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1	REVISION 3
2	Controls of P-T path and element mobility on the formation of corundum pseudomorphs in
3	Palaeoproterozoic high-pressure anorthosite from Sittampundi, Tamil Nadu, India
4	
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ABSTRACT

20	The Archaean Sittampundi Layered Magmatic Complex (SLC) of south India is interpreted as a
21	part of the oceanic crust that formed in a suprasubduction zone setting. The assemblage
22	corundum + anorthite + amphibole (magnesiohornblende to tschermakite to pargasite) +
23	clinozoisite (C ₁ PACz) developed in highly calcic anorthosite of the SLC at the culmination of a
24	c. 2.46 Ga tectonothermal event. Changing physicochemical conditions during this early
25	Palaeoproterozoic (Siderian) event produced spinel + anorthite + second generation amphibole
26	through destabilization of corundum + first generation amphibole. Spinel retains the shape of the
27	corundum that it replaces (spinel pseudomorphing corundum, SCP) and is surrounded by a rind
28	of plagioclase that separates spinel from the matrix amphibole. Development of the assemblage
29	chlorite + clinozoisite + secondary corundum after spinel + anorthite + amphibole marks the
30	terminal metamorphic event in this area. Mass balance calculations on pseudomorphs and
31	modeling of preserved reaction textures show that Na, Mg, Ca and silica were mobile during the
32	formation of the SCP. Al and Fe were mobile in grain scale but remained immobile in the scale
33	of a thin section. Activity adjusted partial petrogenetic grid in the systems Na ₂ O-CaO-Al ₂ O ₃ -
34	SiO ₂ -H ₂ O (NCASH) and Na ₂ O-CaO-MgO-Al ₂ O ₃ -SiO ₂ -H ₂ O (NCMASH) along with the
35	mineralogy of the rocks that were co-metamorphosed with the anorthosite show that (a) the
36	assemblage C ₁ PACz was formed during high pressure metamorphism (11 \pm 1 kbar and 725 \pm 25
37	°C), (b) SCP and the plagioclase rind around it were formed during exhumation of these higher
38	pressure rocks to lower pressure (7 \pm 1 kbar, 675 \pm 50 °C) along steeply decompressive
39	retrograde P-T path and (c) post decompression cooling and hydration at near isobaric condition
40	triggered the formation of the chlorite – clinozoisite – secondary corundum assemblage (6-8
41	kbar, <620 °C). The inferred P-T path is consistent with the view that the studied area that

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represent Archaean oceanic crust of SSZ affinity was subducted and subsequently exhumed during the early Palaeoproterozoic orogeny. Keywords: Sittampundi, anorthosite, corundum pseudomorph, oceanic crust, subduction zone

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INTRODUCTION

Fluid-rock interactions operate in a wide range of geological environments from weathering of 60 supracrustal rocks to metasomatism of the mantle-wedge above a subduction zone (e.g., Philpotts 61 and Ague 2009). Disequilibrium between host-rock and percolating fluid commonly results in 62 63 exchange of materials between solid and fluid that leads to significant change in host-rock composition (Dutrow et al. 1999, 2008; e.g., Philpotts and Ague 2009). At subduction zones, 64 which are potential zones of fluid-rock interaction, the oceanic crust and the entrained sediments 65 66 commonly undergo significant bulk compositional change and develop a sequence of replacement textures over a range of pressure-temperature conditions. Interpretation of these 67 reaction textures is, therefore, likely to provide valuable insight about the subduction zone 68 processes such as fluid circulation, mobility of elements, thermal gradient, burial and upliftment 69 history of the subducted rocks (Berger et al. 2010). Pseudomorphs are a special replacement 70 texture in which the product mineral retains the shape of the mineral that it replaces (reviewed in 71 Putnis 2002). A number of experimental and theoretical studies have confirmed that the 72 formation of pseudomorphs is caused by solution (of reactant phase) and precipitation (of 73 74 product phase) mechanism at nearly constant volume (Putnis 2002, 2009; Putnis et al. 2005; Putnis and Putnis 2007; Putnis and John 2010). This property of pseudomorphs has been used to 75 trace the behavior of elements during the formation of pseudomorphs (Hövelmann et al. 2010). 76 77 Because rocks can develop pseudomorphs during prograde as well as retrograde metamorphism, pseudomorphic replacement textures also provide valuable information on metamorphic P-T path 78 in orogenic belts (Dutrow et al. 2008). 79 In this communication we document pseudomorphic replacement textures (spinel 80

pseudomorphing corundum, SCP) in anorthosite from the Archaean Sittampundi layered

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82	magmatic complex (SLC) of South India. Mass-balance calculations and modeling of the
83	pseudomorphs suggest that several elements including Al were mobile during the formation of
84	the SCP. Pseudomorphs also constrain the metamorphic P-T path and thermal gradient during
85	subduction of an Archaean oceanic crust at the dawn of the Proterozoic.

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GEOLOGICAL BACKDROP

87 Intense geological and geochronological studies in the past two decades have revealed that the granulite terrain of 88 south India can be broadly divided into three segments with contrasting geological history (reviewed in Braun and 89 Kriegsman 2003; Ghosh et al. 2004; Dutta et al. 2011). The northern granulite terrain (NGT) is dominated by felsic 90 orthogneisses with minor mafic, ultramafic rocks and metasediments that witnessed the last high-grade metamorphic 91 event at c. 2.49-2.44 Ga (Ghosh et al. 2004; Sato et al. 2011; Mohan et al. 2012). In contrast to the NGT, the 92 southernmost segment, the Madurai Block (MB), exposes larger amount of metasediments and is affected by high-93 grade metamorphism at c. 0.8-0.5 Ga (reviewed in Braun and Kriegsman 2003; Ghosh et al. 2004; Kooijman et al. 94 2011). A roughly E-W trending curvilinear belt, which separates the NGT from the MB, exposes diverse lithological 95 associations and carries the impressions of protracted geological history for over 2 billion years (c. 2.9-0.5 Ga, 96 reviewed in Ghosh et al. 2004; Dutta et al. 2011). This curvilinear belt is believed to be dissected by a number of 97 crustal scale shear zones that are collectively referred to as the Cauvery Shear System (CSS, Chetty1996), though 98 the existence of a major transcurrent shear zone has been challenged by Mukhopadhyay et al. (2003). In the 99 following section, the salient geological and geochronological features of this belt are described. 100 The oldest components of the CSS include a suite of mafic and ultramafic rocks with local anorthosite 101 (leucogabbro according to IUGS nomenclature) and chromitite (reviewed in Bhaskar Rao et al. 1996; Ghosh et al. 102 2004; Dutta et al. 2011). At several places within the CSS, namely Sittampundi (SLC) and Bhavani Sagar (BLC), 103 layered magmatic complexes are present (Subramanium 1956; Bhaskar Rao et al. 1996; Dutta et al. 2011). Banded 104 Iron Formation (BIF) constitutes the only metasediment within the magmatic suite and is always associated with the 105 mafic rocks (Bhaskar Rao et al. 1996; Ghosh et al. 2004; Dutta et al. 2011). Bhaskar Rao et al. (1996) obtained a Sm-106 Nd whole rock age of c. 2.9 Ga (2935 ± 60 Ma) which they interpreted to be the age of emplacement of the SLC and 107 the BLC. This observation of Bhaskar Rao et al. (1996) has been corroborated by the subsequent study of Ghosh et

108 al. (2004). In a recent communication, Mohan et al. (2012) reported LA-ICP-MS U-Pb zircon age of c. 2.54 Ga 109 $(2541 \pm 13 \text{ Ma})$ that the authors considered to be the age of emplacement of the anorthosite at Sittampundi. The 110 reason for the time difference in the tune of 400Ma between the Sm-Nd whole rock and U-Pb zircon ages remains 111 unclear. Nevertheless, all these studies support a late Archaean mafic magmatism in the CSS. The mafic-ultramafic-112 anorthosite-chromitite suite were intruded by voluminous felsic magmas of calc-alkaline nature during a narrow 113 time span of c. 2.53-2.50 Ga (reviewed in Ghosh et al. 2004; Clark et al. 2009; Saitoh et al. 2011; Mohan et al. 114 2012). Rocks of the layered magmatic complexes, BIF and the invading felsic rocks underwent polydeformation and 115 high-grade metamorphism at c. 2.49-2.44 Ga (Ghosh et al. 2004; Sato et al. 2011; Mohan et al. 2012 and the 116 references cited therein). Important younger events in the CSS are marked by, (1) a thermal event at c. 2.0 Ga 117 (Bhaskar Rao et al. 1996; Meissner et al. 2002), (2) deposition of shale-limestone-quartzite presumably representing 118 shelf sediments with average provenance age of c.1.9 Ga (Meissner et al. 2002), (3) emplacement of carbonatite, 119 syenite at c. 0.7-0.8 Ga (reviewed in Upadhyay et al. 2006), (4) polyphase deformation and upper-amphibolite-120 facies metamorphism of the shelf sediments ($\sim 9 \pm 1$ kbar and 700 ± 50 °C, Meissner et al. 2002; Sengupta et al. 121 2009a) and the quartzofeldspathic rocks (Raith et al. 2010) at c. 0.6-0.5 Ga and (5) intrusion of voluminous granitoid 122 /pegmatoid at c. 0.54-0.50 Ga (Ghosh et al. 2004; Brandt et al. 2003). 123 The Sittampundi Layered Magmatic Complex (SLC), which chiefly comprises mafic, ultramafic and 124 anorthositic rocks with centimeter to meter thick layers of chromitite, occurs as an enclave within a suite of felsic 125 rocks (the protolith of charnockite and enderbite and their retrograde equivalent hornblende-biotite gneiss) (Fig.1). 126 Interpreting the field and petrological features Dutta et al. (2011) argued that the SLC represents a 'fossil oceanic 127 crust' in an Archaean suprasubduction zone (SSZ) setting. Fractionation of hydrous high Al-basaltic magma derived 128 from metasomatized upper mantle led to the formation of the highly calcic anorthosite of the SLC at <2 kbar. At 129 places, mafic rocks (now mafic granulites) of the SLC are intercalated with BIF (Dutta et. al. 2011). Large 130 porphyroblasts of garnet develop in the mafic granulites as well as in BIF (Fig.2a). Petrographic features show that 131 the porphyroblastic garnet grains that are presumed to have developed during culmination of granulite facies 132 metamorphism were partially to completely resorped to a symplectic intergrowth of orthopyroxene, plagioclase and 133 amphibole (Bhaskar Rao et al. 1996, our own data). BIF develop the assemblage garnet + orthopyroxene + magnetite 134 +quartz + clinopyroxene and show no resorption of porphyroblastic garnet (Dutta 2009). Mn-content of garnet and

135 pyroxenes are low (Dutta 2009).Using multiple equilibria convergence technique (TWEEQU), Bhaskar Rao et al.

136 (1996) obtained 11-12 kbar pressure at ~650 °C using the core compositions of the porphyroblastic assemblages in 137 the garnetiferous mafic rocks from the SLC. These authors also obtained a P-T condition of ~7 \pm 1kbar and 700 \pm 50 138 °C for the symplectitic assemblage. Sajeev et al. (2009) reported lenses of high-temperature eclogite (~20kbar, 139 >1000°C) within the anorthosite. At several places, the anorthosite and the interlayered amphibolite develop pink 140 (ruby) to colorless corundum crystals. Infiltration driven metamorphism of corundum-bearing anorthosite developed 141 the assemblage högbomite + clinozoisite + magnetite + chlorite + calcite at 650 \pm 50 °C and 7 \pm 1kbar (Sengupta et 142 al. 2009b).

143

SCP BEARING ANORTHOSITE OF THE STUDIED AREA

144 Mesoscopic features

Three corundum (\pm ruby)-bearing anorthosite (*sensu lato*) samples were chosen for the present 145 146 study. In all the samples, milk-white anorthosite alternates with millimeter to decimeter thick layers that are rich in amphibole (>60-70 vol%, Fig.2b). A prominent planar fabric that is parallel 147 to the penetrative regional foliation is defined by alignment of prismatic amphibole grains 148 149 (Fig.2c). However, the random orientation of a few amphibole grains suggests that the formation of amphibole outlasted the deformation (Fig.2d). One sample shows a layer of chromitite that is 150 151 stretched parallel to the planar fabric defined by amphibole (Fig.2c). Polygonal grains of anorthite (verified by petrography) impart a saccharoidal appearance to the rock. On the basis of 152 153 the relative proportion of plagioclase and amphibole the anorthosite is divided into 'Domain-A' (>70 volume% of plagioclase) and 'Domain-B' (<50 volume% of plagioclase). 154 Colorless and pink corundum crystals (up to ~ 4 cm long), with euhedral to anhedral 155 outline are embedded in the matrix, mostly within Domain-A and less commonly in Domain-B 156 157 (Figs.3a-3d). Corundum grains with both hexagonal (basal/ 0001 face) as well as prismatic outline are observed in the same sample (Fig.3b), suggesting that the corundum crystals are 158 159 randomly oriented within the rock volume. Some prismatic corundum crystals that cut across the

planar fabric of the host rock (Fig.3b). Grains of elongated corundum are boudinaged parallel to 160 their length (Figs.3c and 3d). There is extensive replacement of corundum by spinel but the 161 product spinel retains the external morphology of the host corundum grain (pseudomorphous 162 replacement). The early stage of replacement is manifested by the development of a thin rim of 163 spinel over corundum (Figs.3a-3d). Complete pseudomorphous replacement of corundum by 164 165 spinel marks the advanced stage of replacement (Figs.3b and 3c). At places within Domain-A, broken and boudinaged grains of corundum are partially surrounded by spinel rims of varying 166 thickness (Figs.3cand 3d). The interface between the spinel and the corundum is sharp but highly 167 168 irregular. Coronitic spinel also extends as veins in the interior of the host corundum grain (Fig.3c). The spinel is invariably surrounded by a rind of plagioclase grains that separates the 169 former corundum from amphibole in the matrix (Figs.3a and 3c). Image analyses of several thin 170 sections and observation from randomly cut and polished hand specimens show that the ratio of 171 the thickness of the plagioclase rind to that of the spinel corona ranges between 1.7 and 2.3. 172 173 Compared to Domain-A, Domain-B shows greater thickness of the plagioclase rind.

174

175 **Petrography**

Domain-A is chiefly made up of plagioclase (up to 70 vol%) with minor clinozoisite, chlorite and amphibole (together constituting10-25 vol%). In contrast, amphibole (~50-60 vol%) and plagioclase (~40-50 vol%) constitute the Domain-B. In both the domains, a granoblastic fabric is formed by polygonal grains of amphibole (Am_{mx}) and plagioclase (Pl_{mx} ; Fig.4a). At many places (only in Domain A), dimensional orientation of amphibole and clinozoisite define a crude foliation parallel to the regional foliation. Large corundum grains (Crn₁) in both the

domains are embedded in a matrix consisting of polygonal plagioclase (Pl_{mx}) and amphibole 182 (Am_{mx}) (Fig.4b). Crn₁ is not in direct contact with amphibole and is separated from it by 183 184 successive coronae of green spinel (proximal to corundum) and plagioclase (Pl_m ; toward the amphibole-plagioclase matrix) (Figs.4b and 4c). Where present, clinozoisite (Czo₁) does not 185 show any involvement in the spinel-plagioclase forming reaction. Hence, Czo₁ is considered to 186 187 be stable at this stage. The size of the plagioclase grains in the plagioclase rind (Pl_m) is distinctly larger than the plagioclase grains in the matrix (Pl_{mx}) (Fig.4c). In most cases Crn₁ is partially 188 (Figs.4b and 4c) or completely pseudomorphed by spinel but in rare instances Crn_1 grains do not 189 190 develop spinel corona but are surrounded by a granoblastic fabric formed by Czo₁, Crn₁ and Pl_{mx} (Fig.4d). Contacts among these three phases are obscured by the development of chlorite (Chl) 191 flakes. Aggregates of randomly oriented chlorite flakes and acicular clinozoisite (Czo₂) replace 192 the amphibole and the plagioclase in the matrix (Fig.4e). Locally, coronitic spinel that develops 193 over corundum is replaced by an aggregate of magnetite, corundum (Crn₂) and chlorite 194 195 (Fig.4f). The textural features described above are consistent with the following sequence of 196 mineral growth: Crn_1 +amphibole + Czo_1 + plagioclase (matrix) to spinel + plagioclase (rind) to 197 chlorite + $Czo_2 \sim Crn_2$ +magnetite+chlorite. Clinozoisite appears to be stable throughout the 198 evolution of the studied rock.

199

MINERAL CHEMISTRY

Detail chemical analyses of minerals were carried out in six anorthosite samples. Representative mineral compositions in the pseudomorph domain are presented in Tables 1a-1d. Details of the analytical procedure are presented in the Appendix. In the following section salient

203 compositional characteristics of the different minerals are described.

204 Amphibole

205	Representative amphibole analyses are presented in Table 1a. The amphibole is highly calcic
206	(~1.6-1.9 apfu), magnesian $[X_{Mg} = Mg/(Mg + Fe^{2+}) = ~0.76-0.81$, Table 1a] and aluminous (~2.3-
207	2.7 apfu, Table 1a). Small and variable amount of Cr (up to \sim 0.09 apfu) and Ti (up to \sim 0.03
208	apfu) are noted in the analyzed amphibole (Table 1a). The mineral does not show any
209	compositional zoning. In the classification of Leake et al. (2004), most of the amphibole
210	compositions are plotted within the field of tschermakite with a few data straddling the boundary
211	between tschermakite and magnesiohornblende. In one sample (S160), some amphibole
212	compositions from the amphibole plagioclase matrix are rich in (Na+K) and are plotted in the
213	field of pargasite. In all samples, there is no major difference in the compositions of amphiboles
214	from domains A and B. However, a few amphibole grains (Am_m) that develop close to the SCP
215	are rich in Al_2O_3 (by ~ 2 wt%) than the amphibole (Am_{mx}) present in the amphibole-plagioclase
216	matrix (Table-1a).

217 Spinel

The spinel is rich in Mg $[X_{Mg} = Mg/(Mg+Fe^{2+}) = ~0.53-0.68$, Table 1b] but is low in Cr [up to 0.003 apfu, Cr#= 100 Cr/(Cr+Al)= up to ~0.1], Fe³⁺ [up to ~0.07 apfu, Fe³⁺# = 100 Fe³⁺/(Fe³⁺+Al + Cr)=1.6-3.7], TiO₂ (~up to 0.001 apfu) and ZnO (~upto 0.002 apfu). X_{Mg} of the spinel is significantly lower than the X_{Mg} of the adjoining amphibole (0.76-0.81). Individual

grains of spinel are compositionally homogeneous.

223 Corundum

224	The corundum is Al_2O_3 -rich (>1.97 apfu, Table 1c) with small amount of Fe (up to 0.008 Fe ³)
225	apfu) and Cr (<0.03 apfu, Table 1c). The chromium content imparts blood red color to corundum
226	(ruby).

227 Plagioclase

The plagioclase is highly calcic (An_{≥ 89}, Table 1d) and a few analyses have nearly pure anorthite composition (An₉₉, Table 1d). All the plagioclase analyses show insignificant K. Owing to the extreme calcic nature, no significant compositional difference was noted between the plagioclase grains from different textural settings in the same sample (e.g., matrix and moat plagioclase, in domains A and B). However, the composition of the plagioclase grains varies from one sample to another.

234 Clinozoisite

The clinozoisite contains only 4-6 mol% pistacite molecules ($\sim 0.12-0.18$ Fe³⁺ apfu) and does not show any significant compositional zoning (Table 1c).

237 Chlorite

The chlorite in all the three samples is highly magnesian [$X_{Mg} = Mg / (Mg + Fe^{2+}) = 0.83 - 0.84$

with alumina content varying from ~2.6 to 2.9 Al apfu (Table 1d). Minor and variable amount of

Ti and Cr are noted in the analyses (each up to 0.002 apfu, Table 1d).

241 THE SCP AND ELEMENT MOBILITY- A MASS BALANCE APPROACH

242 Being a product of constant volume process, pseudomorphism provides a reference frame for

studying mobility of elements at least within the volume of the pseudomorph (e.g., Nijland and

244	Touret 2001; Hövelmann et al. 2010). In the following sections we have first discussed the
245	principles of mass-balance approach and then its application to the SCP in the rocks of our study.
246	Following the composition-volume relationship algorithms of Grant (1986) and Gresens
247	(1967) and their subsequent modifications (e.g., Philpotts and Ague 2009), change in
248	concentration of a component 'j' in a mineral during its chemical alteration can be given as:
249	$\Delta C_{j} = (V^{f}/V^{o}) (\rho^{f}/\rho^{o}) (C_{j}^{f}/C_{j}^{o}) - 1 - (1)$
250	Where, ΔC_j – Change in concentration of j
251	C_j^{f} and C_j° – Final and initial concentration of 'j'
252	V ^f and V ^o – volume of the product phase spinel and original corundum grain respectively.
253	ρ^{f} and ρ^{o} — Density of product spinel and original corundum
254	For constant volume process, the equation (1) simplifies to,
255	$\Delta C_{j} = (\rho^{f} / \rho^{o}) (C_{j}^{f} / C_{j}^{o}) - 1 - (2)$
256	If 'j' behaves as an immobile component ($\Delta C_j = 0$), equation (2) further simplifies to,
257	$C_{j}^{f} = (\rho^{o} / \rho^{f}) C_{j}^{o}$ -(3)
258	Equation 3 defines a line in C^{f} vs. C° space that passes through the origin and has a slope of ρ^{o}/ρ^{f} .
259	If we consider the composition of the corundum (Crn1) and spinel (Spl) as 'initial/unaltered' and
260	'final/altered' rock compositions respectively, then equation 3 can be written as,
261	$C_j^{spl} = (\rho^{crn} / \rho^{spl}) C_j^{crn} - (4)$
262	Any chemical species that remains immobile during pseudomorphous replacement of corundum

Any chemical species that remains immobile during pseudomorphous replacement of corundum by spinel will be plotted on the straight line defined by Equation (4). On the other hand, chemical species that are plotted above or below the line mark gain or loss of mass, respectively, during

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pseudomorphous replacement. The densities of corundum and spinel used in the calculations are
3.93g/cm ³ and 3.75g/cm ³ , respectively (see Appendix). It is evident from Figure 5a that none of
the major elements including aluminum falls on or close to the "mass-conserved" line defined by
Equation (4). It is also evident from Figure 5a that FeO, MgO and MnO are added to (mass
gain) and Al ₂ O ₃ , TiO ₂ and Cr ₂ O ₃ have moved out (mass loss) of the volume of the SCP.
Employing Equation 2, we have computed the magnitude of change of concentrations of these
chemical species during the formation of the SCP and the results are presented in Figure 5b.
Figure 5b suggests that to form the SCP \sim 37 wt% Al ₂ O ₃ is lost which is chiefly compensated by
a gain in concentrations of MgO (~188280 wt%) and FeO (~3887wt%). Very high values of
mass change for FeO and MgO are due to their very low concentrations in the reactant
corundum. Concentrations of TiO_2 and Cr_2O_3 are reduced by ~94wt% and ~90wt%, respectively
whereas concentration of MnO is increased by ~91wt% (Fig.5b).
The foregoing analysis, though support mobility of several elements in the volume of
SCP, does not confirm if these chemical species were also mobile in the scale of a thin section.
To evaluate the latter possibility we obtained balanced chemical reactions through textural
modeling of the studied rock and present the results below.
TEXTURAL MODELING OF THE SCP- AN ALGEBRAIC ANALYSIS

Textural features of the anorthosite suggest that the SCP was formed at the expense of corundum 282 and amphibole (Figs.3 and 4c-4f). Algebraic analysis of mineral compositions is a powerful tool 283 to obtain balanced chemical reactions that explain the mineralogy and texture of the rocks 284 formed in open or close systems (Fisher 1989; Lang et al. 2004). Singular value decomposition 285 (SVD) is a simple but robust technique that is widely used by the geoscientists for modeling 286

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metamorphic textures (Lang and Rice 1985; Lang et al. 2004; Sengupta et al. 2009b and the
references cited therein). This technique checks linear dependencies and suggests possible
reactions from a compositional matrix M of m minerals in terms of n components (Lang et al.
2004). In this study, the computer program CSpace (Torres-Roldan et al. 2000) was used to
perform the matrix operation required for SVD. The chemical species whose compositions are
suspected to have changed during the reactions are considered as mobile components during
matrix operation. The mineral compositions that are used for the matrix analyses are indicated by

asterisk mark in the compositional tables (Tables 1a-1d). For the present case, we have altogether

295 15 (16 if two amphiboles Am_{mx} and Am_m are taken) minerals and mobile species (m) that are

defined by 12 system components (n). The CSpace program returns several balanced chemical

reactions solving the m x n matrix. Of the probable reactions, those that satisfy the followingcriteria are likely to explain the formation of the SCP in the studied rocks:

a. The reactant and product phases as deduced from the textures must line on the oppositesides of the reaction(s).

b. Volume ratio of spinel: plagioclase calculated from the modeled chemical reaction would lie close to 1:2 (1:1.7 to 1:2.3 as observed from petrography).

c. The volumes of spinel and corundum in the deduced reactions must be similar. This is an
essential criterion for pseudomorphism (e.g. Putnis 2002).

Modeling chemical reactions that triggered the formation of SCP requires composition of pristine amphibole. Studies have shown that composition of pristine amphibole may change significantly due to complex chemical substitutions with progress of chemical reactions involving amphibole (reviewed in Schumacher 2007). In Sittampundi anorthosite, amphibole compositions do not

309	marked variation between corundum-bearing and corundum- free layers. However, a few
310	amphibole grains that develop proximal to SCP (Am _m) is slightly Al-rich compared to amphibole
311	that develop in the amphibole plagioclase matrix (Am_{mx}) . Exact reason for this compositional
312	variation of amphibole is unclear. One possibility is that Am_m could form along with spinel and
313	moat plagioclase (Pl_m) that separate corundum from matrix plagioclase and amphibole. In view
314	of this, we have used both Am_{mx} and Am_m in textural modeling.
315	Using the aforesaid textural criteria (a-c) as filters the following reactions are obtained:
316	1. 218.494 Crn + 566.949 Am _{mx} + 9.508 Ti + 3.391 Mn + 113.872 Ca + 1.000 K = 85.390
317	$Spl + 54.639 Pl + 561.593 Am_m + 43.709 Al + 59.863 Mg + 23.477 Na + 5.360 H_2O$
318	$(\Delta V_{Crn-Spl} = -0.388 \%; Pl: Spl = 1:1.6; Crn: Am_{mx} = 0.04; Al_2O_3 loss = ~2.4 wt. \%)$
319	2. 130.706 Crn + 205.668 Am _{mx} + 3.088 Ti + 1.000 Mn + 59.714 Ca = 62.152 Spl + 65.242
320	$Pl + 189.215 \text{ Am}_m + 7.117 \text{ Al} + 1.649 \text{ Cr} + 14.071 \text{ Na} + 16.454 \text{ H}_2\text{O}$
321	$(\Delta V_{Crn-Spl} = -0.256 \%; Pl: Spl = 1:2.6; Crn: Am_{mx} = 0.06; Al_2O_3 loss = ~1 wt. \%)$
322	3. 214.286 Crn + 500.000 Am _{mx} + 8.503 Ti + 3.066 Mn + 123.086 Ca + 1.000 K + 57.731
323	$SiO_2 (aq) = 65.534 Spl + 62.023 Pl + 500.000 Am_m + 60.536 Al + 44.067 Mg + 17.523$
324	Na
325	$(\Delta V_{Crn-Spl} = -0.521 \%; Pl: Spl = 1:2.4; Crn: Am_{mx} = 0.04; Al_2O_3 loss = ~ 3.7 wt. \%)$
326	4. 116.479 Crn + 205.697 Am _{mx} + 3.088 Ti + 1.000 Mn + 49.076 Ca = 62.021 Spl + 54.616
327	$Pl + 189.241 \text{ Am}_{m} + 1.450 \text{ Cr} + 47.839 \text{ Mg} + 14.583 \text{ Na} + + 21.451 \text{ SiO}_{2} (aq) + 16.456$
328	H_2O
329	$(\Delta V_{Crn-Spl} = -0.166 \%; Pl: Spl = 1:2.2; Crn: Am_{mx} = 0.05; Al_2O_3 \text{ conserved})$

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330	Am_m and Am_{mx} represent compositions of tschermakite developed close to SCP and in the
331	matrix respectively (Table 1a). For each reaction we have calculated the difference in the
332	volumes of the reactant corundum and the product spinel ($\Delta V_{Crn-Spl}$) and volume ratio of
333	plagioclase: spinel and corundum: matrix amphibole using the molar volume data of minerals at
334	7 kbar and 700 $^{\circ}$ C (see Appendix). The justification for the chosen P-T values will be discussed
335	later. The amount of mobile aluminum (in Al ₂ O ₃ wt%) is calculated from the measured mineral
336	compositions. Modeled chemical reactions 1-4 predict that several elements including Mg and
337	SiO ₂ became mobile during the formation of the SCP. While reactions 1-3 suggest that
338	aluminum too became mobile, reaction 4 predicts Al-conserved reaction during the growth of
339	SCP. Petrological information cannot identify which of the four reactions was responsible for the
340	growth of SCP. The stoichiometry of reactions 1 - 3 suggests that only small amount of Al_2O_3
341	(~1-3.7 wt%) became mobile. In view of that it seems likely that large amount of Al_2O_3 (~37
342	wt%) that was released during the transformation of corundum to spinel was practically locked
343	in the structure of product plagioclase (that developed rind around the SCP) and in \mbox{Am}_m
344	(developed close to plagioclase rind).

345

THE SCP AS A RECORDER OF METAMORPHIC P-T PATH

The mineral assemblages of the corundum-bearing anorthosite are not suitable for application of conventional geothermobarometry. Nevertheless, coexisting ortho- and clinopyroxenes in the adjoining Mn-poor BIF that is co-metamorphosed with the SCP-bearing anorthosite provides some temperature constraint (700 – 750 °C). The deduced temperature is to be treated as minimum temperature during c. 2.46 Ga metamorphism as the pristine pyroxene compositions might have reset during cooling. In the following section an attempt has been made to constrain the physical conditions of formation of the peak metamorphic assemblage corundum (Crn₁) +

353	plagioclase (Pl_{mx}) + amphibole + clinozoisite (Czo_1) (referred to as C_1PACz) and of the
354	retrograde assemblages spinel + plagioclase + clinozoisite (SPCz) and Crn_2 + clinozoisite+
355	chlorite (C ₂ CzCh) that developed in the anorthosite. For this purpose, a partial petrogenetic grid
356	has been constructed in the systems Na ₂ O-CaO-Al ₂ O ₃ -SiO ₂ -H ₂ O (NCASH) and Na ₂ O-CaO-
357	MgO-Al ₂ O ₃ -SiO ₂ -H ₂ O (NCMASH) involving the minerals plagioclase, amphibole, clinozoisite,
358	kyanite, margarite, corundum, spinel, garnet, and chlorite. Most of these minerals form solid
359	solution and hence, their chemical potentials are adjusted for activities calculated from measured
360	chemical composition. As garnet did not develop in the rock, the chemical potential of pure
361	grossular was used. The computation process of the petrogenetic grid and the activity models for
362	the solid solution phases are presented in Appendix. In view of the mineralogy of the studied
363	rock, three invariant points (I_{1-3}) in the system NCMASH and one invariant point (I^*) in the
364	NCASH are considered. Additionally, one univariant reaction in the system NCASH that define
365	the lower pressure stability limit of clinozoisite (clinozoisite \rightarrow grossular + anorthite + corundum
366	+ H ₂ O) is also considered. The topology around the chosen NCMASH and NCASH invariant
367	points is presented in Figures 6a and 6b. Some of the reactions are not shown for clarity. The
368	reaction nets around the chosen invariant points bound P-T fields in which the assemblages
369	C ₁ PACz, SPCz and C ₂ CzCh are stabilized (Fig.6a). It is evident from Figure 6a that the peak
370	metamorphic assemblage (C ₁ PACz) was stabilized within the pressure-temperature range of 8-13
371	kbar and ~650-780 °C. More restricted pressure range (~10-12 kbar) is obtained if the result of
372	two pyroxene thermometry (700-750°C) from the co-metamorphosed BIF is superimposed on the
373	phase diagram (Fig.6a). The topological relations also suggest that reduced water activity that
374	results from dilution of H ₂ O by CO ₂ and/or halide will displace the invariant points of Figure 6
375	to higher pressure and lower temperature. It then follows that the estimated pressure of 10-12

376	kbar (at 700-750 °C) should be treated as the minimum pressure estimate for the stability of the
377	peak metamorphic assemblage C_1 PACz. These P-T values overlap with the P-T values (11-12
378	kbar, ~650 °C) obtained by Bhaskar Rao et al. (1996) from the enclosing garnetiferous mafic-
379	ultramafic rocks (Fig.6b). Topology of Figure 6a also constrains that the assemblage SPCz that
380	includes the SCP was formed in the P-T range of 6-8 kbar, 625-725 °C. Within the uncertainties
381	of calculation, the estimated P-T value for SPCz overlaps with the P-T value obtained for the
382	symplectitic assemblage replacing porphyroblastic garnet in the enclosing mafic-ultramafic rocks
383	$(7 \pm 1 \text{ kbar}, 700 \pm 50 \text{ °C}, \text{Bhaskar Rao et al.} 1996; \text{ our unpublished data; Fig.6b})$. The univariant
384	reactions as depicted in Figure 6a further demonstrate that the assemblage C ₂ CzCh was formed
385	from spinel \pm amphibole- bearing assemblage at temperature \leq 620 °C and pressure 6-8kbar. This
386	pressure-temperature range of the chlorite-bearing assemblage overlaps with the pressure-
387	temperature values (7 \pm 1 kbar, 650 \pm 50 °C) computed for the högbomite + chlorite +
388	corundum- bearing assemblages developed in retrograded anorthosite from Sittampundi
389	(Sengupta et al. 2009b) It is, therefore, likely that the assemblage C ₂ CzCh formed late due to
390	cooling and hydration, presumably under near isobaric condition (Fig.6b). During this hydration
391	event, rocks of the SLC resided at ~7kbar and awaited fresh tectonism that brought them close to
392	the surface of the earth from where weathering and erosion exposed them to the present position.
393	DISCUSSION
394	It is evident from the foregoing analysis that subsequent to its formation as a part of the

Archaean oceanic crust in suprasubduction zone setting (Dutta et al. 2011), the SLC underwent

396 fluid-induced metamorphic reconstitution during c. 2.46 Ga high-grade event. At the first stage,

- 397 the highly calcic anorthosite developed the assemblage C_1PACz . Estimated physical condition of
- metamorphism for the peak assemblage C₁PACz (11 ± 1 kbar, 725 ± 25 °C) points to burial of

the 'fossil' oceanic crust (depth of formation of anorthosite <7 km, Dutta et al. 2011) to a depth 399 of ~33–40km. Mineral reaction that led to stabilization of porphyroblastic corundum in the 400 401 anorthosite and in the interbanded amphibolite is unclear. Features such as, (a) random 402 orientation of Crn_1 throughout the volume of the rock, and (b) absence of the assemblages with kyanite + clinozoisite \pm corundum and corundum + clinopyroxene speak against the idea that the 403 404 corundum-bearing anorthosite represents a ultra-high pressure rock (Morishita et al. 2004; Sajeev 405 et al. 2009). Desilication and decalcification of calcic plagioclase and amphibole appears to explain most of the mesoscopic features of porphyroblastic corundum (e.g., Bucher et al. 2005; 406 407 Raith et al. 2008). Existing tectonic models suggest that burial of oceanic crust to a depth >30km is only possible in subduction zones (Platt 1993; Zhang et al. 2006; Ota and Kaneko 2010; van 408 Hunen and Moyen 2012 and the references cited therein). It then follows that the SLC which was 409 a part of an Archaean suprasubduction zone was transformed to a subduction zone and buried to 410 depth of >30 km at c. 2.46 Ga. The estimated physical condition of formation of C_1PACz (~11 ± 411 412 1kbar and $725 \pm 25^{\circ}$ C) corresponds to a thermal gradient of $17-22^{\circ}$ C/km at the time of the c. 2.46 413 Ga tectonothermal event. Such apparent thermal gradient which overlaps the domain of high pressure metamorphism (≤ 20 °C/km) is sparsely reported from the rocks of early 414 415 Palaeoproterozoic age (>2.0 Ga, reviewed in Brown 2007; Anderson et al. 2012). High heat flow of the ancient earth is deemed responsible for the rarity of high pressure metamorphism at the 416 417 dawn of the Proterozoic and earlier (reviewed in Brown 2007). Our study corroborates the 418 contention of Anderson et al. (2012) that low thermal gradient that is characteristic of the orogenic belts of the Mesoproterozoic and younger time also existed in the south Indian granulite 419 belt at the dawn of Proterozoic. 420

421	In the second stage, the subducted oceanic crust that is represented by high-pressure rock
422	of the SLC was exhumed from 11 ± 1 kbar to 7 ± 1 kbar along a steep P-T path (Figs. 6b).
423	Infiltration-driven processes during this exhumation destabilized the porphyroblastic corundum
424	and the amphibole and triggered the growth of the SCP with plagioclase rind. A large mismatch
425	of crystallographic parameters exist between spinel (cubic) and corundum (hexagonal) and their
426	textural relations are consistent with the idea that solution (of corundum)-precipitation (of spinel)
427	process was instrumental in the formation of the SCP (Putnis 2002, 2009; Putnis et al. 2005;
428	Putnis and Putnis 2007; Putnis and John 2010). Mass-balance calculations performed on SCP
429	show that several chemical species including Al became mobile during the formation of SCP.
430	However, modeling of reaction textures show that aluminum that was released during the
431	formation of SCP was practically locked in the product minerals (plagioclase and amphibole)
432	that develop proximal to SCP. This study therefore supports the low solubility of aluminum in
433	metamorphic fluid.
434	
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LIST OF FIGURE CAPTIONS

Figure 1. Generalized geological map of Cauvery Shear System (CSS; Chetty, 1996) (modified

after the geological map of Tamil Nadu, 1: 250 000 scale, published by the Geological Survey of

India 1995). The studied area is marked by a square in the inset. Various shear zones in CSS and

- ⁵⁹⁷ adjoining areas are shown in the inset. DC- Dharwar Craton, FL- Fermore line separating
- northern DC from the Southern India Granulite Terrane, NGT- Northern Granulite Terrane,
- 599 MSZ- Moyar shear zone, BSZ- Bhavani shear zone, MBASZ- Moyar-Bhavani-Attur shear zone,
- 600 PCSZ- Palghat- Cauvery shear zone, MB- Madurai Block, KKPTSZ- Karur-Kumbum-Panivu-
- 601 Trichur shear zone (Ghosh et al., 2004), ACSZ- Achankovil shear zone, KKB- Kerala khondalite
- 602 belt, BLC- Bhavani layered complex, SLC- Sittampundi layered complex.
- 603

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604	Figure 2. (a)- Dismembered band of clinopyroxenite dykes (dark) within anorthosite (white).
605	Note the large porphyroblastic garnet (Grt) grains in the clinopyroxenite dyke. (b)- Amphibole
606	(Am) rich layers (dark) within anorthosite (white). (c)- Dimensional orientation of amphibole
607	(Am) grains defining the foliation within anorthosite. In the middle of the slab a cm-thick
608	chromite (Chr) layer is present within the anorthosite. Note that the chromite (Chr) layer is
609	stretched parallel to the foliation defined by amphibole (Am). Pink corundum (Crn_1) with a rim
610	of spinel is seen within anorthosite in the lower part of the slab. (d)- Haphazard orientation of
611	large amphibole (Am) grains within anorthosite (white). The Mineral abbreviations are after
612	Kretz et al. (1983).

613

614 **Figure 3.** (a)- Large corundum (Crn₁) with hexagonal outline is embedded within amphibole rich (dark) domain within anorthosite. Note that Spinel (Spl) that rims Crn₁ also retains the hexagonal 615 shape of the original Crn₁ (pseudomorph). Also note that a rind of plagioclase (Pl_m) separates Spl 616 617 from matrix amphibole (Am_{mx}) + plagioclase (Pl_{mx}) . Domain-B. See text. (b)- Prismatic Crn₁ (ruby) cuts the foliation defined by Am (dark green) in Domain-B. In Domain-A (lower half) 618 619 Crn₁ shows oval to hexagonal outline. These features are consistent with haphazard orientation 620 of Crn_1 in the rock volume. Spl rim on Crn_1 grains are also seen. Note that some Crn_1 grains are completely pseudomorphed by Spl. See text. (c)- Development of coarse Crn_1 in Am-Pl_{mx} 621 622 matrix. Crn₁ develops Spl rims of variable thickness. Spl retains the shape of Crn₁ and is surrounded by Pl_m near Am. Coronal Spl send vein towards the interior and fill fractures within 623 624 the Crn₁ grains. See text. Complete pseudomorphic replacement of Crn₁ by Spl is also seen. The mineral abbreviations are after Kretz et al. (1983). (d)-Boudinaged prismatic Crn₁ (ruby) crystal 625

partially replaced by Spl within plagioclase rich domain (Domain-A). Note that Spl retains the shape of the Crn_1 boudins. Patches of amphibole (Am_m) are seen close to the Crn_1 -Spl domain.

628

Figure 4. (a)- Granoblastic fabric defined by polygonal grains of plagioclase (Pl_{mx}) and 629 630 amphibole (Am_{mx}) grains in the matrix of anorthosite. Plane polarized light. (b)- Partial replacement of Crn₁ by Spl. Note the development of Pl_m around Spl. Plane polarized light.(c)-631 Same as Fig.(b) note that grains of Pl_m has larger size than that of Pl_{mx}. Domain-B, anorthosite. 632 633 Plane polarised light .(d)- Granoblastic texture shown by corundum (Crn_1), plagioclase (Pl_{mx}) 634 and clinozoisite (Czo₁). Note the development of haphazard chlorite (Chl) flakes along the 635 contacts of the porphyroblastic phases. Crossed nicols. (e)- Aggregate of clinozoisite (Zzo_2) + 636 chlorite (Chl) separate Pl_{mx} and amphibole (Am_{mx}). Domain-A. Crossed nicols. (f)- Breakdown of coronitic Spl by into an aggregate of corundum (Crn₂; black) + magnetite (Mag; bright) + 637 chlorite (Chl; flaky) against plagioclase rind (Pl_m). Domain-A. BSE image. The abbreviations for 638 phases are same as in Figure 2 and 3 (after Kretz et al. 1983). 639

640

Figure 5. (a)- C_j^{spl} vs. C_j^{crn} diagram demonstrating the gains and losses of different elements during the formation of spinel with corundum pseudomorphs (SCP). Initial concentration of various species in corundum (C_j^{crn}) is plotted against the final concentration in spinel (C_j^{spl}). Elements whose concentrations remain conserved should be plotted on the 'mass-conserved' line having slope given by (ρ^{crn}/ρ^{spl}). See Equation 4 in the text. Species plotting above or below 'mass-conserved' Line infer mass gain or loss during the formation of SCP. Note that the

formation of SCP was accompanied by the loss of Al₂O₃, Cr₂O₃ and TiO₂ which in turn is
compensated by the gain of MgO, FeO and MnO. (b)- Percentages of mass change undergone by
individual species during the formation of SCP. Species having negative values indicate mass
loss while those having positive values indicate mass gain. The extremely high positive values
for FeO and MgO (plots outside the shown scale) are related to the low concentration of these
species in corundum.

653

654 Figure 6. (a) Activity adjusted partial petrogenetic grid in the system Na₂O-CaO-Al₂O₃-SiO₂-H₂O (NCASH) and Na₂O-CaO-MgO-Al₂O₃-SiO₂-H₂O (NCMASH) involving the minerals those 655 656 are relevant to this study. P-T stability fields of the peak assemblage $Crn_1+Pl+Am+Czo_1$ 657 (C_1PACz) and retrograded assemblages Spl+Pl+Czo (SPCz) and Crn₂+Czo+Chl (C₂CzCh) of the 658 studied anorthosite are shaded. Lines marked (a) and (b) represent the temperature range estimated from the enclosing BIF. I₁₋₃ and I* are the invariant points in the NCMASH and 659 NCASH systems respectively. (b) Metamorphic P-T path deduced from the SCP-bearing 660 661 anorthosite. 'x' and 'y' represent the P-T ranges for the peak and retrograde assemblages as 662 obtained from the mafic granulites by Bhaskar Rao et al. 1996 (see text). The bold and dashed 663 line with an arrow head represents the probable P-T path traversed by the studied rock. Some of the reaction lines and labels are omitted for clarity. The abbreviations for phases are after Kretz 664 665 et al. (1983).

666

APPENDIX

667 Mineral abbreviation

(DOI will not work until issue is live.) DOI: http://dx.doi.org/10.2138/am.2013.4350 The mineral name abbreviations used here are after Kretz et al. 1983. Amphibole is

abbreviated as 'Am'. Subscript 'm' and 'mx' are used after mineral abbreviation (Am and Pl) to

670 indicate the presence of the phase near or within SCP and within matrix respectively. Different

generations of the same mineral is denoted by mentioning '1' or '2' for first or second generation

respectively in the subscript of the mineral abbreviation e.g., Crn_1 and Crn_2 .

673 Microprobe analysis

668

674 Representative compositions of the minerals in the pseudomorph forming domains were

675 measured with CAMECA-SX 100 at Geological Survey of India, Kolkata. Analyses were carried

out with an electron beam (1-2 μ m diameter) operated at 15kv and 15 nA. Details of the

analytical procedure and the standard used for analyses are given in Sengupta et al. (2011).

678 Activity-composition relations used for Figure 6

For construction of activity adjusted topologies in the system Na₂O-CaO-MgO-Al₂O₃-

680 SiO₂-H₂O (NCMASH) and Na₂O-CaO-Al₂O₃-SiO₂-H₂O (NCASH), A-X program of Holland

and Powell (2001) is used.

682 Molar volumes and densities of minerals

683 The molar volume (V) and density (ρ) of the minerals that are used in this study are

calculated at 7 kbar, 700 °C, the mean pressure-temperature estimated for the SCP. The

- thermodynamic data of Holland and Powell (1998 updated in 2002) and the computer program of
- 686 PERPLEX (Connolly, 2005) are used to obtain the molar volume and density data.

Phases	Crn	Spl	Pl(An)	Am(Ts)	

9/4

687	V(J/mol/bar)	2.593	4.060	10.106	27.094
688	$\mathbf{p}(a/am^3)$	3.93	3.75		
689	$\mathbf{\rho}(g/cm^3)$	3.95	5.75		

690

691

For spinel, which is essentially a solid solution of $MgAl_2O_4$ and $FeAl_2O_4$ (Table 1b), molar

693 volume and density is calculated by the relation –

694
$$V_{spinel} = [(X_{MgAl2O4} \times V^{MgAl2O4}) + (X_{FeAl2O4} \times V^{FeAl2O4})]$$

695
$$\rho_{spinel} = [(X_{MgAl2O4} \times \rho^{MgAl2O4}) + (X_{FeAl2O4} \times \rho^{FeAl2O4})]$$

where, $X_{FeAl2O4}$ represents molar mole fraction of $FeAl_2O_4$ etc. The values of the used inputs in

697 the above calculation are - $X_{MgAl2O4} = 0.68$; $X_{FeAl2O4} = 0.32$; $V^{MgAl2O4} = 4.030 \text{ g/cm}^3$; $V^{FeAl2O4} = -1000 \text{ g/cm}^3$

698 4.124 g/cm³;
$$\rho^{MgAl2O4} = 3.53$$
 g/cm³; $\rho^{FeAl2O4} = 4.215$ g/cm³.

699

700



Figure 1



Figure 2



Figure 3


Figure 4a-4f





Figure 5b



Figure 6a



Figure 6b

Sample	S135-83	S135-84	S135-102	S140-100	S160-28*	S160-62	S160-231
SiO ₂	45.75	46.29	45.27	45.24	43.40	43.83	44.35
TiO ₂	0.04	0.08	0.21	0.21	0.23	0.16	0.10
Al_2O_3	13.96	13.78	13.21	15.21	15.53	15.31	14.53
Cr ₂ O ₃	0.13	0.11	0.78	0.02	0.56	0.26	0.47
MgO	15.69	15.42	15.85	15.91	14.98	15.68	15.69
FeO	8.47	8.52	6.76	6.96	6.66	6.82	7.15
CaO	10.92	11.17	11.24	11.57	11.95	11.33	11.07
MnO	0.13	0.10	0.12	0.09	0.15	0.11	0.10
Na ₂ O	1.99	2.04	2.02	2.19	1.89	2.24	2.13
K ₂ O	0.13	0.13	0.14	0.06	0.13	0.10	0.06
Total	97.22	97.64	95.60	97.46	95.48	95.84	95.65
Cations base	ed on 23 oxygen	5					
Si	6.549	6.595	6.565	6.427	6.318	6.348	6.435
Ti	0.005	0.009	0.023	0.022	0.025	0.017	0.011
Al	2.355	2.315	2.258	2.548	2.664	2.613	2.485
Cr	0.015	0.013	0.089	0.002	0.064	0.029	0.054
Mg	3.347	3.275	3.426	3.370	3.250	3.384	3.394
Fe	1.014	1.016	0.820	0.826	0.811	0.826	0.867
Ca	1.674	1.706	1.746	1.761	1.865	1.758	1.722
Mn	0.016	0.012	0.015	0.011	0.018	0.014	0.012
Na	0.552	0.563	0.568	0.603	0.533	0.628	0.600
Κ	0.023	0.023	0.026	0.012	0.025	0.019	0.012
Cation S	15.550	15.525	15.536	15.583	15.572	15.637	15.591
X_{Mg}	0.77	0.76	0.81	0.80	0.80	0.80	0.80
Species**	Tsch	MH	MH	Tsch	Tsch _m	Parg _m	Tsch _{mx}

Table 1a. Representative microprobe analyses of amphibole.

 $X_{Mg} = Mg / (Mg + Fe^{2+})$; Tsch-Tschermakite, MH- Magnesiohornblende, Parg-Pargasite * Analyses used for reaction modeling (m= amphibole near SCP; mx= matrix amphibole, see text) **Amphibole species nomenclature is after Leake et. al. (2004).

S160-234	S160-243*
44.39	43.83
0.11	0.08
14.71	14.02
0.47	0.50
16.13	15.62
7.19	6.98
11.32	11.05
0.08	0.10
2.20	2.01
0.11	0.12
96.71	94.31
6.383	6.453
0.012	0.008
2.493	2.433
0.053	0.058
3.456	3.427
0.865	0.859
1.744	1.743
0.010	0.012
0.613	0.574
0.020	0.023
15.649	15.591
0.80	0.80
Tsch _{mx}	Tsch _{mx}

Table 1b. Representative microprobe analyses of spinel (Spl).

Sample	S135-7	S135-16	S140-149	S160-2	S160-3	S160-16*
SiO ₂	0.00	0.02	0.03	0.02	0.00	0.00
TiO ₂	0.00	0.00	0.04	0.00	0.00	0.00
Al ₂ O ₃	61.57	61.48	62.92	64.62	65.13	64.14
Cr_2O_3	0.02	0.00	0.05	0.12	0.08	0.11
FeO	23.38	23.46	20.60	17.99	18.47	17.89
MnO	0.33	0.30	0.10	0.07	0.07	0.06
MgO	13.16	13.75	15.55	16.68	16.85	17.77
CaO	0.00	0.01	0.01	0.00	0.00	0.00
ZnO	0.00	0.00	0.08	0.00	0.00	0.05
Na ₂ O	0.00	0.00	0.00	0.01	0.00	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.01	0.00
Total	98.47	99.03	99.37	99.52	100.60	100.01
Cations bas	ed on 4 oxygen	is				
Si	0.000	0.000	0.001	0.000	0.000	0.000
Ti	0.000	0.000	0.001	0.000	0.000	0.000
Al	1.943	1.926	1.938	1.965	1.961	1.935
Cr	0.000	0.000	0.001	0.003	0.002	0.002
Fe ³⁺	0.057	0.073	0.058	0.032	0.038	0.063
Fe ²⁺	0.467	0.448	0.392	0.356	0.356	0.320
Mn	0.007	0.007	0.002	0.002	0.001	0.001
Mg	0.525	0.545	0.606	0.642	0.641	0.678
Zn	0.000	0.000	0.002	0.000	0.000	0.001
Ca	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.000	0.000	0.000	0.001	0.000	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000
Total	3.000	3.000	3.000	3.000	3.000	3.000
Mg#	53	55	61	64	64	68
Cr#	0.0	0.0	0.1	0.1	0.1	0.1

Al#	97	96	97	98	98	97
Fe ³⁺ #	2.8	3.7	2.9	1.6	1.9	3.1

 $\begin{array}{l} Mg\# = 100 \ Mg \ / \ (Mg + Fe^{2^{+}}); \ Cr\# = 100 \ Cr \ / \ (Cr + Al); \ Al\# = 100 \ Al \ / \ (Cr + Al + Fe^{3^{+}}); \ Fe^{3^{+}}\# \\ = 100 \ Fe^{3^{+}} \ / \ (Cr + Al + ^{Fe^{3^{+}}}) \\ * \ Analysis used for reaction modeling \end{array}$

Sample	S135-25	S135-26	S140-163	S160-14*	S160-105	S135-67	<u>\$135-68</u>	S135-69
Mineral	$\frac{5135-23}{\text{Crn}_1}$	Crn ₁	Crn ₁	Crn ₁	Crn ₁	Czo ₁	Czo ₁	Czo ₁
SiO ₂	0.10	0.01	0.00	0.00	0.01	39.21	38.94	38.60
TiO ₂	0.02	0.00	0.00	0.03	0.02	0.00	0.34	0.00
Al_2O_3	98.55	97.02	97.50	96.73	97.34	31.20	31.21	30.44
	0.07	0.17	1.01	1.05	1.74	0.00	0.00	0.18
Cr_2O_3								
Fe ₂ O ₃	0.34	0.50	0.18	0.43	0.64	1.92	2.39	2.97
MgO	0.02	0.02	0.00	0.01	0.00	0.03	0.01	0.05
CaO	0.06	0.01	0.00	0.02	0.01	25.12	25.55	25.11
MnO	0.00	0.00	0.03	0.03	0.01	0.10	0.00	0.00
ZnO	0.00	0.00	0.03	0.01	0.04	0.00	0.00	0.00
Na ₂ O	0.02	0.00	0.01	0.00	0.01	0.01	0.04	0.08
K ₂ O	0.01	0.00	0.01	0.00	0.00	0.02	0.00	0.00
Total	99.18	97.73	98.79	98.30	99.82	97.61	98.48	97.43
Oxygen Basis	3	3	3	3	3	12.5	12.5	12.5
Si	0.002	0.000	0.000	0.000	0.000	3.010	2.973	2.985
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.020	0.000
Al	1.991	1.990	1.983	1.979	1.967	2.823	2.809	2.775
Cr	0.001	0.002	0.014	0.014	0.024	0.000	0.000	0.011
Fe ³⁺	0.004	0.007	0.002	0.006	0.008	0.111	0.137	0.173
Mg	0.000	0.000	0.000	0.000	0.000	0.003	0.001	0.006
Ca	0.001	0.000	0.000	0.000	0.000	2.066	2.090	2.081
Mn	0.000	0.000	0.000	0.000	0.000	0.007	0.000	0.000
Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.001	0.000	0.000	0.000	0.000	0.001	0.006	0.012
K	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000
Cation 	2.000	2.000	2.001	2.000	2.000	8.024	8.037	8.042
Pistacite (mole %)						4	5	6

Table 1c. Representative microprobe analyses of corundum (Crn₁) and clinozoisite (Czo₁).

Pistacite (mole %) = 100 Fe³⁺/ (Fe³⁺ + Al)

* Analysis used for reaction modeling

Sample	<u>8135-90</u>	<u>S135-95</u>	<u>S135-99</u>	<u>S135-3</u>	<u>S140-130</u>	<u>S160-70*</u>	<u>S140-152</u>
Mineral	P1	P1	Pl	Pl	Pl	Pl	Chl
SiO ₂	46.27	45.30	45.64	42.35	43.63	43.16	27.70
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Al_2O_3	33.61	33.93	34.05	35.93	34.21	35.53	21.99
Cr_2O_3	0.01	0.02	0.01	0.01	0.00	0.00	0.02
MgO	0.00	0.00	0.00	0.00	0.00	0.00	26.39
FeO	0.10	0.08	0.11	0.08	0.05	0.08	9.05
CaO	18.49	18.74	18.59	20.15	19.95	20.00	0.03
MnO	0.00	0.00	0.00	0.05	0.00	0.00	0.03
ZnO	0.00	0.04	0.02	0.00	0.05	0.00	0.05
Na ₂ O	1.29	1.05	1.15	0.06	0.40	0.53	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.77	99.16	99.58	99.39	98.31	99.30	85.27
Oxygen basis	8	8	8	8	8	8	14
Si	2.138	2.109	2.115	1.993	2.058	2.017	2.744
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.002
Al	1.831	1.862	1.860	1.993	1.902	1.958	2.567
Cr	0.000	0.001	0.000	0.000	0.000	0.000	0.001
Mg	0.000	0.000	0.000	0.000	0.000	0.000	3.896
Fe	0.004	0.003	0.004	0.003	0.002	0.003	0.750
Ca	0.916	0.935	0.923	1.016	1.008	1.001	0.003
Mn	0.000	0.000	0.000	0.002	0.000	0.000	0.002
Zn	0.000	0.001	0.001	0.000	0.002	0.000	0.004
Na	0.116	0.095	0.103	0.006	0.036	0.048	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cation S	5.005	5.007	5.007	5.013	5.009	5.028	9.970
X _{An}	89	91	90	99	97	95	
Mg#							0.84

Figure 1d. Representative microprobe analyses of plagioclase (Pl) and chlorite (Chl).

$$\begin{split} X_{An} &= 100 \text{ Ca } /(\text{Ca} + \text{Na} + \text{K}); \text{ Mg\#} = \text{Mg} / (\text{Mg} + \text{Fe}^{2*}) \\ * \text{ Analysis used for reaction modeling} \end{split}$$

<u>S140-165</u>
Chl
26.40
0.02
24.75
0.02
24.71
8.98
0.03
0.04
0.01
0.04
0.00
85.01
14
2.620
0.002
2.896
0.002
3.655
0.745
0.004
0.003
0.001
0.008
0.000
9.934

0.83