

# Plastic deformation and post-deformation annealing in chromite: mechanisms and implications

(Revision 5)

Biswajit Ghosh<sup>1,3\*</sup>, Santanu Misra<sup>2</sup>, Tomoaki Morishita<sup>3</sup>

<sup>1</sup>Department of Geology, University of Calcutta, 35 Ballygunge Circular Road, Kolkata, India

<sup>2</sup>Department of Earth Sciences, Indian Institute of Technology, Kanpur, UP-208016, India

<sup>3</sup>School of Natural System, College of Science and Engineering, Kanazawa University, Japan

## Abstract

Plastic deformation in chromite is not frequently reported in literature. We present a detailed microstructural analysis of this mineral from massive chromitite of the Neoarchaean Sittampundi Complex, southern India. The study reveals intracrystalline plasticity is dominantly active in this mineral and it produces distinctive features corresponding to at least two different microstructural regimes. The Regime 1 is deformation-related and it commenced with recovery of strained grains and formation of new grains, corresponding to subgrain rotation recrystallization. This was followed by nucleation of strain-free new grains in regions of high strain. The Regime 2 appears to be post-deformational and dominantly temperature-controlled, producing distinctive features of static annealing of already deformed grains. This regime corresponds to grain boundary migration recrystallization resulting coarsening of strain-free faceted, new grains at the expense of high dislocation density subgrains. The resultant micro-features resemble closely what is known as ‘*abnormal grain growth*’, not yet documented for chromites. These coarse grains, in places, also feature accommodation of deformation by displaying very low angle subgrain boundaries. The movement of high-angle grain boundaries in Regime 2 through precursor strained grains provided high diffusivity paths for the rapid exchange of components, producing compositional heterogeneity between grains dominated by deformation features and faceted, new grains. These microstructural observations coupled with chemical heterogeneity provide new directions in interpreting the deformation mechanism of chromite, and its annealing history at the post-deformation stage.

**Keywords:** Chromite, Plastic deformation and recrystallization, Strain-free new grain, Annealing, Abnormal grain growth.

\*Corresponding Author. E-mail: [bghosh\\_geol@hotmail.com](mailto:bghosh_geol@hotmail.com) Tel: +91-33-2461-4891

## 34 INTRODUCTION

35 The general absence of substructures in chromites from mantle peridotites and chromitites  
36 (Christiansen, 1985) and subsequent recognition of stress-induced Al-Cr multipolar zoning in  
37 ophiolitic chromites prompted to believe that dislocation creep is not a dominant mechanism in  
38 the deformation of chromite (Ozawa, 1989). Instead, diffusion creep is thought to be the  
39 principal mechanism in its deformation. The lack of appreciation of chromite crystal plasticity  
40 owes to the fact that chromite, among the cubic minerals, has low stacking fault energy, like  
41 garnet, and hence struggles to develop dislocation based microstructures. While using  
42 backscatter electron (BSE) channeling pattern and orientation contrast in scanning electron  
43 microscopy, chromites from Oman ophiolite have served to provide evidences favoring limited  
44 dislocation creep mechanisms at high temperature during mantle flow (Christiansen, 1986), well  
45 constrained natural examples of crystal-plastic deformation in the dislocation creep regime were  
46 absent until recently, when Vukmanovic et al. (2013) described chromite microstructures in the  
47 stratiform chromitite layer from the Meerensky Reef. Soon after, chromite crystal plasticity was  
48 documented from podiform mantle chromitites in ophiolitic setting (Ghosh et al., 2014). Very  
49 recently fluid-assisted chromite deformation, promoting chemical and textural modification has  
50 also been reported (Satsukawa et al., 2015a).

51 Our study focuses on trench samples of foliated stratiform chromitites (Fig. 1a) occurring  
52 as seams containing 60–70 modal% of porphyroclastic chromites with the remaining matrix,  
53 constituted dominantly by amphiboles, mainly tschermakitic hornblende with accessory  
54 phlogopites from the Sittampundi Layered Complex (SLC), southern India which is thought to  
55 be equivalent to Fiskenaesset complex of West Greenland (Ghisler, 1970). The SLC is a  
56 deformed, anorthosite-dominated layered igneous complex within Palghat–Cauvery Shear Zone

57 (PCSZ) that represents a geosuture amalgamating two crustal blocks (Santosh et al., 2009;  
58 Santosh and Kusky, 2010) with different isotopic characteristics, age, structure, metamorphism  
59 and magmatism (Meissner et al., 2002). The SLC was formed in Neoproterozoic (Bhaskar Rao et  
60 al., 1996) and was subjected to eclogite facies metamorphism ( $>1000\text{ }^{\circ}\text{C}$  and  $>20\text{ kbar}$ )  
61 corresponding to 65 km paleo-depth, near to the crust-mantle boundary and later exhumed in the  
62 latest Neoproterozoic–Cambrian (Sajeev et al., 2009). Structurally, the Sittampundi complex was  
63 initially considered as a single stratigraphic unit (Subramanian, 1956; Naidu, 1963). A detailed  
64 work (Ramadurai, 1975) later, however, suggested that the complex consists of a repeated  
65 stratigraphic sequence resulted from a tight (isoclinal) anticline structure of the region.

66 In order to know the impact of deformation at such high pressure and temperature on  
67 chromites, we carried out a detailed microstructural study on chromitites sampled from different  
68 stratigraphic horizons using high resolution optical microscopy, Back Scattered Electron (BSE)  
69 imaging, quantitative chemical analysis, elemental mapping and Electron Back Scattered  
70 Diffraction (EBSD) techniques. Our results imply that chromite, like pyrite, is more ductile than  
71 generally inferred (Barrie et al., 2010), and we demonstrate the intracrystalline plastic  
72 deformation mechanisms in this mineral. We have identified two distinct microstructural  
73 regimes; Regime 1 and Regime 2 based on characteristic features and attributed them as  
74 functions of relative magnitude of deformation and temperature respectively. This work differs  
75 from related one, performed experimentally on other minerals in that our observations here is  
76 made on natural samples and not constrained in controlled conditions exclusive to each of these  
77 microstructural regimes and to their transitions. Therefore, the observations made here are based  
78 entirely on relict micro-features arrested in some grains.

## 79 **SAMPLING AND ANALYTICAL METHODS**

80 Based on estimation of intensity of foliation observed in the field and their outcrop  
81 location, we collected 12 samples, 4 from each 3 different chromitite seams (KPT5: N11°16'04",  
82 E77°59'58", BL-SII: N11°14'17", E77°57'21" and CPT6: N11°15'40" E77°58'56") corresponding to  
83 different stratigraphic horizons around Karungalpatti area (Fig. 1b). We initially analyzed all of  
84 them on thin sections cut perpendicular to foliation (Fig. 2a) for BSE imaging, and based on the  
85 output we finally selected 3 samples, each representing a seam for detailed quantitative  
86 orientation analysis (EBSD) analysis. We emphasize here that the observed micro-features (see  
87 next) corresponding to two regimes (Regime 1 and 2, discussed later), do not occur in all the  
88 seams. Those related to the Regime 1 are restricted to seams at the upper and middle horizons  
89 (sample locations KPT5 and BL-SII, respectively) whereas, those related to the Regime 2 are  
90 specific only to the bottom horizon (sample location CPT6). However, some features of Regime  
91 1 are preserved in samples that exhibit regime 2 features.

92 BSE imaging, quantitative chemical point analysis and elemental mapping were carried out  
93 at Kanazawa University, Japan using an electron probe micro-analyzer (JEOL JXA-8800  
94 Superprobe). The analyses were performed under an accelerating voltage of 15 kV and beam  
95 current of 20 nA, using a beam diameter of 3  $\mu\text{m}$ . EBSD analysis was carried out at Electron  
96 Microscopy Center at ETH, Zurich (EMEZ) with FEI Quanta 200. The chromitite samples were  
97 cut perpendicular to the foliation (A2-A3 plane, Fig. 2a), impregnated in epoxy and polished for  
98 EBSD analysis. The EBSD patterns and data were generated by the vertical incidence of electron  
99 beams on the polished surface of the sample, tilted at 70° with respect to the horizontal plane of  
100 the scanning electron microscope. The scheme of the sample orientation with respect to the  
101 EBSD analysis is shown in Figure 2. The acceleration voltage and probe current were set at 20

102 kV and 8.2 ( $\pm 0.2$ ) nA, respectively and the working distance was 18-20 mm. Diffraction patterns  
103 were automatically collected with 40-45 fps, indexed (initial indexing rate  $\sim 90\%$ ) and analyzed  
104 using an orientation imaging microscopy software (TSL OIM) from the quadrangle areas of the  
105 samples, using step sizes of 5 or 7  $\mu\text{m}$  (depending on the average grain size of the region being  
106 mapped). The automatic data processing converted non-indexed data-points (pixels) to indexed  
107 with respect to the index-patterns of the neighbouring pixels. Only data with a high level of  
108 reliability (confidence index  $\text{CI} > 0.2$ ) were used in the statistical orientation analysis presented in  
109 this paper. A series of TSL OIM built-in “clean-up” steps were used to replace non-indexed data  
110 points with reliable orientations from the neighbouring pixels. For grain dilation default  $5^\circ$  grain  
111 tolerance angle and 2 pixels minimum grain size were set under single iteration. A similar  
112 protocol applied for Grain CI and grain fit standardizations. For neighbour CI and orientation  
113 correlations the minimum confidence index was set to 0.2.

114 In the following discussions related to EBSD analysis we have presented three major map  
115 types – i) Image Quality (IQ), ii) Inverse Pole Figure (IPF) and iii) Kernel Average  
116 Misorientation (KAM) maps. The IQ maps show the quality of the diffraction pattern obtained  
117 during a scan, and thus they provide information and visualization of microstructures,  
118 particularly the misorientation of the grains. In our analysis we have defined boundary as any  
119 adjacent point pair with misorientation exceeding  $2^\circ$ . We have mapped the boundaries in three  
120 segments – subgrains (misorientation-boundaries  $\leq 5^\circ$ ); intermediate grains (misorientation-  
121 boundaries from  $5$ - $15^\circ$ ) and recrystallized grains (misorientation-boundaries  $\geq 15^\circ$ ). The  
122 recrystallized grains may have partial subgrain/intermediate grain boundaries. They are  
123 apparently strain-free with internal misorientations less than  $1$ - $2^\circ$ . The IQ maps are highlighted  
124 to show several analytical directions (transects) used in this study. The IPF maps are color-coded

125 based on the orientation of the grains. Red, green and blue colors are designated to grains whose  
126  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  axes, respectively, are parallel to the projection of the IPF. All other  
127 orientations are color-coded and are assigned blends of these three basic colors based on  
128 orientation. The IPF maps are projected along the z direction, which is equivalent to A1 (Fig. 2a)  
129 of the sample geometry. Like the IQ maps the IPF maps are also highlighted with the grain  
130 boundaries. The KAM maps obtained from the EBSD data reveal the average misorientation  
131 angle at any point taking into account of all the neighbouring analysis points. We have selected  
132 up to 10<sup>th</sup> nearest neighbours with maximum misorientation angle of 5°. The KAM maps are  
133 useful to interpret the internal strain which is represented by concentration of low angle  
134 boundaries. We have also made profiles across grains to show change in orientation relative to  
135 the starting point along specific directions.

## 136 **OBSERVATIONS**

137 Based on the pattern and the mutual disposition of grains we have classified the observed  
138 microstructures in two major regimes. The Regime 1 shows significant change in orientation  
139 within individual grains with presence of subgrain boundaries. The Regime 2 is characterized by  
140 abundance of large ( $\sim 300\text{-}400\mu$ ) grains that exhibit little to no crystal lattice bending and  
141 straight grain boundaries. A detailed account of the observed microstructures is provided below.

### 142 **Regime 1**

143 The porphyroclastic chromite grains of the upper chromitite seam (KPT5) are little  
144 deformed and do not show much evidence of intra-grain lattice distortion (recovery) except at the  
145 marginal part (Figs. 3 and 4). These grains seldom preserve micro-fractures within them. The IQ,  
146 IPF and KAM maps illustrate low angle grain boundaries within the parent grains (Figs. 3A-C

147 and 4A-C). The texture-component maps (Figs. 3D and 4D) were prepared by considering  
148 orientations ranging within  $30^\circ$  from the orientation of the parent grain measured at the center.  
149 These maps reveal that the edges of the parent grains are represented by subgrains. The  
150 recrystallized grains are little larger than the subgrains. They are characterized by  $120^\circ$  triple  
151 junction boundaries and display both daughter and neighbor-daughter dispositions (Halfpenny et  
152 al., 2006; Fig. 4) with comparable size range. The misorientation angle data measured from the  
153 central part of the parent grains to their edge reveal a maximum deviation of about  $10^\circ$  (Figs. 3E  
154 and 4E). The profiles show distinct plateaus in some subgrains but also continuous lattice  
155 bending.

156 The chromitite samples collected from the middle horizon (BL-SII) are more deformed  
157 compared to the KPT5 samples; also correspond to Regime 1. The shape of the precursor  
158 porphyroclastic grains is slightly elongated and the aggregate of smaller grains appears like  
159 ribbon. The outer margin of individual precursor grain shows highest concentration of  
160 substructures of similar size range, which gradually diminishes towards the inner part (Figs. 5  
161 and 6). The parent grains are internally strained with development of low angle misorientations  
162 within them (Figs. 5A, B and 6A, B). They show an overall increase in misorientation from their  
163 centres to the rims (Figs. 5D, E and 6D, E). The recrystallized grains are relatively larger,  
164 compared to those observed in KPT5 and have internal misorientations less than  $1^\circ$  (Fig. 5E,  
165 inset). Here too the boundaries between the substructures are commonly straight and form  $120^\circ$   
166 triple junctions (Fig. 5C, arrowheads). The recrystallized grains are bounded partly by high-angle  
167 and partly by subgrain/intermediate grain boundaries. All these substructures commonly  
168 surround the relict of the precursor grain (parent), giving rise to typical core-mantle structure.  
169 Following the nomenclature by Halfpenny et al. (2006) the neighbor-daughters are mostly

170 subgrains and/or intermediate grains and the daughters are new recrystallized grains. Further, the  
171 daughters and the neighbor-daughters have comparable size range. Another set of new grains  
172 with very high-angle grain boundaries ( $>15^\circ$ ) begin to form next in the sequence in this regime  
173 near the rims of the parent grains i.e., the regions of high strain (Fig. 6A, arrowheads). The  
174 regions of high strain are marked by high crystal lattice bending as evident in KAM map (Fig.  
175 6C). These grains are typical in the sense that they occur within the parent grains not similar to  
176 those of daughters and are inclusion-free. Part of the grain boundaries of these grains are straight  
177 (idioblastic) and other sections are serrated. Similar inclusion-free recrystallized grains of  
178 chromite were reported earlier from the Fiskenaesset deposit of West Greenland (Ghisler, 1976),  
179 Oman ophiolite complex (Christiansen, 1985) and recently from Luobusa ophiolite (Satsukawa  
180 et al., 2015b).

## 181 **Regime 2**

182 The chromitite seams at the bottom horizon (CPT6) are intensely deformed corresponding  
183 to Regime 2 (Figs. 7 and 8). The relict precursor grains are mostly occupied by subgrains  
184 whereas, the peripheral parts are decorated by dynamically recrystallized chromite grains of  
185 smaller grain size (Figs. 7A, B and 8A, B). The KAM maps (Figs. 7C and 8C) also support the  
186 observation that the parent grains are relatively more deformed compared to those of KPT5 and  
187 BL-SII samples. The misorientation data from core to the grain boundaries show a gradual  
188 increase, however with sudden jumps (Figs. 7F and 8D). The most interesting observation in  
189 these samples is abundance of relatively large strain-free faceted grains (Figs. 7 and 8). These  
190 large idioblastic and faceted (Fig. 7 D, E) grains are different from the grains with significant  
191 internal crystal bending (e.g. high KAM values) and are bounded by both straight and serrated  
192 grain boundaries. The misorientation data across these large grains reveal maximum

193 misorientation deviation less than  $1^\circ$  (Figs. 7E inset and 8E). However, there are occasional  
194 presence of feeble substructures within the large grains (Fig. 8F).

195 A compositional distinction at this regime between the large idioblastic crystals and the  
196 remains of the precursor grain is documented earlier (Ghosh and Konar, 2012). This distinction  
197 is evident from the tonal difference in the high contrast BSE image (Fig. 9). In terms of  
198 elemental distribution these new large grains contain less Cr and more Al in comparison to the  
199 parent grains which is also reflected in their Cr# [= Cr/(Cr + Al) atomic ratio] values whereas,  
200 the correlation with Mg and Fe is not so apparent (Fig. 9).

## 201 **DISCUSSION**

202 The microstructures in Sittampundi chromites revealed distinct domains with characteristic  
203 features. The changing microstructural pattern as evident from the characteristic features  
204 corresponding to two regimes might be attributed to deformation and temperature gradient as  
205 well. Given the scale of the field area and previous studies there is no strong evidence to justify  
206 that these two factors were mutually exclusive, however, there could be dominance of one over  
207 another in respective regions, the reason of which is still unknown. The deformation event might  
208 have followed by heating or some fluid influx at least in the local scale.

### 209 **Origin of Regime 1**

210 The Regime 1 is deformation related and the dominant strain accommodating mechanism  
211 commenced with recovery-accommodated dislocation creep (Tullis and Yund, 1985). Because of  
212 increasing ease of diffusion in the crystal lattice in this regime and owing to faster mobility of  
213 newly formed dislocations, the plastic deformation commenced with the onset of recovery that  
214 eventually lead to subgrain rotation recrystallization in presence of deformation (Figs. 3 - 6). The

215 primary evidence for subgrain rotation recrystallization is core and mantle structure, where the  
216 cores of precursor grains pass out transitionally into the mantle with increasing subgrain  
217 development and misorientation (Halfpenny et al., 2006; 2012), which is the case for  
218 Sittampundi chromites in Regime 1. Additionally, the increasing misorientation angles from the  
219 core to the boundary of the parent grains justify the mechanism of subgrain rotation  
220 recrystallization in this domain. The presence of distinct plateaus with continuous lattice bending  
221 in the profiles speaks strongly in favour of ongoing progressive recrystallization and crystal  
222 plasticity. This recrystallization process is an extension of the recovery where the driving force is  
223 a reduction of the internal strain energy of the deforming aggregate. Dislocation climb perhaps  
224 dominated over glide alike garnet deformation in this regime (Prior et al., 2000). In terms of  
225 kinetics, Regime 1 was purely rotational and temporally continual, persistent until the end of  
226 deformation (Drury and Urai, 1990).

## 227 **Origin of Regime 2**

228 From the general lack of substructures in large strain-free grains the Regime 2 appears to  
229 be post-deformational and is dominantly temperature controlled. These relatively large crystals  
230 are often bounded by straight grain boundaries indicating lower internal free energy prevailing  
231 along those straight growth-lines and thus can be termed qualitatively as faceted grain  
232 boundaries (Gottstein and Shvindlerman, 2010). A quantitative analysis of two such grains (Fig.  
233 7 D, E) also shows the face parallel grain growth. The microstructural features in this regime  
234 closely resemble what is known in the literature as ‘abnormal or exaggerated grain growth’  
235 (Kang, 2005; Omori et al., 2013), also referred to as ‘discontinuous grain growth’ (Stockhert and  
236 Duyster, 1999), commonly related to annealing of pre-deformed grains. In this regime rotational  
237 and migration related recrystallization process operated simultaneously. Regime 2 is

238 discontinuous, in contrary to the earlier regime. This discontinuous nature of the migration  
239 related recrystallization produced large strain-free regions in the microstructure which was likely  
240 favored by solute escape from the high-angle migration front. The growth morphology of the  
241 boundaries of new grains was controlled by interfacial energy of cubic crystals as evident from  
242 their polygonal habit. However, the occasional presence of feeble substructures within the large  
243 faceted grains (Fig. 8) either signifies a continuum of their growth at the very end stage of  
244 deformation or it demonstrates growth related defects (Piazolo et al., 2005). As a whole the  
245 Regime 2 characterizes microstructural features of static annealing conditions of already  
246 deformed grains. During this stage the stored free energy of such system is reduced through  
247 vacancy diffusion and also grain growth which is facilitated by grain boundary migration (Baker,  
248 2000). In general, grain boundary migration is driven by curvature which is related to the  
249 requirement to reduce total boundary surface area, and also strain energy which is related to the  
250 difference in unbound dislocation density either side of a boundary (Piazolo et al., 2006). Since,  
251 grain growth driven by reduction of grain boundary energy becomes the dominant process only  
252 when all grains are relatively dislocation-free (Humphreys and Hatherly, 1995; Urai et al., 1986),  
253 the driving force in Regime 2 for Sittampundi chromites originated partly due to a difference in  
254 the dislocation density across the grain boundary (Hirth and Tullis 1992). However, in solid  
255 solution minerals, grain boundary migration is not only driven by internal strain energy, but also  
256 by chemical driving potentials in terms of compositional changes of minerals associated with  
257 dynamic recrystallization (Kirby and Kronenberg, 1984; Urai et al., 1986; Berger and Stunitz,  
258 1996; Passchier and Trouw, 2005). Since there is a compositional difference between crystals of  
259 the same phase on either side of a migrating boundary chemical free energy might have played a  
260 significant role in considering the driving force in this regime. This process is referred to as

261 diffusion-induced grain boundary migration (DIGM) (Hay and Evans, 1987). The kinetics of  
262 migration depends upon the magnitude of the driving force and the boundary mobility, which in  
263 turn is function of boundary structure, impurity effects and fluid effects (Urai, 1983).

#### 264 **Origin of strain-free grains**

265 The formation of strain-free new grains might occur in deformed minerals by subgrain  
266 growth in regions of high dislocation density. Such development has been reported from natural  
267 rocksalt samples (Desbois, 2010) and also experimentally revealed in case of feldspar (White,  
268 1975), pyrite (Cox et al., 1981), olivine (Toriumi and Karato, 1985) and also in synthetic rocksalt  
269 (Piazolo et al., 2006). Recrystallization in all these experiments involved a progressive stage of  
270 new high-angle grain boundary formation by subgrain rotation, followed by a stage of new grain  
271 development along newly-formed grain boundaries. However, because of the strain-free grains in  
272 our samples do not always occur in subgrain-rich domains and the general lack of evidences of  
273 dominant subgrain growth, classical nucleation recrystallization may be considered as a possible  
274 alternative where a cluster of atoms spontaneously takes on a new orientation owing to the action  
275 of thermally activated fluctuations. It is more likely because chemical driving forces were also  
276 involved (Hay and Evans, 1987; Etheridge and Hobbs, 1974).

#### 277 **Compositional heterogeneity**

278 Deformation might increase the rate of compositional exchange between minerals (Yund  
279 and Tullis, 1991). Stress induced kinetic demixing of solid solution minerals is reported for  
280 feldspar (Yund and Tullis, 1991), amphibole (Stunitz, 1998), pyroxene (Stunitz, 1998), olivine  
281 (Hirth and Kohlstedt, 1995), garnet (Wang and Ji, 2000; Storey and Prior, 2005; Bestmann et al.,  
282 2008; Smit et al., 2011) and chromite (Ozawa, 1989; Sammis, 1989). We describe the change in

283 composition across the high-angle grain boundaries of the faceted strain-free new grains in our  
284 samples in terms of chemical diffusion which is a temperature sensitive process. These grains  
285 after their nucleation at the end of Regime 1 grew by outward grain boundary migration all  
286 through the next regime, which was likely to be a higher temperature event. Volume diffusion  
287 (Nabarro-Herring creep) is more effective for relatively finer grain size because of ease of  
288 travelling shorter distances. Considering the relatively larger sizes of the faceted strain-free  
289 grains in our samples we propose the model of grain boundary diffusion (Coble creep) to explain  
290 the elemental reequilibration (Fig. 10). During recrystallization the high-angle grain boundaries  
291 sweep through strained grains to remove dislocations and possibly subgrain boundaries  
292 (Passchier and Trouw, 2005; Hay and Evans, 1987). It is equally applicable even for  
293 temperature-induced grain boundary migration in static recrystallization. This movement of high-  
294 angle grain boundaries through strained grains provides high diffusivity paths for the rapid  
295 exchange of components, like Al - Cr during deformation and this might have produced  
296 compositional heterogeneity in the recrystallized grains. Interestingly, the relatively small  
297 recrystallized grains which were produced by progressive subgrain rotation during recovery-  
298 accommodated dislocation do not show compositional reequilibration because they were not  
299 swept by high-angle grain boundaries (Stunitz, 1998).

300 Thus, high mobility of preexisting dislocations during annealing in a later heating event  
301 might have promoted grain boundary migration and thereby facilitating diffusion, which in turn  
302 induced grain boundary migration. This perhaps defined a cause and effect loop in this process  
303 and once boundary migration initiated because of some other means, like contrast in dislocation  
304 density across the boundary, it became self-driven in the rest of the deformation.

## 305 **IMPLICATIONS**

306       Although of low average modal abundance, chromite is a significant mineral phase  
307 considering the chromium reservoir of the bulk earth, the upper mantle in particular. The  
308 identification and characterization of deformation mechanisms in this mineral are of interest  
309 because these mechanisms govern the rheological response of chromite dominated rocks (viz.  
310 chromitite) (Frost and Ashby, 1982). For example, deformation via dynamic recrystallization  
311 will result in strain softening (Poirier, 1985). The composition of chromite is widely used as i) a  
312 petrogenetic and geotectonic indicator (Dick and Bullen, 1984), ii) a geospeedometer (Ozawa,  
313 1985), iii) a geothermometer (Fabries, 1979) and also iv) an oxygen geobarometer (Wood and  
314 Virgo, 1989). While subsolidus and/or metamorphic reequilibration is taken into account in  
315 many instances, the core compositions of large chromite grains from massive chromitite are  
316 considered unaffected because of the notion that massive chromitite minimizes the effects of  
317 reequilibration with adjacent silicates (Suita and Streider, 1996). Our study on Sittampundi  
318 massive chromitites demonstrates how deformation may induce intra-phase compositional  
319 reequilibration in chromite, producing compositional heterogeneity throughout. This constrains  
320 on extensive use of chromite composition in many petrologic studies without much adherence to  
321 microstructural consideration which in most of the cases are lacking. This lacuna is mainly due  
322 to the fact that chromite is isotropic and predominantly opaque, posing difficulties in recognizing  
323 the substructures during routine microscopic studies. We emphasize the importance of a  
324 reconnaissance microstructural study using orientation contrast imaging before applying its  
325 composition for petrologic purposes. Further, annealing microstructures from geological samples  
326 are not commonly reported. This study on Sittampundi chromites stands as a natural example of  
327 recognizing behavior of this mineral during deformation and also in post-deformational heating

328 event, not yet documented in the literature. Proper identification of annealed microstructures in  
329 massive chromitite is immensely important because extreme development of the faceted new  
330 grains in association with other recrystallized grains with  $120^\circ$  triple junctions may give rise to a  
331 pseudo adcumulate texture, common to many early magmatic rocks.

332 Summarizing, this study provides an account of plastic deformation mechanism of chromite  
333 from natural samples that substantially enhances our understanding of the physiochemical  
334 behavior of this mineral at the crust-mantle boundary. Whilst this study was unable to set the  
335 limits of natural variables at the transitions of successive microstructural regimes it leaves a  
336 scope for further experimental investigations to constrain these parameters well in preparing the  
337 deformation mechanism map for this mineral.

#### 338 **ACKNOWLEDGEMENTS**

339 The authors thank Zoja Vukmanovic and one anonymous reviewer for their insightful  
340 comments and suggestions that improved the quality of the text and figures. Editorial handling  
341 and constructive criticism by Sandra Piazzolo is greatly acknowledged. Shashank Shekhar is  
342 acknowledged for his critical reading of the manuscript. Karsten Kunze from Scientific Center  
343 for Optical and Electron Microscopy (ETZ Zurich) assisted in obtaining and analyzing the EBSD  
344 data. B.G. acknowledges the financial support received from UGC-DRS Phase-II, 2013-18,  
345 Government of India and JSPS Invitation Fellowship (FY 2015). SM thanks the infrastructural  
346 facilities provided by IIT Kanpur.

347 **REFERENCES CITED**

- 348 Baker, I., (2000) Recovery, recrystallization and grain growth in ordered alloys. *Intermetallics*, 8,  
349 1183–1196.
- 350 Barrie, C.D., Boyle, A.P., Cook, N.J., and Prior, D.J., (2010) Deformation mechanisms and  
351 textural changes in pyrite (FeS<sub>2</sub>) in the massive sulphide deposits of the Norwegian  
352 Caledonides. *Tectonophysics*, 283, 269–286.
- 353 Berger, A., and Stunitz, H., (1996) Deformation mechanisms and reactions of hornblende:  
354 examples from the Bergell tonalite (Central Alps). *Tectonophysics*, 257, 149-174.
- 355 Bestmann, M., Habler, G., Heidelbach, F., and Thöni, M., (2008) Dynamic recrystallization of  
356 garnet and related diffusion processes. *Journal of Structural Geology*, 30, 777–790.
- 357 Bhaskar Rao, Y.J., Chetty, T.R.K., Janardhan, A.S., and Gopalan, K., (1996) Sm–Nd and Rb–Sr  
358 ages and P–T history of the Archean Sittampundi and Bhavani layered meta-anorthosite  
359 complexes in Cauvery shear zone, South India: evidence for Neoproterozoic reworking of  
360 Archean crust. *Contributions to Mineralogy and Petrology*, 125, 237–250.
- 361 Christiansen, F.G., (1985) Deformation fabric and microstructures in ophiolitic chromitites and  
362 host ultramafics, Sultanate of Oman. *Geologische Rundschau*, 74, 61–76.
- 363 Christiansen, F.G., (1986) Deformation of chromite: S.E.M. investigations. *Tectonophysics*, 121,  
364 175-196.
- 365 Cox, S.F., Etheridge, M.A., and Hobbs, B.E., (1981) The experimental ductile deformation of  
366 polycrystalline and single crystal pyrite. *Economic Geology*, 76, 2105-2117.
- 367 Desbois, G., Zavada, P., Schleder, Z., and Urai, J.L., (2010) Deformation and recrystallization  
368 mechanisms in actively extruding salt fountain: Microstructural evidence for a switch in

- 369 deformation mechanisms with increased availability of meteoric water and decreased  
370 grain size (Qum Kuh, central Iran). *Journal of Structural Geology*, 32, 580-594.
- 371 Dick, H.J.B., and Bullen, T., (1984) Chromian spinel as a petrogenetic indicator in abyssal and  
372 alpine-type peridotites and spatially associated lavas. *Contributions to Mineralogy and  
373 Petrology*, 86, 54–76.
- 374 Drury, M.R., and Urai, J.L., (1990) Deformation-related recrystallization processes.  
375 *Tectonophysics*, 172, 235-253.
- 376 Etheridge, M.A., and Hobbs, B.E., (1974) Chemical and deformational controls of  
377 recrystallization of mica. *Contributions to Mineralogy and Petrology*, 43, 111-124.
- 378 Fabries, J., (1979) Spinel-olivine geothermometry in peridotite from ultramafic complex.  
379 *Contributions to Mineralogy and Petrology*, 69, 329-336.
- 380 Frost, H.J., and Ashby, M.F., (1982) Deformation-mechanism Maps. *The Plasticity and Creep of  
381 Metals and Ceramics*. Pergamon Press, New York.
- 382 Ghisler, M., (1970) Pre-metamorphic folded chromite deposits of stratiform type in the early  
383 Precambrian of West Greenland. *Mineralium Deposita*, 5, 223–236.
- 384 Ghisler, M., (1976) The geology, mineralogy and geochemistry of the pre-orogenic Archaean  
385 stratiform chromite deposits at Fiskenaasset, West Greenland. *Monograph Series.  
386 Mineralium Deposita*, 14, 156.
- 387 Ghosh, B., and Konar, R., (2012) Textural developments in chromite deforming under eclogite-  
388 facies conditions from the Neoproterozoic Sittampundi anorthosite complex, southern India.  
389 *Geological Journal*, 47, 253-262.

- 390 Ghosh, B., Ray, J., and Morishita, T., (2014) Grain-scale plastic deformation of chromite from  
391 podiform chromitite of the Naga–Manipur ophiolite belt, India.: Implication to mantle  
392 dynamics. *Ore Geology Reviews*, 56, 199–208.
- 393 Gottstein, G., and Shvindlerman, L.S. (2010) *Grain Boundary Migration in Metals:*  
394 *Thermodynamics, Kinetics, Applications*, 2nd ed., CRC Press, Boca Raton, FL.
- 395 Halfpenny, A., Prior, D.J., and Wheeler, J., (2006) Analysis of dynamic recrystallization and  
396 nucleation in a quartzite mylonite. *Tectonophysics*, 427, 3-14.
- 397 Halfpenny, A., Prior, D.J., and Wheeler, J., (2012) Electron backscatter diffraction analysis to  
398 determine the mechanisms that operated during dynamic recrystallisation of quartz-rich  
399 rocks. *Journal of Structural Geology*, 36, 2-15.
- 400 Hay, R.S., and Evans, B., (1987) Chemically induced grain boundary migration in calcite:  
401 temperature dependence, phenomenology, and possible applications to geologic systems.  
402 *Contributions to Mineralogy and Petrology*, 97, 127-141.
- 403 Hirth, G., and Kohlstedt, D.L., (1995) Experimental constraints on the dynamics of the partially  
404 molten upper mantle: Deformation in the diffusion creep regime. *Journal of Geophysical*  
405 *Research*, 100(B2), 1981–2001.
- 406 Hirth, G., and Tullis, J., (1992) Dislocation creep regimes in quartz aggregates. *Journal of*  
407 *Structural Geology*, 14, 145-159.
- 408 Humphreys, F.J., and Hatherly, M., (1995) *Recrystallization and related annealing phenomena.*  
409 Oxford, Pergamon.
- 410 Kang, S.J.L., (2005). *Sintering: densification, grain growth, and microstructure.* Elsevier,  
411 Butterworth-Heinemann.

- 412 Kirby, S.H., and Kronenberg, A.K., (1984) Diffusion induced grain boundary motion (DIGM)  
413 and diffusion induced recrystallization (DIR): applications to the rheology of rocks. *Eos*,  
414 *Transactions American Geophysical Union*, 65, 1098.
- 415 Meissner, B., Deters, P., Srikantappa, C., and Köhler, H., (2002) Geochronological evolution of  
416 the Moyar, Bhavani and Palghat shear zones of southern India: implications for East  
417 Gondwana correlations. *Precambrian Research*, 114, 149–175.
- 418 Naidu, P.R.J., (1963) A layered complex in Sittampundi, Madras state, India. *Mineralogical*  
419 *Society of America Special Paper* 1, 116–123.
- 420 Omori, T., Kusama, T., Kawata, S., Ohnuma, I., Sutou, Y., Araki, Y., Ishida, K., and Kainuma,  
421 R., (2013) Abnormal Grain Growth Induced by Cyclic Heat Treatment. *Science*, 341,  
422 1500-1502.
- 423 Ozawa, K., (1985) Olivine-spinel geospeedometry: Analysis of diffusion-controlled Mg-Fe<sup>2+</sup>  
424 exchange. *Geochimica et Cosmochimica Acta*, 48, 2597-2611.
- 425 Ozawa, K., (1989) Stress-induced Al–Cr zoning of spinel in deformed peridotites. *Nature*, 338,  
426 141– 144.
- 427 Passchier, C.W., and Trouw, R.A.J., (2005) *Microtectonics*, 2nd edn. Springer, Berlin.
- 428 Piazzolo, S., Bestmann, M., Prior, D.J., and Spiers, C.J., (2006) Temperature dependent grain  
429 boundary migration in deformed-then-annealed material: Observations from  
430 experimentally deformed synthetic rocksalt. *Tectonophysics*, 427, 55-71.
- 431 Piazzolo, S., Prior, D.J., and Holness, M.D., (2005) The use of combined Cathodoluminescence  
432 and EBSD analysis: A case study investigating grain boundary migration mechanisms in  
433 quartz. *Journal of Microscopy*, 217, 152-161.

- 434 Prior, D.J., Wheeler, J., Brenker, F.E., Harte, B., and Matthews, M., (2000) Crystal plasticity of  
435 natural garnet: New microstructural evidence. *Geology*, 28, 1003-1006.
- 436 Poirier, J-P., (1985) *Creep of Crystals*. Cambridge University Press, Cambridge.
- 437 Ramadurai, S., Sankaran, M., Selvan, T.A., and Windley, B.F., (1975) The stratigraphy and  
438 structure of the Sittampundi complex, Tamil Nadu. *Journal of the Geological Society of*  
439 *India*, 16, 409–414.
- 440 Sajeev, K., Windley, B.F., Connolly, J.A.D., and Kon, Y., (2009) Retrogressed eclogite (20 kbar,  
441 1020°C) from the Neoproterozoic Palghat–Cauvery suture zone, southern India.  
442 *Precambrian Research*, 171, 23–36.
- 443 Sammis, C.G., (1989) Stress-induced segregation. *Nature*, 338, 114-115.
- 444 Santosh, M., and Kusky, T., (2010) Origin of paired high pressure–ultrahigh temperature  
445 orogens: a ridge subduction and slab window model. *Terra Nova*, 22, 35-42.
- 446 Santosh, M., Maruyama, S., and Sato, K., (2009) Anatomy of a Cambrian suture in Gondwana:  
447 Pacific-type orogeny in southern India? *Gondwana Research*, 16, 321-341.
- 448 Santosh, M., and Sajeev, K., (2006) Anticlockwise evolution of ultrahigh-temperature granulites  
449 within continental collision zone in southern India. *Lithos*, 92, 447-464.
- 450 Satsukawa, T., Piazzolo, S., González-Jiménez, J.M., Colás, V., Griffin, W.L., O'Reilly, S.Y.,  
451 Gervilla, F., Fanlo, I., and Kerestedjian, T N., (2015a) Fluid-present deformation aids  
452 chemical modification of chromite: Insights from chromites from Golyamo Kamenyane,  
453 SE Bulgaria. *Lithos*, 228, 78-89.
- 454 Satsukawa T., Griffin, W.L., Piazzolo, S. and O'Reilly, S.Y., (2015b) Messengers from the  
455 deep:Fossil wadsleyite-chromite microstructures from the Mantle Transition Zone.  
456 *Scientific Reports*, 5, doi:10.1038/srep16484.

- 457 Smit, M.A., Scherer, E.E., John, T., and Janssen, A., (2011) Creep of garnet in eclogite:  
458 Mechanisms and implications. *Earth and Planetary Science Letters*, 311, 411-419.
- 459 Stöckhert, B., and Duyster, J., (1999) Discontinuous grain growth in recrystallised vein quartz-  
460 implications for grain boundary structure, grain boundary mobility, crystallographic  
461 preferred orientation, and stress history. *Journal of Structural Geology*, 21, 1477-1490.
- 462 Storey, C.D., and Prior, D.J., (2005) Plastic deformation and recrystallization of garnet: a  
463 mechanism to facilitate diffusion creep. *Journal of Petrology*, 46, 2593-2613.
- 464 Stunitz, H., (1998) Syndeformational recrystallization – dynamic or compositionally induced?  
465 *Contributions to Mineralogy and Petrology*, 131, 219-236.
- 466 Subramaniam, A.P., (1956) Mineralogy and petrology of the Sittampundi complex, Salem  
467 district, Madras State, India. *Bulletin Geological Society of America*, 67, 317–390.
- 468 Suita, M.T., and Streider, A.J., (1996) Cr-spinels from Brazilian mafic-ultramafic complexes:  
469 metamorphic modifications. *International Geology Review*, 38, 245–267.
- 470 Toriumi, M., and Karato, S., (1985) Preferred orientation development of dynamically  
471 recrystallized olivine during high temperature creep. *Journal of Geology*, 93, 407-417.
- 472 Tullis, J., and Yund, R.A., (1985) Dynamic recrystallization of feldspar: a mechanism for ductile  
473 shear zone formation. *Geology*, 13, 238-241.
- 474 Urai, J.L., (1983) Water assisted dynamic recrystallization and weakening in polycrystalline  
475 bischofite. *Tectonophysics*, 96, 125-157.
- 476 Urai, J.L., Means, W.D., and Lister, G.S., (1986) Dynamic recrystallization of minerals, in,  
477 Hobbs, B.E., and Heard, H.C., eds., *Mineral and rock deformation: laboratory studies*.  
478 *American Geophysical Union Monograph*, 36, 161-199.

- 479 Vukmanovic, Z., Barnes, S.J., Reddy S.M., Godel, B., and Fiorentini, M.L., (2013) Morphology  
480 and microstructure of chromite crystals in chromitites from the Merensky Reef  
481 (Bushveld Complex, South Africa). *Contributions to Mineralogy and Petrology*, 165,  
482 1031-1050.
- 483 Wang, Z., and Ji, S., (2000) Diffusion creep of fine-grained garnetite: implications for the flow  
484 strength of subducting slabs. *Geophysical Research Letters*, 27, 2333-2336.
- 485 White, S.H., (1975) Tectonic deformation and recrystallization of oligoclase. *Contributions to*  
486 *Mineralogy and Petrology*, 50, 287-304.
- 487 Wood, B.J., and Virgo, D., (1989) Upper mantle oxidation state: ferric iron contents of lherzolite  
488 spinels by  $^{57}\text{Fe}$  Mossbauer spectroscopy and resultant oxygen fugacities. *Geochimica et*  
489 *Cosmochimica Acta*, 53, 1277-1291.
- 490 Yund, R.A., and Tullis, J., (1991) Compositional changes of minerals associated with dynamic  
491 recrystallization. *Contributions to Mineralogy and Petrology*, 108, 346-355.
- 492

493 **Figure Captions**

494 **FIGURE 1.** (A) The generalized geological map of Sittampundi Layered Complex (modified  
495 from Subramaniam, 1956) showing disposition of various lithomembers. The inset map (after  
496 Santosh and Sajeev, 2006) shows tectonic framework of southern India. PCSZ: Palghat–Cauvery  
497 Suture Zone; CSZ: Chennamalai Shear Zone; ACSZ: Achankovil Shear Zone. (B) The exposures  
498 of the chromite seams in the field at three different locations (marked by different symbols in A)  
499 used in this study. Sample location KPT5, BL-SII and CPT6 occur stratigraphically in upper,  
500 middle and lower horizons, respectively.

501 **FIGURE 2.** A schematic representation of the sample processing and geometry for the EBSD  
502 analysis. (A) The foliation plane was set to A1-A2 plane and cut perpendicular to the A1 axis for  
503 observation on A2-A3 plane. (B) The sample (shaded area in A) then prepared for the EBSD  
504 analysis and placed in the SEM chamber for data collection keeping A1 axis projected towards  
505 the phosphor screen.

506 **FIGURE 3.** EBSD analysis for sample KPT5. Dark grey tones in these maps represent non-  
507 indexed areas dominated by amphibole. (A)-(C) Image quality (IQ), inverse pole figure (IPF),  
508 projected along the z direction, and kernel average misorientation (KAM) maps, respectively  
509 showing concentration of the deformation at the parent grain boundary. B and C also mark the  
510 subgrain, intermediate grain and recrystallized grain boundaries following the definition  
511 provided in the text. (D) The texture-component map considering orientations ranging within 30°  
512 from the orientation of the parent grain measured at the center. The orientations within 30° are  
513 coloured proving that the origin of the subgrains are from the parent grains. (E) Misorientation  
514 profiles showing the gradual change of misorientations relative to the first point (considering 0°

515 misorientation) of the profile. The misorientation values are added to the first point with the  
516 direction of transect. Individual profiles are highlighted by different color with reference to the  
517 profile lines shown by arrowheads in (A).

518 **FIGURE 4.** EBSD analysis for sample KPT5. The description of individual figures and  
519 illustrations (A-E) are similar to those given in Figure 3.

520 **FIGURE 5.** EBSD analysis for sample BL-SII. The description of individual figures and  
521 illustrations (A-E) are similar to those given in Figure 3. Note the development of new  
522 recrystallized (neighbor-daughter) grains along the boundaries of the parent grains. The KAM  
523 map (C) shows the new grains are strain free and form 120° triple junctions. Their internal  
524 misorientation angle is less than 1° (E, inset). In (D), five parent grains are indemnified (marked  
525 with 1-5) in the texture-component maps; coded with similar color effect (rainbow) performed in  
526 separate steps.

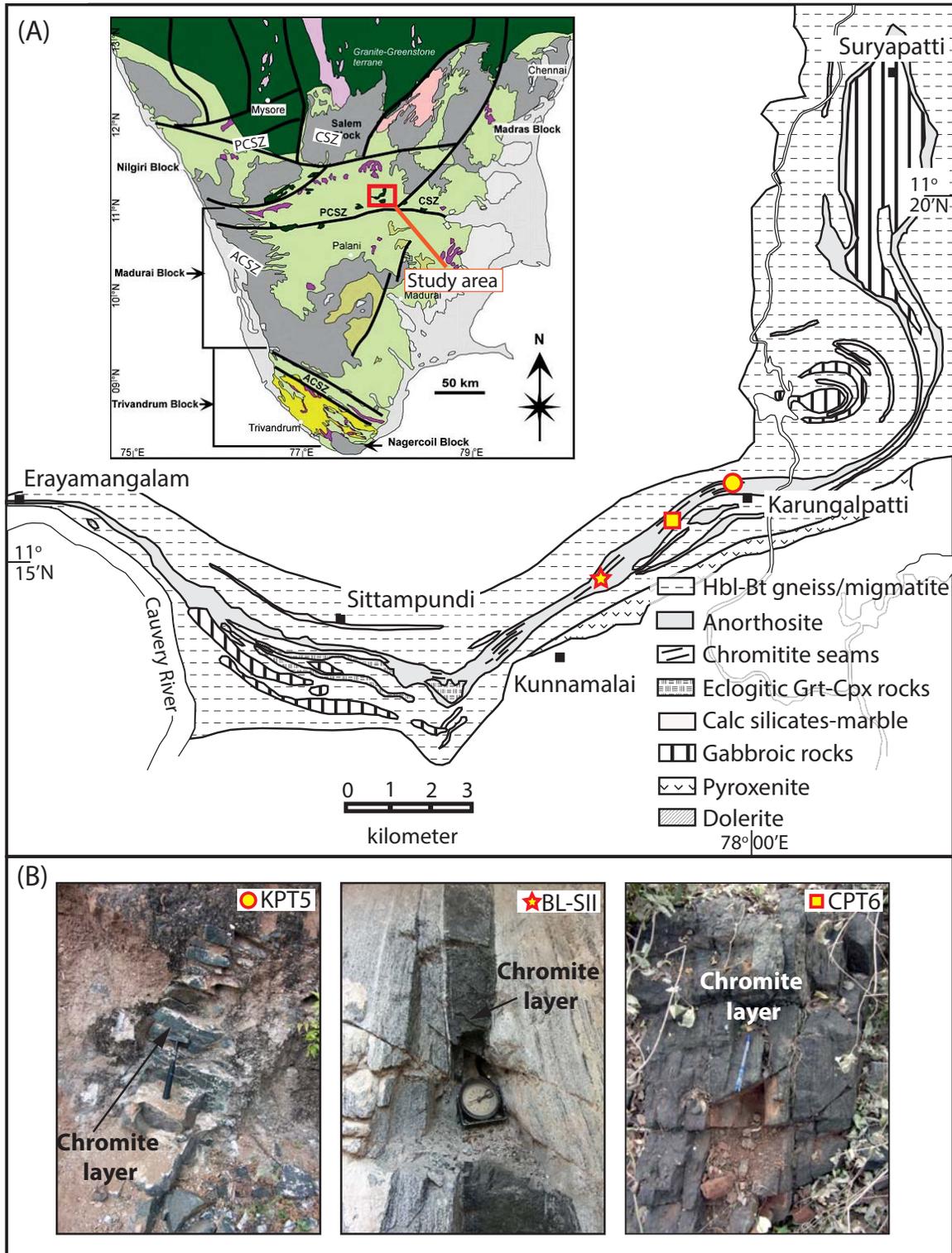
527 **FIGURE 6.** EBSD analysis for sample BL-SII. The description of individual figures and  
528 illustrations (A-E) are similar to those given in Figure 3. The growth initiation of strain-free  
529 grains at the edge of the parent grains are marked by white arrowheads. The misorientation  
530 angles also increased and the boundaries are marked by sharp jumps (E).

531 **FIGURE 7.** EBSD analysis for sample CPT6. The description of individual figures and  
532 illustrations (A-D and F) are similar to those given in Figure 3. The white arrowheads in B point  
533 to the new strain free “abnormal grain growths”. In D, two such crystals are marked with plane  
534 trace overlay showing the orientation of the crystal for {111} planes.

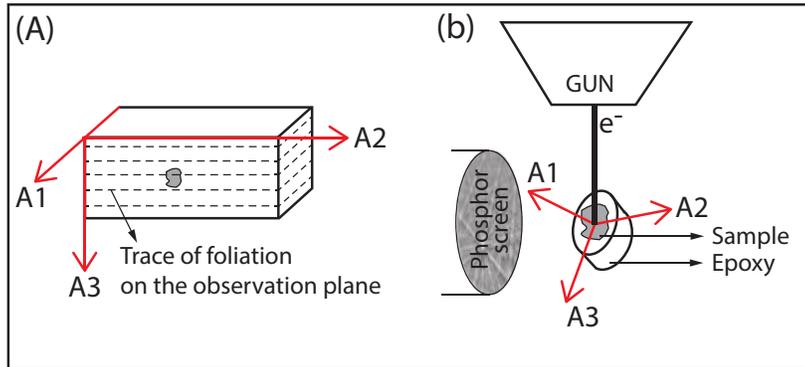
535 **FIGURE 8.** EBSD analysis for sample CPT6. The description of individual figures and  
536 illustrations (A-C) are similar to those given in Figure 3. The abnormal grain growth and intense  
537 deformation in the parent grain is prominent. The transects show a general trend of increasing  
538 misorientation angles from the core to edge of the parent grain (D), however, sharp jump of  
539 misorientation is common. Unlike the other abnormal grain growths, shown in Figure 7, one  
540 grain in this section shows weak deformation by showing the development of feeble sub-grain  
541 boundary (highlighted by dashed line in A and pointed by white arrowhead). This is further  
542 confirmed by the transect misorientation data shown in (E) and (F).

543 **FIGURE 9.** The high contrast BSE image (sample location CPT6) at the top represents overall  
544 compositional heterogeneity in terms of tonal difference. The boundaries of the recrystallized,  
545 strain-free new grains are shown by yellow dashed lines. Note, the Cr# value is less in the new  
546 grains compared to the parent grain. The four plates at the bottom show compositional maps (X-  
547 ray) of the same sample. Note, the distribution of Cr and Al has a variation across the region,  
548 while Mg and Fe does not show any spatial change.

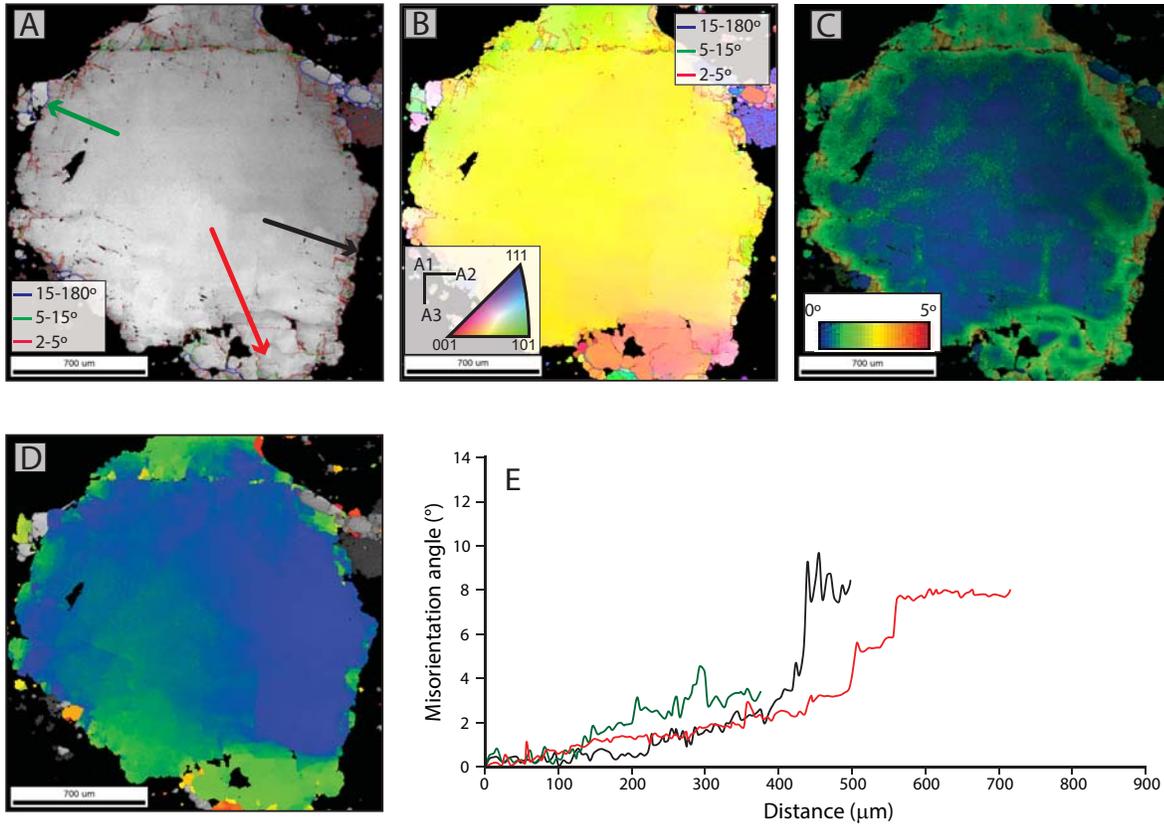
549 **FIGURE 10.** A schematic illustrations showing chemical diffusion at very high-angle grain  
550 boundary of one faceted new grain. This grain grows at the expense of subgrains by outward  
551 migration of its high-angle grain boundaries. At the left illustration, I, II, III, IV are representing  
552 parent-grain, subgrain, neighbor-daughter and abnormal grain growths, respectively. At the left,  
553 HAGB and LAGB are indicating high-angle and low-angle grain boundaries, respectively.



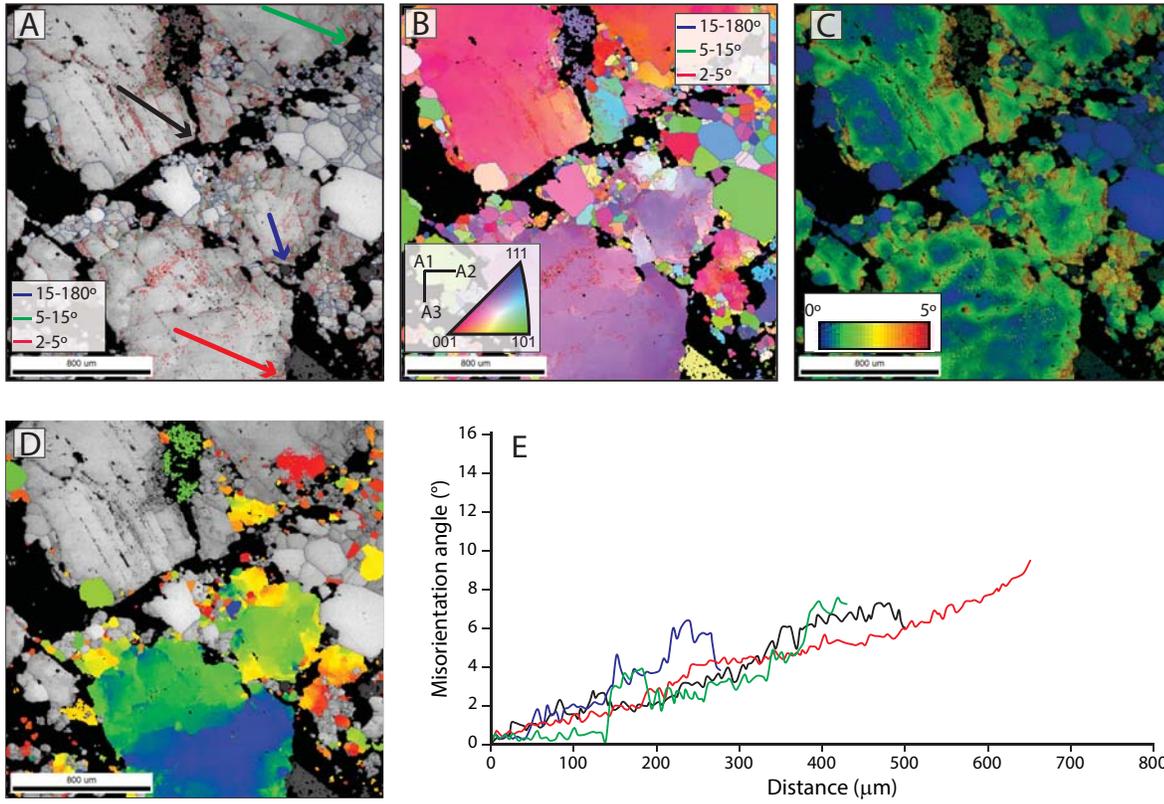
↑ Figure 1



↑ Figure 2



↑  
Figure 3



↑  
Figure 4

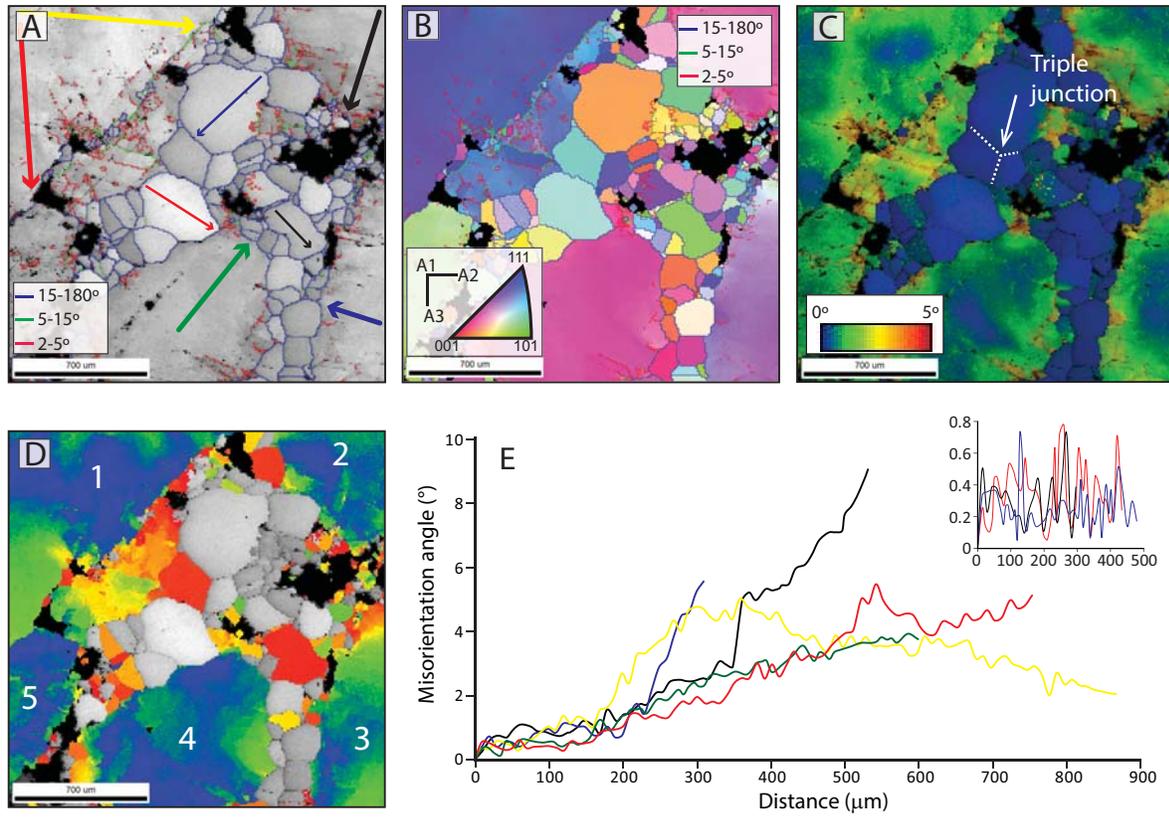
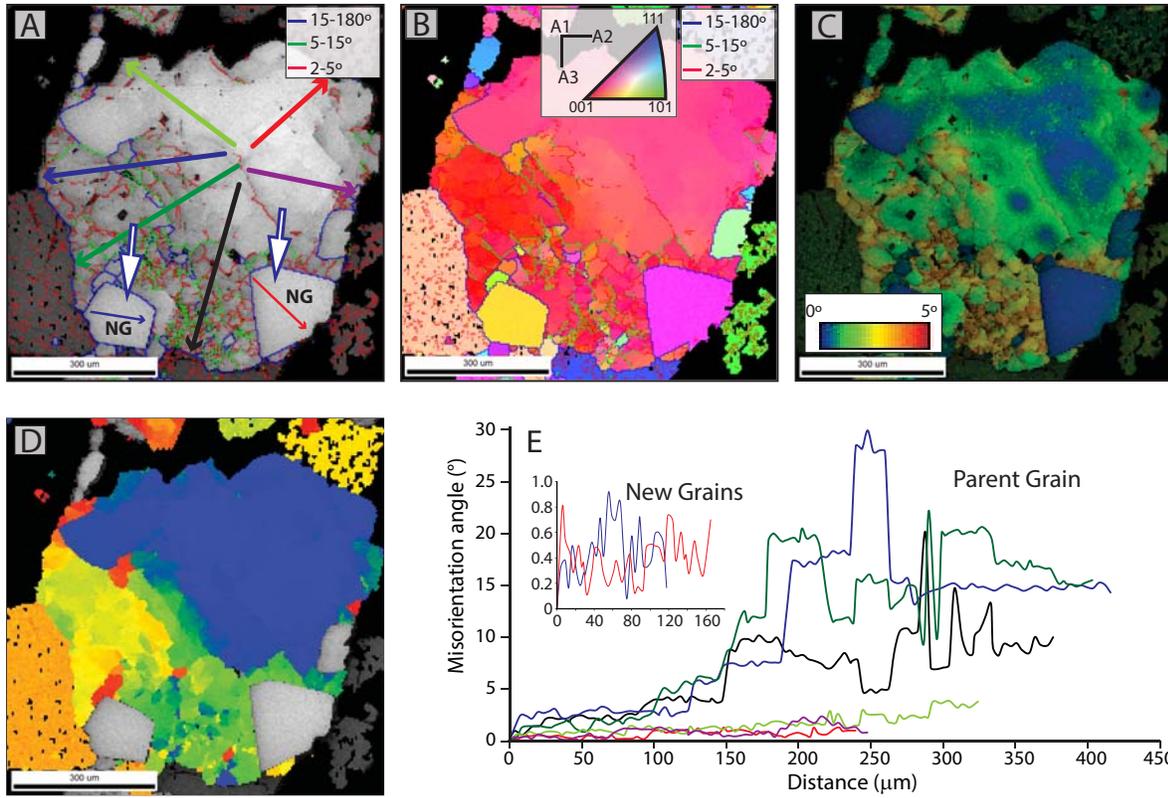
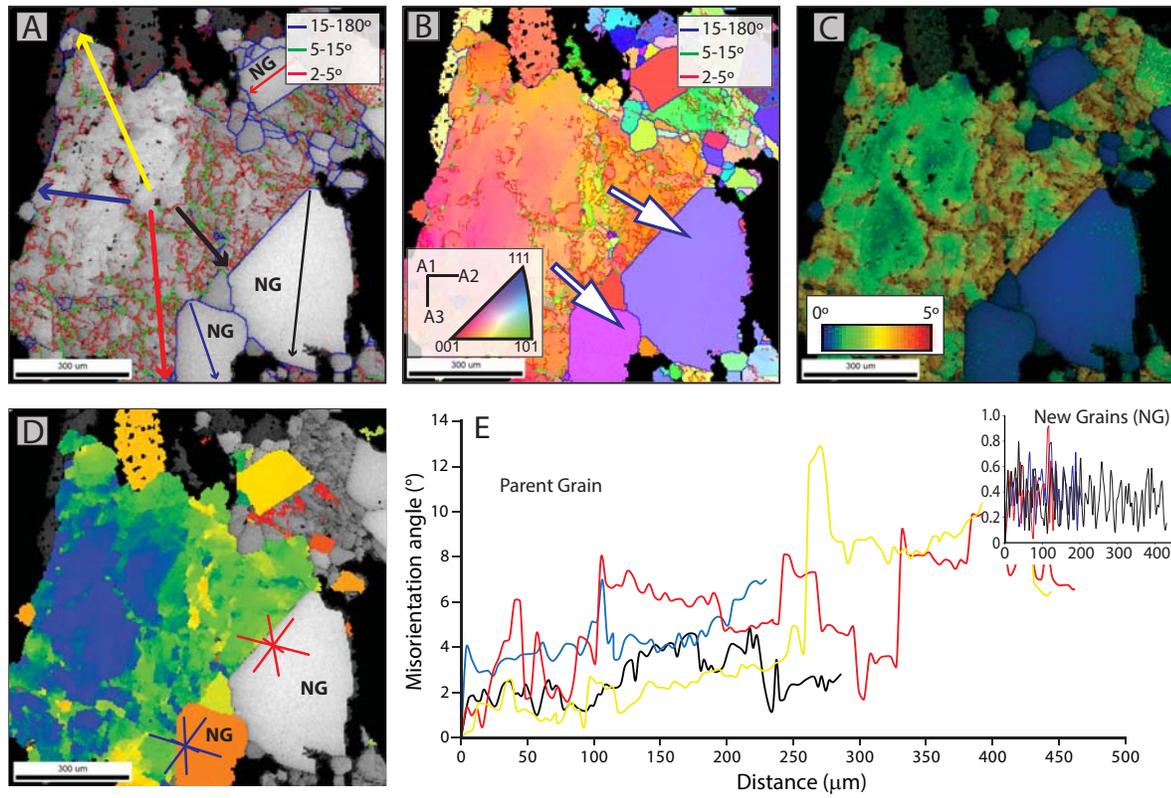


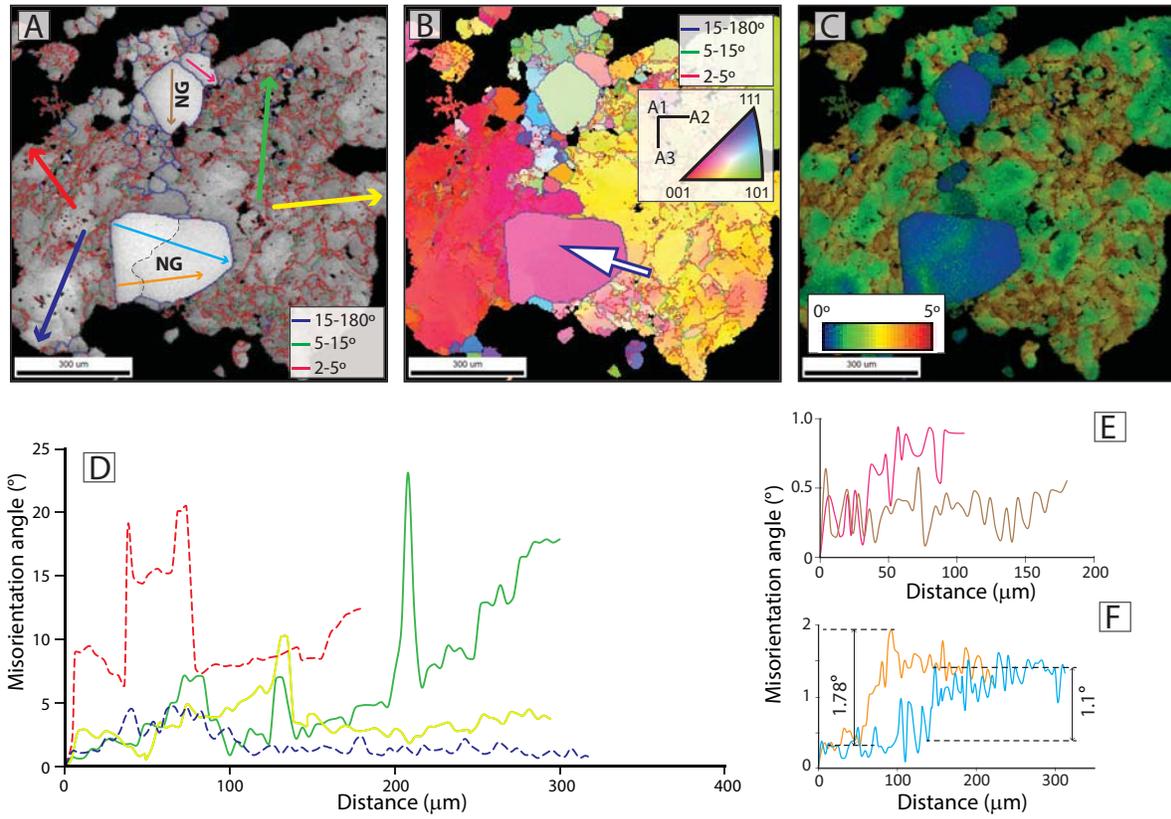
Figure 5



↑  
Figure 6



↑  
Figure 7



↑  
Figure 8

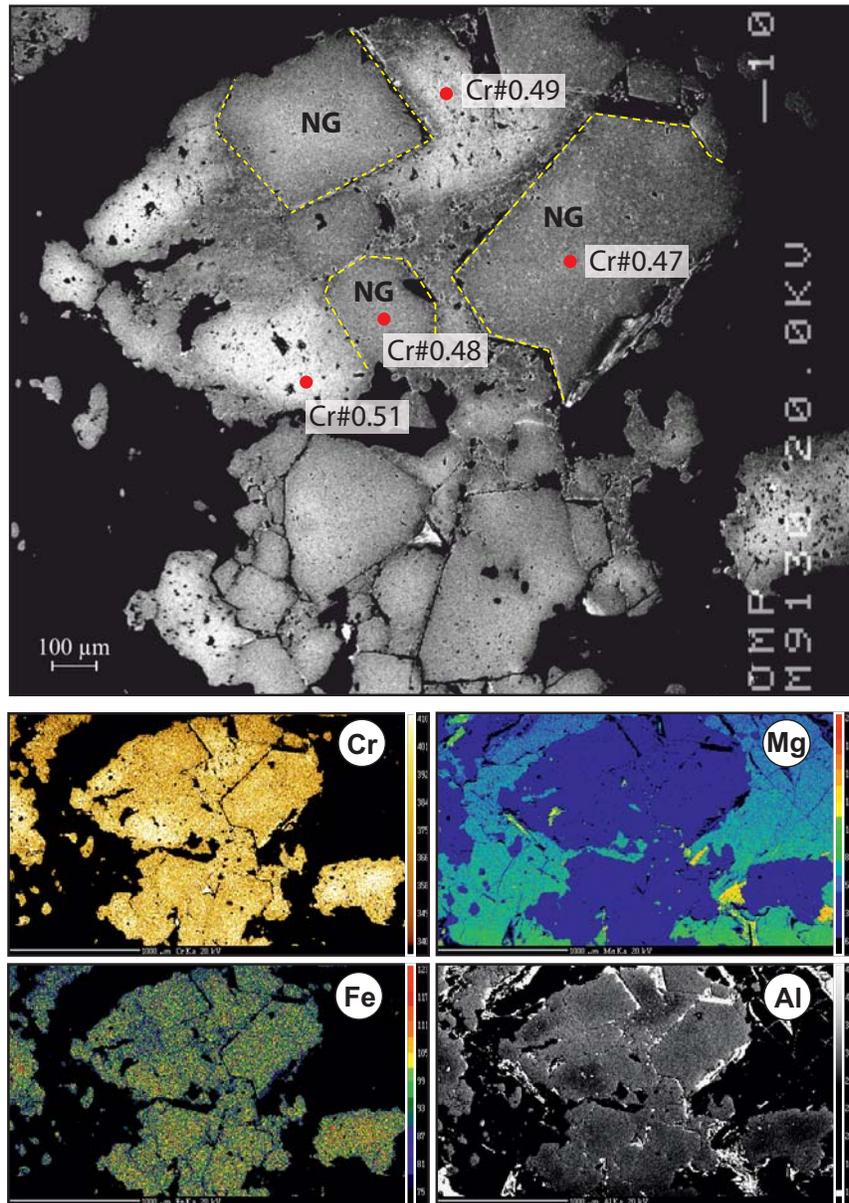


Figure 9

