12.64	12.10	11.76	11.86	11.28	12.75
CaO	11.47	11.65	11.41	11.32	11.49	11.38	11.84
MnO	0.17	0.00	0.14	0.16	0.13	0.17	0.09
Na <sub>2</sub> O	1.82	1.66	1.61	1.82	1.78	1.61	2.02
K₂O	0.27	0.26	0.28	0.27	0.25	0.25	0.20
F	0.00	0.00	0.01	0.00	0.01	0.01	0.00
CI	0.03	0.02	0.00	0.01	0.01	0.01	0.01
Total	98.49	98.33	97.83	98.78	99.34	98.68	99.68
Si	6.58	6.67	6.69	6.59	6.56	6.72	6.42
AI <sup>(IV)</sup>	1.42	1.33	1.31	1.41	1.44	1.28	1.58
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum T	8.00	8.00	8.00	8.00	8.00	8.00	8.00
AI <sup>(VI)</sup>	0.49	0.49	0.46	0.42	0.38	0.42	0.45
Ті	0.17	0.14	0.15	0.17	0.17	0.19	0.14
Cr <sup>+3</sup>	0.04	0.03	0.02	0.00	0.01	0.00	0.00
Fe <sup>+3</sup>	0.26	0.25	0.28	0.35	0.41	0.27	0.44
Mg	2.51	2.73	2.63	2.55	2.56	2.45	2.73
Fe <sup>+2</sup>	1.54	1.36	1.45	1.51	1.48	1.67	1.25
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum C	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe <sup>+2</sup>	0.05	0.07	0.06	0.08	0.09	0.06	0.07
Mn	0.02	0.00	0.02	0.02	0.02	0.02	0.01
Са	1.79	1.81	1.79	1.77	1.78	1.78	1.82
Na	0.13	0.12	0.13	0.14	0.12	0.14	0.10
Sum B	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.38	0.35	0.32	0.38	0.38	0.31	0.47
К	0.05	0.05	0.05	0.05	0.05	0.05	0.04
Sum A	0.43	0.40	0.37	0.43	0.43	0.36	0.50
TOTAL	15.43	15.40	15.37	15.43	15.43	15.36	15.50
X <sub>Mg</sub>	0.61	0.66	0.64	0.62	0.62	0.59	0.67
Group	Calcic group	Calcic group	Calcic group	Calcic group	Calcic group	Calcic group	Calcic group
Sub-Group	Magnesio- hornblend	Magnesio- hornblend	Magnesio- hornblend	Magnesio- hornblend	Magnesio- hornblend	Magnesio- hornblend	Pargasite

Table 4: Representative microprobe analyses and calculated cations of amphibole based on 23 oxygens

SM128A1
Am-8
Amp <sub>0</sub>
43.83
1.56
11.92
0.30
15.34
11.85
11.65
0.02
1.99
0.29
0.00
0.02
98.86
6.39
1.61
0.00
8.00
0.43
0.17
0.38
2 57
1.41
0.00
5.00
0.00
0.08
0.00
1.82
0.10
2.00
0.00
0.47
0.05
0.52
15.52
0.63
Calcic group
Pargasite

Sample	SM128A1 <sup>DM2</sup>	SM128A <sup>DM1</sup>	SM128A1 <sup>DM2</sup>	SM128A1	SM128A1	SM128A <sup>DM1</sup>	SM128A	SM128A
Sr. no.	Tn-1	Tn-2	lm-1	lm-2	lm-3	lm-4	lm-5	lm-6
Phase	Ttn	Ttn	Ilm	Ilm	Ilm	Ilm	Ilm	Ilm
SiO <sub>2</sub>	29.84	30.35	0.05	0.000	0.00	0.04	0.02	0.02
TiO <sub>2</sub>	38.67	39.35	51.03	52.134	52.39	51.18	51.63	51.81
$AI_2O_3$	1.41	1.09	0.16	0.165	0.19	0.15	0.13	0.19
$Cr_2O_3$	0.01	0.00	0.21	0.038	0.00	0.03	0.00	0.04
$Fe_2O_3^*$	0.52	0.45	3.10	3.090	1.38	2.00	2.60	2.22
FeO*	0.00	0.00	42.74	44.063	42.67	43.53	44.49	44.79
MgO	0.04	0.00	1.20	1.134	1.57	0.74	0.72	0.62
CaO	28.98	28.64	0.11	0.050	0.17	0.20	0.17	0.10
MnO	0.09	0.05	0.53	0.569	0.49	0.42	0.38	0.58
Na <sub>2</sub> O	0.02	0.01	0.00	0.000	0.02	0.02	0.02	0.00
F	0.06	0.00	0.03	0.011	0.00	0.04	0.00	0.00
$P_2O_5$	0.56	0.00	0.00	0.000	0.01	0.00	0.00	0.00
Total	100.20	99.94	99.16	101.25	98.88	98.36	100.15	100.36
Oxygen	5.00	5.00	3.00	3.000	3.00	3.00	3.00	3.00
Si	0.96	0.99	0.00	0.000	0.00	0.00	0.00	0.00
Ті	0.94	0.96	0.97	0.970	0.99	0.98	0.97	0.98
Al	0.05	0.04	0.00	0.005	0.01	0.00	0.00	0.01
Cr	0.00	0.00	0.00	0.001	0.00	0.00	0.00	0.00
Fe <sup>+3</sup> *	0.01	0.01	0.06	0.058	0.03	0.04	0.05	0.04
Fe <sup>+2</sup> *	0.00	0.00	0.90	0.911	0.89	0.93	0.93	0.94
Mg	0.00	0.00	0.05	0.042	0.06	0.03	0.03	0.02
Са	1.00	1.00	0.00	0.001	0.00	0.01	0.00	0.00
Mn	0.00	0.00	0.01	0.012	0.01	0.01	0.01	0.01
Na	0.00	0.00	0.00	0.000	0.00	0.00	0.00	0.00
F	0.01	0.00	0.00	0.001	0.00	0.00	0.00	0.00
Р	0.02	0.00	0.00	0.000	0.00	0.00	0.00	0.00

\*Fe<sub>2</sub>O<sub>3</sub> and Fe<sup>+3</sup> is recalculated after the scheme of Droop (1987)

SM128B2	Sample	SM128A1
Rt-1	Point	10
Rt	Phase	Ap
0.00	SiO2	0.033
98.14	TiO2	0.024
0.35	AI2O3	0
0.03	Cr2O3	0
0.86	FeO	0.278
0.00	MgO	0.026
0.02	CaO	56.038
0.02	MnO	0.048
0.00	Na2O	0.05
0.00	К2О	0
0.04	P2O5	42.155
0.00	F	1.657
99.46	Cl	0.24
2.00	Sum	100.55
0.00	O=F	0.70
0.97	O=Cl	0.05
0.97 0.01	O=Cl Revised SUM	0.05 99.80
0.97 0.01 0.00	O=Cl Revised SUM Si	0.05 99.80 0.00
0.97 0.01 0.00 0.01	O=Cl Revised SUM Si Ti	0.05 99.80 0.00 0.00
0.97 0.01 0.00 0.01 0.00	O=Cl Revised SUM Si Ti Al	0.05 99.80 0.00 0.00 0.00
0.97 0.01 0.00 0.01 0.00 0.00	O=Cl Revised SUM Si Ti Al Cr	0.05 99.80 0.00 0.00 0.00 0.00
0.97 0.01 0.00 0.01 0.00 0.00 0.00	O=Cl Revised SUM Si Ti Al Cr Ca	0.05 99.80 0.00 0.00 0.00 0.00 4.72
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2	0.05 99.80 0.00 0.00 0.00 4.72 0.02
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.0	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2 Mn	0.05 99.80 0.00 0.00 0.00 4.72 0.02 0.00
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.0	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2 Mn Mg	0.05 99.80 0.00 0.00 0.00 4.72 0.02 0.00 0.00
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.0	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2 Mn Mg Na	0.05 99.80 0.00 0.00 0.00 4.72 0.02 0.00 0.00 0.00
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.0	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2 Mn Mg Na K	0.05 99.80 0.00 0.00 0.00 4.72 0.02 0.00 0.00 0.01 0.00
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.0	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2 Mn Mg Na K P	0.05 99.80 0.00 0.00 0.00 4.72 0.02 0.00 0.00 0.00 0.01 0.00 2.81
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.0	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2 Mn Mg Na K P SUM	0.05 99.80 0.00 0.00 0.00 4.72 0.02 0.00 0.00 0.01 0.00 2.81 7.57
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.0	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2 Mn Mg Na K P SUM F	0.05 99.80 0.00 0.00 0.00 4.72 0.02 0.00 0.00 0.01 0.00 2.81 7.57 0.41
0.97 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.0	O=Cl Revised SUM Si Ti Al Cr Ca Fe+2 Mn Mg Na K P SUM F SUM F Cl	0.05 99.80 0.00 0.00 0.00 4.72 0.02 0.00 0.00 0.01 0.00 2.81 7.57 0.41 0.03

Minerals in equilibrium		Dataset	Thermometry (GC <sup>1</sup> )	
winerais in equilibrium	No.	Phases used	P (ref)	Т
	1	G-1; Px-1; Pl-1;		865°C
	2	G-3; Px-3; Pl-3;		825°C
Rt + Spn + Grt <sub>c</sub> + Cpx <sub>1</sub> + Pl <sub>1</sub>	3	G-5; Px-5; Pl-5;	13kbar	830°C
	4	G-7; Px-7; Pl-7;		844°C
	5	G-9; Px-9; Pl-9;		857°C
	6	G-2; Px-2; Pl-2;		654°C
	7	G-4; Px-4; Pl-4;		693°C
Ilm + Cpx <sub>2</sub> + Grt <sub>r</sub> + Opx + Pl <sub>2</sub>	8	G-6; Px-6; Pl-6;	7kbar	645°C
	9	G-8; Px-8; Pl-8;		690°C
	10	G-10; Px-10; Pl-10;		713°C

Table 6: P-T estimates through conventional thermobarometric calculations

 $^1\mbox{GC:}\xspace$  Garnet – clinopyroxene geothermometer (Ellis and Green 1979).

<sup>2</sup>GCPS: Garnet – clinopyroxene – plagioclase – quartz barometer (Eckert et al. 1991).

Barometry (GCPS <sup>2</sup> )				
T (ref) P				
	12.6kbar			
	12.7kbar			
850°C	13.0kbar			
	13.1kbar			
	12.6kbar			
	7.4kbar			
	6.4kbar			
700°C	6.8kbar			
	7.9kbar			
	6.8kbar			



Figure 2



## Figure 3



### Figure 4













