1 **<u>Revision 1</u>**

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3 Compositional zoning in dolomite from lawsonite-bearing eclogite (SW Tianshan, China):

4 Evidence for prograde metamorphism during subduction of oceanic crust

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ABSTRACT

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17   Dolomite with compositional zoning was discovered in carbonate-lawsonite-bearing eclogites

18   in the Tianshan (ultra-)high-pressure/low-temperature metamorphic belt, northwestern China.

19   The eclogite-facies dolomite occurs as matrix porphyroblast and as inclusion in garnet, both

20   of which display the same chemical zoning pattern. The dolomite contains inclusions of

21   calcite (probably after aragonite), magnesite, glaucophane, lawsonite (and its pseudomorphs),

22   allanite, epidote, paragonite, phengite and omphacite. The chemical zoning in dolomite is

23   well defined by a continuous core–to–rim Mg increase and Fe–Mn decrease. The

24   concentrations of transition metal elements, REE and Y also decrease from core to rim of the

25   dolomite. Thermodynamic modeling demonstrates that the Fe–Mg zoning of dolomite is

26   largely temperature dependent and, thus, is interpreted as prograde growth zoning, which

27   developed during subduction of carbonate-bearing oceanic crust. It is suggested that dolomite

28   in equilibrium with garnet formed as a result of changing matrix compositions due to

29   increasing temperatures. In addition, thermodynamic modeling demonstrates that during

30   subduction at high-pressure conditions prograde-formed aragonite and dolomite were

31   transformed to dolomite and magnesite. Furthermore, Fe-rich magnesite inclusions in matrix

32   dolomite and in dolomite inclusions in garnet are shown to have formed during high-pressure

33   conditions prior to peak metamorphic conditions and, therefore caution is warranted using

34   Fe-bearing magnesite occurrences in eclogite-facies rocks as an unambiguous ultrahigh

35   pressure indicator as previously suggested.

36   **Keywords:** prograde zoning, dolomite, magnesite, eclogite, high pressure, Tianshan

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INTRODUCTION

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40   Carbonates are common minerals in some blueschists and eclogites in (ultra-)high-

41   pressure/low-temperature ((U)HP/LT) metamorphic terranes. Coesite inclusions in dolomite

42   in eclogite-facies calc-silicate rocks and metabasalts from the Dabie ultrahigh-pressure (UHP)

43   belt were interpreted as evidence for the subduction of continental crust (including sediments)

44   to mantle depths (>100 km) and that coexisting dolomite and magnesite are stable mineral

45   phases under UHP conditions (Schertl and Okay 1994; Zhang and Liou 1996). Coexisting

46   magnesite, aragonite and calcite inclusions in dolomite have also been reported to occur in

47   eclogites from several high-pressure (HP) and UHP metamorphic terranes and are regarded to

48   be an UHP indicator (e.g., Wang and Liou 1993; Zhang and Liou 1994; Zhang et al. 2003).

49   However, the coexistence of magnesite and dolomite as well as magnesite inclusions in

50   dolomite in blueschists and eclogites were also interpreted to have formed under HP

51   conditions (e.g., Klemd 2003; Smit et al. 2008; Li et al. 2012).

52   Compositional zoning is a distinctive feature that is commonly observed in petrographical

53   and chemical studies of minerals, and it may provide important information on the minerals

54   growth history and geological conditions during mineral formation. Compositional zoning,

55   involving the variations in both trace and major elements, is most suitable for studying the

56   dynamics of crystal growth (Tracy 1982). Different types of compositional zoning in

57   dolomite, including concentric zoning, sector zoning and oscillatory zoning, were studied

58   through imaging techniques such as cathodoluminescence (CL), back scattered electron

59   imaging (BSE) and X-ray topographs in some sedimentary rocks (e.g., Farr 1989; Reeder and

60   Prosky 1986; Reeder 1991; Wogelius et al. 1992; Shore and Fowler 1996). However, to our

61   knowledge the compositional zoning of eclogite-facies dolomite has not been reported and

62   thermodynamically modeled yet. Nonetheless it was rarely observed in other metamorphic

63   carbonates (*cf.*, Jones and Ghent 1971; Reinecke et al. 2000).

64   In the present study, we present concentric Fe–Mg zoning of dolomite from HP lawsonite-

65   carbonate-bearing eclogites in the southwest Tianshan (U)HP/LT metamorphic belt. The

66   petrography and mineral chemistry of the dolomite and its inclusions were studied in detail

67   by means of electron microprobe and laser ablation inductively coupled plasma mass

68   spectrometry (LA–ICP–MS). Furthermore   we   conducted   detailed   textural   and

69   thermodynamic modeling studies of the dolomite and its inclusions in order to shed some

70   light on the carbonate-phase formations and transitions in subducted oceanic crust.

71   **GEOLOGICAL SETTING AND PETROGRAPHY**

72   The Chinese Tianshan (U)HP/LT metamorphic belt extends for >200 km along the South

73   Tianshan suture zone separating the Yili (-Central Tianshan) block to the north and the Tarim

74   block to the south (see Fig. 1a in Li et al. 2012; Gao et al. 1998, 2011; Han et al. 2011). It

75   mainly consists of blueschist-, eclogite- and greenschist-facies meta-sedimentary and some

76   mafic metavolcanic rocks, the latter of which have N-MORB, E-MORB, OIB and arc basalt

77   affinities (Gao et al. 1999; Gao and Klemd 2003; John et al. 2008). Peak metamorphism of

78   some eclogites was estimated to have occurred under high-pressure conditions between 14

79   and 23 kbar at 480 and 580°C (e.g., Gao et al. 1999; Klemd et al. 2002; Wei et al. 2003; Li et

80   al. 2012), while coesite relics were identified in other eclogites or eclogite-facies rocks

81   indicating that these rocks underwent UHP metamorphism (e.g., Lü et al. 2008, 2009; Lü and

82   Zhang 2012). The intimate interlayering of HP and UHP rocks on a meter scale (Lü et al.

83   2009) was interpreted to be due to juxtaposition processes during subduction and exhumation

84   in the subduction channel (Klemd et al. 2011). The timing of peak metamorphism was

85   determined by multi-point Lu–Hf isochron ages from four blueschist- or eclogite-facies rocks

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86 yielding consistent garnet-growth ages of *ca.* 315 Ma (Klemd et al. 2011). This age is in

87 agreement, within error, with U–Pb SIMS ages of *ca.* 320 Ma on metamorphic zircon rims

88 from eclogites (Su et al. 2010). White mica ^{40}Ar–^{39}Ar and Rb–Sr ages of eclogite-facies

89 metavolcanic rocks and omphacite-bearing blueschists cluster at *ca.* 311 Ma and were found

90 to represent a major post-eclogite-facies episode of cooling or recrystallization (Klemd et al.

91 2005).

92   Marbles and carbonate-bearing HP metabasalts, metapelites are commonly observed in the

93 Tianshan (U)HP/LT metamorphic belt. The occurrence of magnesite and calcite inclusions in

94 dolomite in eclogites and metapelites was considered as evidence for UHP metamorphism

95 (Zhang et al. 2002, 2003), but the petrological interpretation of carbonate/silicate mineral

96 assemblages in (U)HP rocks is often highly controversial due to disequilibrium,

97 crystallographical or textural considerations (e.g., Klemd et al. 1994; Klemd 2003; Smit et al.

98 2008; Hammouda et al. 2011). More recently, interlayered dolomite- and magnesite-bearing

99 eclogite and blueschist in the Tianshan were interpreted to have coexisted at the same peak

100 metamorphic HP conditions due to different bulk-rock compositions (Li et al. 2012).

101   This study focuses on the chemical zoning of dolomite from a previously described HP

102 carbonate-lawsonite-bearing eclogite (sample L0910, Li et al. 2013). The peak metamorphic

103 *P–T* conditions of the eclogite are estimated at 580–590 ºC and 2.2–2.4 GPa. The eclogite

104 consists of garnet (*ca.* 16 vol.%), omphacite (*ca.* 45%), carbonate (*ca.* 13%), white mica (*ca.*

105 13%), epidote (*ca.* 5%), glaucophane (*ca.* 3%), sulfide (*ca.* 2%), quartz (*ca.* 1%) and

106 accessory minerals such as rutile, titanite, lawsonite and apatite. Porphyroblastic garnet

107 contains barroisite/glaucophane, epidote, paragonite, quartz and albite in the core domain and

108 omphacite, dolomite/magnesite and rutile in the mantle domain while the rim domain usually

109 is inclusion-free. Occasionally, lawsonite and magnesite were found to be enclosed by

110 dolomite inclusions in garnet porphyroblasts. Omphacite is often orientated parallel to the

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111   weak foliation as defined by phengite. Furthermore, some glaucophane inclusions were

112   detected in the omphacite cores. Significantly, the eclogite contains *ca.* 13 vol.% carbonates,

113   mainly dolomite and minor magnesite and calcite (Table 1). The dolomite occurs as

114   idioblastic/subidioblastic coarse-grained porphyroblastic matrix mineral and as inclusion in

115   garnet (Fig. 1). The matrix dolomite (0.2–1 mm in diameter) contains inclusions of omphacite,

116   glaucophane, lawsonite, phengite, paragonite, epidote, allanite, chlorite, calcite, magnesite

117   and quartz (Fig. 1), while dolomite inclusions in garnet contain magnesite, paragonite and

118   lawsonite inclusions (Fig. 1a–b; *cf.*, Li et al. 2013). Magnesite occurs as inclusion in matrix

119   dolomite and in dolomite inclusions in garnet (Fig. 1a–c). Calcite intergrown with chlorite,

120   phengite and paragonite occurs in the core of idioblastic matrix dolomite only (Fig. 1d).

121   Magnesite occasionally contains glaucophane inclusions (Fig. 1c). Epidote, which usually has

122   an allanite core, occurs as matrix mineral and as inclusion in dolomite prophyroblasts (Fig. 1d

123   and f). Lawsonite and its pseudomorphs (epidote-paragonite assemblages) were also

124   identified as inclusions in matrix dolomite (Fig. 1g).

ANALYTICAL METHODS

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126   *In situ* major element compositions of carbonates and inclusion minerals were obtained

127   from polished thin sections by electron microprobe analysis (JEOL JXA 8200) at the

128   GeoZentrum Nordbayern (GZN) of the University Erlangen–Nürnberg, Erlangen, Germany.

129   Quantitative major element analyses were performed with an acceleration voltage of 15 kV, a

130   beam current of 15 nA, a beam diameter of 3 μm and 10–30s counting time, while qualitative

131   mapping of Ca, Fe, Mg and Mn in dolomite was conducted using an energy-dispersive X-ray

132   detector with an acceleration voltage of 15 kV, a beam current of 230 nA, a 3–5 μm pixel size

133   and dwell time of 100 ms. Natural minerals and synthetic oxides were used as standards, and

134   a program based on the ZAF procedure was used for data correction. Representative

6

135   microprobe analyses for the minerals in this study are presented in Table 1. In order to

136   determine the nature of the $CaCO_3$ polymorph occurring as inclusions in dolomite and garnet,

137   Laser-Raman spectroscopy was performed at Department of material in the same university.

138   The laser beam (wavelength of 533 nm) was focused on the $CaCO_3$ inclusions by means of

139   50× objectives of a polarizing microscope. The laser spot size was focused to 1 μm.

140   *In situ* trace element analyses of zoned dolomite and inclusions were performed by LA–

141   ICP–MS at the GZN using a single collector quadrupole Agilent 7500i ICP–MS equipped

142   with an UP193Fx Argon Fluoride New Wave Research Excimer laser ablation system. The

143   glass reference material NIST SRM 612 was used as standard for external calibration. LA–

144   ICP–MS measurements were conducted using a spot size of 25µm in diameter, a laser

145   frequency of 15 Hz and 0.63 GW/cm^2 and a fluence of 3.32 J/cm^2. The carrier gas consists of

146   a mixture of 0.65 l/min helium and 1.10 l/min argon. Acquisition time was 20 s for the

147   background and 25 s for the mineral analysis. The Ca-content of the carbonates determined

148   by EMP analysis was used as internal standard. Reproducibility and accuracy, which were

149   determined for NIST SRM 610, are usually <8% and <6%. The trace element concentrations

150   were calculated by GLITTER Version 3 (van Achterbergh et al. 2000). Representative trace

151   element analyses of the carbonate minerals are given in Table 2.

152   **MINERAL CHEMISTRY**

153   Garnet has a prograde compositional growth zoning with a continuous increase of the

154   pyrope component from 4.9 to 11.4 % and a decrease of the spessartine component from 4.2

155   to 1.6 % from the core towards the rim (Table 1). Omphacite inclusions in garnet and

156   dolomite and matrix omphacite have a similar jadeite component of between 32.8 mol.% and

157   46.5 mol.%. The Si–content of phengite is between 3.45–3.51 pfu and the Na-content of

158   paragonite at *ca.* 0.80 pfu (Table 1). The glaucophane and epidote-group minerals display

159   rather uniform compositions either as matrix or inclusion minerals (Table 1). For more

160   detailed microprobe data concerning the silicates in the eclogite see Li et al. (2013).

161   The dolomite studied here is a dolomite-ankerite solid solution (dolomite$_{s.s.}$) that contains

162   20–35 mol.% ankerite [$CaFe(CO_3)_2$] component due to the substitution of Fe^{2+} for Mg (Table

163   1). This type of dolomite always contains small but variable amounts of Mn and less

164   commonly minor Sr, Pb, Ni and Zn (Table 2). LA–ICP–MS data show that the dolomite

165   contains high amounts of transition metal elements (e.g., Co: 18–60 ppm; Ni: 54–264 ppm

166   and Zn: 114–147 ppm), Sr (449–1633 ppm), Pb (2.17–27.8 ppm), P (23–28 ppm) and minor

167   Li, Ba, REE and Y (Table 2). The magnesite inclusions in the dolomite are magnesite-siderite

168   solid solutions (magnesite$_{s.s.}$) with a high siderite [$FeCO_3$] component (44–47 mol.%) and

169   about 1 mol.% $CaCO_3$ and even less $MnCO_3$ (Table 1). Magnesite hosts higher amounts of

170   transition metal elements (e.g., Co: 127–252 ppm; Ni: 181–533 ppm and Zn: 161–449 ppm)

171   but much lower Sr (0.110–5.17 ppm), Pb, HREE and Y concentrations than the dolomite

172   (Table 2). The HFSE concentrations in dolomite and magnesite are always below the

173   detection limit (Table 2). The $CaCO_3$ phase occurring as inclusions in dolomite is calcite

174   according to Raman spectrometry (Fig. 1d) and contains minor Mg, Fe and Mn contents

175   (Table 1). However, the stability of aragonite instead of calcite at HP/LT metamorphic

176   conditions is suggested by the thermodynamic modeling (see below) which is in agreement

177   with experimental studies (*cf.*, Carlson 1980). Thus, the calcite inclusions are thought to have

178   formed at the expense of former aragonite at low-*P* and high-*T* during post peak metamorphic

179   conditions (e.g., Carlson 1980; Proyer et al. 2008).

180

181   **COMPOSITIONAL ZONING OF DOLOMITE**

182   **Major elements**

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183   The zoning of dolomite is petrographically displayed by a change in color from core to rim

184   in the BSE images (here displayed by changes of the gray intensity, Fig. 1d). The dolomite

185   core contains inclusions of calcite (probably after aragonite), magnesite$_{s.s.}$, phengite,

186   paragonite, epidote, lawsonite, epidote and paragonite intergrowth (possibly after lawsonite)

187   and occasionally omphacite. Omphacite, phengite and allanite inclusions occur in the darker

188   rim domains (Fig. 1d and f). The Ca content of dolomite is rather homogeneous with a slight

189   increase at the outer-rim (Figs. 2 and 3a). The Fe content continuously decreases from core

190   (12.66 wt.%) to rim (7.51 wt.%) while the Mg content increases from 13.29 wt.% to 16.97

191   wt.% (Table 1). Thus X_{Fe} (=Fe/(Fe+Mg)) decreases accordingly (Fig. 3a). The Mn content

192   decreases from the dolomite core (0.53 wt.%) towards the inner-rim (0.18 wt.%) while it

193   increases at the outermost rim (0.40 wt.%). In addition, a subtle oscillatory Mn zoning occurs

194   in the inner-rim domain (Fig. 2). Magnesium and Fe show a good negative correlation in the

195   Mg *vs.* Fe plot (Fig. 3b). Interestingly, Mn shows a negative correlation with Mg and a

196   positive correlation with Fe when neglecting the outer-rim Mn composition (Fig. 3c–d). The

197   large scale mapping images document that the dolomite inclusions in garnet and matrix

198   dolomite grains share the same compositional core–to–rim zoning pattern; however, the

199   dolomite inclusions in garnet lack the (mantle-) rim domain in contrast to the matrix dolomite

200   (Fig. 4).

201

202   **Trace elements**

203   The Sr and Pb concentrations decrease gradually from the dolomite core to the mantle and

204   increase from the mantle to the inner-rim with an abrupt decrease at the outer-rim (Fig. 5a).

205   Lithium, Ba and Sr display similar distribution patterns throughout the zoning profile (Fig.

206   5a). Manganese and Co exhibit a general decrease from core to rim and a slight oscillatory

207   zoning at the inner-rim and an increase at the outermost rim (Fig. 5b). Zinc displays a flat

208   pattern. Vanadium, Cr and Ni concentrations decrease from core to mantle and then increase

209   towards the rim with a significant drop at the outermost rim (Fig. 5b). In general, the

210   dolomite core contains higher REE and Y concentrations than the mantle and rim (Fig. 5c and

211   d). The chondrite-normalized REE diagram displays a MREE (especially Eu) enrichment

212   relative to the LREE and HREE (Fig. 5d). The REE patterns presented here are in accordance

213   with those of dolomite from other Tianshan eclogites (van der Straaten et al. 2008) but are

214   quite different with the flat REE patterns in dolomite from Central Dabie coesite-bearing

215   eclogites (Sassi et al. 2000). This discrepancy is believed to be due to different chemical bulk

216   compositions of the protoliths (e.g. oceanic crust *vs.* continental crust) and/or the different

217   rock mineralogy, which strongly controls the trace element distributions. The magnesite

218   shows a relative HREE enrichment compared to the LREE and MREE (Fig. 5e).

219

THERMODYNAMIC MODELING

221   In order to obtain information on the carbonate-phase transitions as well as compositional

222   variation of carbonates during HP/LT metamorphism, thermodynamic modeling of the

223   carbonate-bearing eclogite L0910 was undertaken in the NMnCaKFMASCHO (Na_2O–MnO–

224   CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–CO_2–H_2O–Fe_2O_3) model system using the Perple_X

225   software (Connolly 1990, 2005) and an internally consistent thermodynamic dataset (Holland

226   and Powell 1998; and update) based on the effective bulk-rock composition (Table 3).

227   Mineral solid-solution models are *Gt(WPH)* for garnet (White et al. 2007), *Omph(GHP)* for

228   omphacite (Green et al. 2007), *Amph(DPW)* for amphibole (Dale et al. 2005), *Mica(CHA)* for

229   phengite (Coggon and Holland 2002), *Chl(HP)* for chlorite (Holland and Powell 1998),

230   *Ep(HP)* for epidote (Holland and Powell 1998), and *F* for H_2O–CO_2 fluid solution (Connolly

231   and Trommsdorff 1991). In particular, the recently developed solid-solution model

232   *odCcMS(EF)* for ternary Ca–Fe–Mg carbonates (Franzolin et al. 2011) was used to determine

233   compositional variations in dolomite, the transition of carbonate minerals and the effect of Fe

234   on carbonate stabilities during subduction conditions. For more details concerning the

235   pseudosection calculations see Li et al. (2013).

236   A calculated phase equilibrium diagram is presented in Figure 6a. Omphacite, phengite and

237   garnet are stable phases over the whole shown *P–T* range, while lawsonite occurs in the low–

238   *T* range from which epidote-group minerals are absent. Amphibole is absent in the HT/HP

239   stability fields. Dolomite is stable over a wide *P–T* range, while magnesite occurs in the

240   higher-pressure and aragonite in the LP/LT fields only (Fig. 6b). The modal amounts of

241   dolomite, aragonite, magnesite, chlorite, amphibole, omphacite, lawsonite and garnet, along

242   with the X_{Fe} isopleths of magnesite*s.s.* and dolomite*s.s.* were contoured in the modeled

243   pseudosection (Fig. 6). The modal amount of dolomite increases and that of aragonite

244   decreases with increasing *P* and *T* in the aragonite-dolomite transition area (Fig. 6a). The

245   modal amount of magnesite decreases and that of dolomite increases with increasing *T* in the

246   magnesite-bearing *P–T* range of 550 to 600°C (Fig.6a). The X_{Fe} isopleths of magnesite*s.s.* are

247   parallel to the *P*-axis and decrease in value from low to high temperatures in the amphibole-

248   absence field (Fig. 6b). Similarly, the X_{Fe} isopleths of dolomite*s.s.* are parallel to those of

249   magnesite and also decrease from low to high temperatures in this field (Fig. 6b). The

250   chemical changes as displayed by the X_{Fe} contents of the dolomite*s.s.* are in agreement with

251   the compositional variations observed in the zoned dolomite in the lawsonite-bearing eclogite

252   (Figs. 2 and 3a). The *P–T* paths of the studied eclogite and nearby eclogites (*cf.*, Li et al. 2012,

253   2013) indicate that the low temperature/low pressure aragonite was progradely transformed to

254   dolomite*s.s.* and then to dolomite*s.s.* and magnesite*s.s.* during increasing *P–T* conditions (Fig. 6b,

255   Table 3). The modal amount of omphacite (and of dolomite*s.s.* and magnesite*s.s.*) increases at

256   the expense of chlorite and amphibole with increasing *P–T* conditions (Fig. 6b–d). Garnet

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257 growth at the expense of lawsonite started at temperatures between 550 and 600°C (Fig. 6f

258 and g).

259

DISCUSSION

261 **Formation of dolomite and its prograde compositional zoning**

262 Significant amounts of carbonates are introduced into mafic oceanic curst by hydrothermal

263 alteration prior to subduction (e.g., Staudigel 2003). The crystallographically-bound CO_2 that

264 preferentially occurs in carbonates in the slab rocks is carried down to great mantle depths

265 without prominent decarbonation (Kerrick and Connolly 2001). Dolomitic carbonates are

266 generally stable at pressures of up to 2–7 GPa in mafic eclogites (e.g., Yaxley and Green

267 1994; Molina and Poli 2000; Poli et al. 2009). High-pressure experimental data on the

268 carbonate stability based on a basaltic composition in the presence of a H_2O–CO_2 mixed fluid

269 demonstrate that calcite is stable at P ≤ 1.4 GPa, dolomite at P between 1.4 and 1.8 GPa, and

270 dolomite and magnesite at P ≥ 1.8 GPa (Molina and Poli 2000). These results are in

271 accordance with the presented modeling which suggests the stability of aragonite at T ≤

272 450°C, P ≤ 1.7 GPa, of dolomite at 1.7 ≤ P ≤ 2.1 GPa and of dolomite and magnesite at even

273 higher pressures (e.g., P ≥ 2.1 GPa) (Fig. 6).

274 The occurrence of calcite (after aragonite)-chlorite inclusions in dolomite core domains in

275 the studied sample (Fig. 1d) and calcite (after aragonite)-chlorite-dolomite inclusions in

276 garnet cores (Fig. 1h) in adjacent eclogite (*cf.*, Li et al. 2012) suggest the prograde formation

277 of dolomite at LT–LP conditions (400 ≤ T ≤ 480°C, 1.5 ≤ P ≤ 2.1 GPa) according to the

278 continuous reaction:

279 arag + chl + amp → dol$_{s.s.1}$ + omp + H_2O (1),
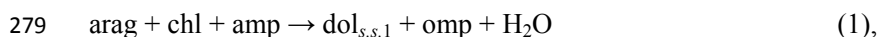
280 this reaction corresponds to a decrease in the modal amounts of aragonite, chlorite and

12

281   amphibole and an increase of dolomite and omphacite in the pseudosection (see hatched area

282   A; Fig. 6a and c–e). During increasing P–T conditions dolomite partly reacts to magnesite

283   (hatched area B) according to the reaction:

284    $\text{dol}_{s.s.1} + \text{chl} + \text{amp} \rightarrow \text{mag}_{s.s.} + \text{omp} \pm \text{grt} + H_2O$ (2),
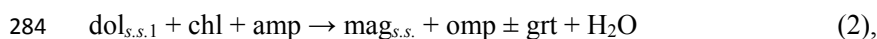
285   this reaction is displayed by increasing modal amounts of magnesite and omphacite (and

286   garnet) which formed at the expense of chlorite and amphibole along the P–T path (hatched

287   area B in the pseudosection, Fig. 6a–e). This is supported by glaucophane inclusions in

288   magnesite (Fig. 2c). The lawsonite and magnesite$_{s.s.}$ inclusions in matrix dolomite (Figs. 1c

289   and g) and in dolomite inclusions in garnet (*cf.*, Li et al. 2013) suggest that with increasing

290   temperatures and pressures dolomite formed at the expense of magnesite (e.g., $550 \leq T \leq$

291    $600^{\circ}C$, $P \geq 2.1$ GPa) according to the continuous reaction:

292    $\text{mag}_{s.s.} + \text{dol}_{s.s.1} + \text{law} + \text{omp} \rightarrow \text{dol}_{s.s.2} + \text{grt} + q + H_2O$ (3),

293   corresponding with gradually decreasing modal abundances of magnesite and lawsonite (Fig.

294   6a and f) and increasing modal amounts of dolomite and garnet (Fig. 6a and g) in the

295   pseudosection (hatched area C; Fig. 6b). The change in the modeled chemical composition

296   (X_{Fe}) of the dolomite (Fig. 6b) is in good agreement with that of the EPM-analyses of the

297   dolomite$_{s.s.2}$ (Table 1, No. 4–8; Fig. 3a). In addition, the measured chemical composition of

298   the magnesite$_{s.s.}$ inclusions ($X_{Fe} \approx 0.47$) in dolomite (Table 1, No. 9–10) corresponds with that

299   of the modeled magnesite$_{s.s.}$ ($X_{Fe} = 0.40$–0.50) in the pseudosection (area B–C; Fig. 6b).

300   Chemical zoning in metamorphic minerals relates to the changing effective bulk rock

301   composition and the precipitating fluid during changing pressures and/or temperatures (e.g.,

302   Tracy 1982). In case of a closed chemical system chemical zoning is directly related to the

303   availability of reactants and the degree of reaction completion. Reaction (3) suggests that

304   dolomite and garnet formed simultaneously. The garnet in eclogite L0910 shows distinctive

305   prograde growth zoning with continuously decreasing Fe- and Mn-contents and a gradually

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306   increasing Mg-content from core to rim, respectively (Li et al. 2013). X-ray maps and

307   composition profiles display that the dolomite porphyroblasts exhibit the same compositional

308   zoning as the garnets (Figs. 2 and 3a). The symmetric concentric chemical zoning occurs both

309   in matrix dolomite and dolomite inclusions in garnet (Fig. 4) suggesting that the zoning is the

310   product of prograde growth processes. This assumption is supported by the following

311   evidence: 1) the dolomite contains mineral inclusions of glaucophane, lawsonite (and its

312   pseudomorphs), chlorite, allanite, epidote, white mica and omphacite (Fig. 1) indicating that

313   the growth of dolomite may have occurred during the blueschist-facies to eclogite-facies

314   stages; 2) the thermodynamic modeling reveals that the Fe substitution of Mg in dolomite

315   decreases during the prograde *P–T* evolution (Fig. 6), which is in agreement with the

316   observed Fe–Mg zoning in dolomite; and 3) matrix dolomite grains and dolomite inclusions

317   in garnet have the same core (-mantle) compositional zoning pattern (Fig. 4).

318   Decreasing Fe and increasing Mg contents from core to rim of the dolomite are believed to

319   be the result of a changing matrix bulk rock composition during temperature increase as

320   revealed by the thermodynamic modeling (Fig. 6). The prograde chlorite and amphibole

321   breakdown supply the Mg for the dolomite formation and at the same time the garnet

322   crystallization reduces the Fe concentration in the system. However, the core–to–inner rim

323   Mn decrease of the dolomite is thought to be the result of fractional crystallization, which

324   was already proposed for similar zoned siderite porphyroblasts from greenschist-facies

325   phyllites of the Esplanade Range and Northern Dogtooth Mountains in British Columbia

326   (Jones and Ghent 1971). Trace element zoning of dolomite such as decreasing core–to–rim

327   concentrations of Sr, Pb, transition metal elements, REE (Fig. 5a–d) and Y (*cf.*, garnet,

328   Hollister 1966), is believed to be further evidence for fractional crystallization of the

329   dolomite. The abrupt Mn increase at the outer-rim of the dolomite accompanied by large

330   compositional changes of the Fe- and Mg-contents (Figs. 2 and 3) along with the sudden

14

331 variations of trace elements (Fig. 5a–c), may be attributed to variations in the equilibrium

332 fluid composition or to disequilibrium crystallization during the last porphyroblastic growth

333 stages (*cf.*, Jones and Ghent 1971).

334

335 **The occurrence of magnesite in dolomite in the Tianshan eclogites**

336 The occurrence of magnesite ± calcite (aragonite) inclusions in dolomite was interpreted as

337 evidence for UHP metamorphism in excess of 5 GPa for eclogite-facies-rocks from the

338 Tianshan orogen (Zhang et al. 2002, 2003). These authors referred to the equilibrium reaction

339 dolomite = magnesite + aragonite in order to deduce these exceptionally high UHP conditions

340 (*cf.*, Hammouda et al. 2011, and references therein). The stability of magnesite at ultrahigh

341 pressure conditions (e.g., >5GPa) was confirmed by a series of experiments (Hammouda et al.

342 2011, and references therein) and some field observations (e.g., Zhang and Liou 1994;

343 Messiga et al. 1999). On the other hand, Fe-rich magnesite$_{s.s.}$ and dolomite$_{s.s.}$ were

344 experimentally shown to be stable at HP as well as UHP conditions in mafic Fe-rich eclogites.

345 However, the influence of Fe on the carbonate structure and thus their stability was not

346 discussed in detail by these studies (e.g., Dasgupta et al. 2004; Yaxley and Brey 2004),

347 although recently it was experimentally shown that the Fe-content plays an decisive role in

348 effecting the ordering-disordering state of dolomite (Franzolin et al. 2012) and, thus, has a

349 considerable effect on the magnesite-aragonite-dolomite stability relationship (Hammouda et

350 al. 2011). In Fe-bearing systems, experimental results suggest that the nucleation of aragonite

351 and magnesite occurs prior to that of dolomite at relatively low-pressure/low-temperature

352 conditions. Furthermore, a relatively high Fe proportion is expected to shift the aragonite +

353 magnesite$_{s.s.}$↔ dolomite reaction toward higher temperatures, enlarging the stability field of

354 aragonite and magnesite$_{s.s.}$ (Franzolin et al. 2012). For instance, aragonite and magnesite$_{s.s.}$

355 are stable between 400 and 450°C at *ca.* 2 GPa and react to highly disordered dolomite only

15

356   at temperatures > 450°C in Fe-rich systems (see Fig. 10 in Hammouda et al. 2011). In the

357   present study, the application of a new thermodynamic solid-solution model for Ca–Mg–Fe

358   carbonate provides an opportunity to investigate the transition of carbonate minerals during

359   subduction zone metamorphism. In the modeled complex system using a particular bulk

360   chemistry (Fig. 6a) aragonite occurs in the low temperature/low pressure stability fields in the

361   phase equilibrium diagram while magnesite$_{s.s.}$ appears only at P > 2.0 GPa (Fig. 6) indicating

362   that Fe-rich magnesite (in equilibium with dolomite) is stable under high-pressure conditions

363   (P ≤ 2.5 GPa, T ≤ 600°C), but is expected to react out to dolomite at temperatures > 600°C

364   (Fig. 6).

365   Thus, the reported magnesite$_{s.s.}$ inclusions in dolomite$_{s.s.2}$ (Table 1) from the Tianshan HP

366   eclogites may have formed prograde in equilibrium with dolomite$_{s.s.1}$ and not during

367   decompression as previously proposed (Zhang et al. 2003). This interpretation is also

368   supported by glaucophane inclusions in the magnesite (Fig. 1c) and the occurrence of

369   dolomite-rimmed magnesite inclusions in the core domain of prograde garnet porphyroblasts

370   (Fig. 1a–b) (see also Li et al. 2012). These textural observations indicate that Fe-magnesite

371   formed at the expense of glaucophane between 500 and 560°C at 2.0 ≤ P ≤ 2.3 GPa and was

372   then transformed to dolomite prior to or simultaneously with the pervasive garnet growth

373   during increasing *P–T* conditions. Consequently caution is warranted in interpreting

374   magnesite occurrences in dolomite in eclogite facies rocks as unambiguous evidence for UHP

375   metamorphism (see also Smit et al. 2008). Alternatively, fluid flow along micro cracks may

376   enter the inner part of garnet (or other container minerals) and thus may change the carbonate

377   composition of inclusions forming pseudomorph after older minerals. In addition, it should be

378   kept in mind that magnesite and dolomite assemblages cannot be treated as an absolute

379   pressure indicator without a strict control of the relative amounts of volatile and non-volatile

380   components in multi-component Fe-bearing systems (Poli et al. 2009).

381 **IMPLICATIONS**

382   Compositionally zoning was observed in dolomite in a lawsonite-bearing eclogite from the

383   western Tianshan HP–UHP metamorphic belt. Evidence from mineral inclusions,

384   thermodynamic modeling and textures suggest the zoning formed during prograde dolomite

385   growth under HP metamorphism. To our knowledge the compositional zoning of carbonate is

386   very rare in metamorphic rocks, and this is the first report showing the possibility to retrieve

387   such a long history from high-pressure carbonates, which are generally believed to record

388   only the latest stages of the metamorphic evolution of eclogite-facies rocks. The core–to–rim

389   Mg–Fe–Mn zoning of dolomite formed contemporaneously with garnet thereby suggesting

390   that the dolomite, like garnet, also experienced fractional crystallization during the HP

391   metamorphism. Therefore more attention should be paid to the carbonates when considering

392   mineral equilibrium and effective bulk-rock composition calculations in HP–UHP carbonate-

393   bearing rocks. In addition, our findings show that the chemical zoning in dolomite is largely

394   temperature dependent and thus the analysis of major and trace elements in carbonates from

395   blueschists and eclogites may bear important thermobarometric implications.

396   The present study shows that carbonates in subducted oceanic crust may experience

397   gradual aragonite $\rightarrow$ dolomite $\rightarrow$ dolomite+magnesite transition stages during blueschist- to

398   eclogite-facies conditions. The occurrence of magnesite$_{s.s.}$ inclusions in dolomite enclosed in

399   garnet indicates that the magnesite$_{s.s.}$ had formed already under HP conditions. Fe content in

400   magnesite determines its stability at lower pressures. Thus, caution is warranted using

401   magnesite occurrences in eclogite-facies rocks as unambiguous evidence for UHP

402   metamorphism, in particular in a multi-component Fe-bearing system.

403

17

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584   **FIGURE CAPTIONS**

585   **Figure 1** Representative photomicrographs and BSE images of dolomite in carbonate-

586   lawsonite-bearing eclogite in the Tianshan (U)HP/LT metamorphic belt. All=allanite, Cal

587   =calcite, Chl=chlorite, Dol=dolomite, Ep=epidote, Gln=glaucophane, Grt=garnet,

588   Law=lawsonite, $Mag_{s.s.}$=magnesite-siderite$_{s.s.}$, Omp=omphacite, Phn=phengite,

589   Pg=paragonite, Py=pyrite, Qtz=quartz, Ttn=titanite. (a, b) Dolomite inclusions in garnet and

590   coarse-grained matrix dolomite, both enclosing $Mag_{s.s.}$ inclusions. (c) $Mag_{s.s.}$ inclusions in

591   dolomite containing glaucophane inclusions. (d) The zoned porphyroblastic dolomite

592   contains inclusions of calcite, chlorite, phengite, paragonite, allanite and omphacite. The

593   calcite was identified by the representative Raman shifts at 154 cm^{-1}, 279 cm^{-1}, 713 cm^{-1} and

594   1085 cm^{-1}. (e) Glaucophane inclusions in dolomite. (f) Phengite, allanite/epidote, omphacite

595   and quartz inclusions in matrix dolomite. (g) Lawsonite inclusions and its pseudomorph

596   (epidote+paragonite assemblages) in the core domain of matrix dolomite. (h) Calcite-chlorite-

597   dolomite inclusions in garnet in nearby carbonate-bearing eclogite, see also Fig. 3d from Li et

598   al. (2012).

599   **Figure 2** X-ray intensity maps of Ca, Fe, Mg and Mn in the dolomite porphyroblast from Fig.

600   1d. The compositional zoning is displayed by core–to–rim gradually increasing Mg and

601   decreasing Fe and Mn, whereas Ca is rather homogeneous (for profile A–B see Fig. 3a). The

25

602   numbered circles represent LA–ICP–MS spots, the data of which are listed in Table 2.

603   **Figure 3** Chemical composition profile of the dolomite porphyroblast from Fig. 2. (a) Fe and

604   Mn decrease from core to rim while Mg increases and Ca is constant. Towards the outermost

605   rim Ca and Mn increase slightly. (b) Good negative correlation of Mg and Fe. (c, d) Mn

606   shows a negative correlation with Mg and a positive correlation with Fe, respectively.

607   **Figure 4** X-ray maps of Ca, Fe, Mg and Mn of dolomite grains from Fig. 1a–b. The dolomite

608   inclusions in garnet shows the same compositional zoning as the core (-mantle) domain of

609   matrix dolomite.

610   **Figure 5** Trace elements in the zoned matrix dolomite porphyroblast from Fig. 2 and the

611   magnesite inclusions in dolomite. (a–c) Trace element concentrations along a profile from

612   core to rim in the dolomite. (a) Li–Ba–Sr–Pb. (b) Transition metal elements. (c) REE and Y.

613   (d) Chondrite-normalized rare earth element patterns. The dolomite core contains higher REE

614   contents (especially HREE) contents than the rim. (e) Chondrite-normalized rare earth

615   element patterns of magnesite inclusions in dolomite. Normalization values are after Sun and

616   McDonough (1989).

617   **Figure 6** (a) $P–T$ pseudosection (using Perple_X) in the system NMnCaKFMASCHO for the

618   eclogite based on an effective bulk composition. The pseudosection is contoured for aragonite,

619   dolomite$_{s.s.}$ and magnesite$_{s.s.}$ modal abundances (vol.%). (amp = amphibole; arag = aragonite;

620   chl = chlorite; dol = dolomite; ep = epidote; f = fluid; grt = garnet; law = lawsonite; mag =

621   magnesite; omp = omphacite; phn = phengite; q = quartz; rhc = rhodochrosite; zoi = zoisite).

622   For more mineral assemblages see Table 3. (b) The $P–T$ path (for details see Li et al. 2012,

623   2013) indicates that carbonates in subducted oceanic crust undergo the aragonite → dolomite

624   → dolomite+magnesite transitions during prograde subduction zone metamorphism. The

625   pseudosections are contoured with X_{Fe} isopleths in magnesite$_{s.s.}$ and dolomite$_{s.s.}$. The

626   isopleths are largely T-dependent in area C: the Fe-content decreases and the Mg-content

26

627   increases from low-T to high-T, which is in agreement with the measured compositional

628   zoning in eclogite-facies dolomite of this study. (c–g) The contoured modal amounts (vol.%)

629   of chlorite (c), amphibole (d), omphacite (e), lawsonite (f) and garnet (g).

27

Table 1
Representative major element composition of minerals in dolomite-bearing eclogite

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Mineral	Grt	Grt	Grt	Dol	Dol	Dol	Dol	Dol	Mag	Mag	Cal	Omp	Omp	Gln	Gln	Phn	Phn	Pg	Ep	Ep	All	Law	Chl
Location	core	mantle	rim	core	mantle	mantle	inner-rim	outer-rim	in Dol	in Dol	in Dol	matrix	in Dol	in Grt	in Mag	matrix	in Dol	in Dol	matrix	in Dol	in Dol	in Dol	in Dol
SiO_2	35.01	37.64	37.33	0.01	0.02	0.00	0.02	0.01	0.01	0.00	0.07	56.69	55.87	55.68	56.53	53.06	53.52	46.83	39.20	38.88	34.20	38.82	26.18
TiO_2	0.09	0.03	0.03	0.00	0.05	0.03	0.02	0.03	0.00	0.00	0.00	0.05	0.04	0.02	0.49	0.26	0.18	0.04	0.44	0.00	0.12	0.48	0.00
Al_2O_3	23.13	21.58	21.99	0.04	0.01	0.00	0.01	0.00	0.01	0.02	0.03	10.72	10.03	11.19	10.32	26.38	25.57	39.23	26.35	28.58	20.21	30.76	18.53
Cr_2O_3	0.11	0.07	0.08	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.15	0.09	0.01	0.16	0.07	0.07	0.01	0.13	0.02	0.12	0.00	0.16
FeO	29.68	29.84	27.10	12.66	11.69	10.02	9.57	7.51	34.32	33.40	1.93	7.81	9.50	12.79	11.94	2.31	3.18	0.45	8.25	5.11	11.89	0.79	29.99
MnO	1.87	1.72	0.73	0.53	0.38	0.26	0.15	0.40	0.54	1.36	0.40	0.07	0.02	0.01	0.08	0.02	0.03	0.00	0.15	0.10	0.00	0.00	0.25
MgO	1.22	2.23	2.91	13.29	14.14	15.59	15.29	16.97	21.35	20.71	0.95	5.98	5.40	8.64	9.64	3.66	3.62	0.08	0.08	0.09	0.20	0.01	13.29
CaO	8.80	7.82	9.87	27.67	28.60	28.84	28.88	30.38	0.59	0.67	59.24	10.93	9.53	1.15	0.72	0.05	0.06	1.19	22.89	23.86	17.62	17.41	0.05
Na_2O	0.02	0.02	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.01	8.43	9.35	7.18	7.47	0.62	0.28	6.46	0.04	0.00	0.05	0.00	0.03
K_2O	0.02	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.00	0.00	0.08	0.00	0.00	0.01	0.01	10.23	10.48	0.84	0.01	0.01	0.01	0.00	0.00
Total	99.95	100.95	100.05	54.22	54.90	54.74	53.98	55.33	56.83	56.16	62.71	100.83	99.83	96.68	97.20	112.66	97.00	95.16	97.53	96.65	84.45	88.27	88.48
Si	2.798	2.973	2.942	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.002	2.006	1.993	7.761	7.851	3.478	3.510	3.001	3.044	3.028	3.084	2.553	2.809
Al	2.177	2.007	2.041	0.002	0.001	0.000	0.000	0.000	0.000	0.001	0.001	0.447	0.421	1.836	1.688	2.036	1.975	2.960	2.410	2.621	2.146	2.382	2.000
Cr	0.007	0.004	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.003	0.001	0.018	0.004	0.004	0.001	0.008	0.001	0.009	0.000	0.014
Ti	0.005	0.002	0.002	0.000	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.001	0.001	0.002	0.051	0.013	0.009	0.002	0.025	0.000	0.008	0.024	0.000
Fe^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.111	0.234	0.575	0.262	0.000	0.000	0.000	0.540	0.330	0.900	0.000	0.000
Fe^{2+}	1.984	1.971	1.786	0.349	0.316	0.267	0.258	0.194	0.931	0.920	0.048	0.120	0.050	0.915	1.125	0.127	0.174	0.024	0.000	0.000	0.000	0.043	2.691
Mn	0.127	0.115	0.049	0.015	0.010	0.007	0.004	0.011	0.015	0.038	0.010	0.002	0.001	0.001	0.009	0.001	0.002	0.000	0.010	0.007	0.000	0.000	0.023
Mg	0.145	0.263	0.342	0.654	0.680	0.740	0.735	0.784	1.032	1.017	0.042	0.315	0.287	1.795	1.996	0.358	0.354	0.008	0.009	0.010	0.027	0.001	2.125
Ca	0.754	0.662	0.833	0.979	0.989	0.984	0.998	1.008	0.021	0.024	1.892	0.414	0.364	0.172	0.107	0.004	0.004	0.082	1.905	1.991	1.703	0.000	0.006
Na	0.003	0.003	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.578	0.647	1.940	2.012	0.079	0.036	0.803	0.006	0.000	0.009	1.227	0.006
K	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.003	0.000	0.000	0.002	0.002	0.855	0.877	0.069	0.001	0.001	0.001	0.000	0.000
Cation	8	8	8	2	2	2	2	2	2	2	2	4	4	15	15	6.955	6.945	6.950	7.958	7.989	7.887	6.230	9.674
O	12	12	12	6	6	6	6	6	6	6	6	6	6	23	23	12	12	12	12.5	12.5	12.5	10	14
X_{Fe}	0.00	0.00	0.00	0.35	0.32	0.27	0.26	0.20	0.47	0.47	WEF	42.41	35.18						Ps	0.18	0.11	0.30	
Alm	66.15	65.62	59.49								JD	46.11	41.46										
Grs	24.78	21.81	27.50								AE	11.48	23.37										
Prp	4.85	8.74	11.39																				
Sps	4.22	3.83	1.62																				

(i) $X_{Fe} = Fe^{2+}/(Fe^{2+}+Mg)$; Alm: almandine, Grs:grossular, Prp:pyrope, Sps: spessartine, WEF: wollastonite+enstatite+ferrosilite, JD: jadeite, AE: aegirine, Ps: pistacite. (ii) Fe^{3+} was calculated assuming stoichiometric mineral compositions.

Table 2

Representative trace element composition (in ppm) of dolomite and magnesite. Aanlyses 1-15 refer to the profile in dolomite (Fig. 2 Mn).

Min.	Dolomite															Magnesite		
Pos.	core							→							rim	in matrix	Dol	Dol/Gt
No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	19	21	23
Li	2.26	2.14	2.50	2.51	1.75	2.18	2.75	1.67	1.12	1.73	2.08	5.76	4.09	5.53	2.00	bdl	bdl	bdl
P	28.4	27.7	24.8	26.8	26.2	22.6	25.2	28.1	22.9	27.7	30.2	25.9	25.9	28.1	23.6	26.6	28.2	13.0
Si	bdl*	bdl	bdl	365	bdl	bdl	bdl	bdl	433	419	bdl	bdl	bdl	bdl	bdl	bdl	723	bdl
Ti	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
V	2.35	2.13	2.17	1.87	1.88	1.63	1.98	1.65	0.950	0.940	0.865	1.33	1.41	1.77	1.17	0.664	0.973	0.401
Cr	5.29	5.16	5.33	2.92	2.45	4.73	4.12	2.96	2.17	2.22	2.93	1.71	4.11	4.57	1.50	bdl	3.12	1.43
Mn	3993	3646	3763	3538	3021	2824	2587	2517	2068	1916	1625	1633	1936	1232	1975	3559	5860	5293
Co	59.5	57.4	53.0	52.7	50.7	51.4	43.0	38.5	30.3	29.0	32.2	24.6	17.9	19.1	29.1	252	250	127
Ni	264	230	202	185	168	179	153	155	183	178	194	216	215	213	53.7	533	351	181
Cu	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.49	bdl	2.06
Zn	132	132	132	130	138	132	134	136	130	136	130	142	141	147	114	449	280	161
Rb	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Sr	1275	1280	1344	1305	1274	1224	1274	1410	1160	1236	1531	1633	1411	1533	449	0.227	0.110	5.17
Y	10.9	6.36	4.27	1.63	1.28	0.757	0.261	0.225	0.305	0.151	0.174	0.090	0.123	0.093	0.108	0.607	0.583	0.102
Zr	bdl	bdl	bdl	bdl	15.3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.76	bdl	bdl
Nb	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Mo	0.135	0.225	0.161	0.107	bdl	bdl	bdl	bdl	0.093	bdl	bdl	0.076	0.075	bdl	bdl	0.317	0.278	0.111
Cs	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ba	1.90	1.95	2.19	1.87	2.50	1.63	1.56	1.24	0.957	0.885	1.29	1.42	0.791	1.33	0.244	bdl	bdl	0.888
La	0.316	0.252	0.239	0.100	0.121	0.317	0.138	0.163	0.154	0.126	0.146	0.248	0.117	0.144	bdl	0.062	bdl	0.084
Ce	1.05	0.690	0.733	0.330	0.385	0.738	0.397	0.301	0.498	0.486	0.481	0.750	0.349	0.338	0.049	0.224	bdl	0.078
Pr	0.174	0.140	0.138	0.066	0.088	0.107	0.075	0.060	0.082	0.109	0.093	0.164	0.037	0.049	0.008	0.038	bdl	0.013
Nd	1.31	1.06	1.08	0.493	0.375	0.787	0.258	0.619	0.679	0.429	0.687	0.972	0.349	0.364	bdl	bdl	bdl	bdl
Sm	0.711	0.687	0.661	0.266	0.326	0.259	0.149	0.171	0.347	0.253	0.346	0.326	0.169	0.122	bdl	bdl	bdl	bdl
Eu	0.596	0.458	0.473	0.483	0.442	0.381	0.375	0.348	0.236	0.226	0.220	0.256	0.171	0.182	bdl	bdl	bdl	bdl
Gd	2.14	1.40	1.29	0.445	0.721	0.447	0.156	0.153	0.417	0.206	0.229	0.297	0.072	0.089	bdl	bdl	bdl	bdl
Tb	0.381	0.256	0.208	0.086	0.068	0.066	0.019	0.014	0.032	0.020	0.009	0.028	bdl	0.021	bdl	bdl	bdl	0.009
Dy	2.39	1.66	1.14	0.410	0.287	0.249	0.104	bdl	bdl	0.047	bdl	bdl	0.049	0.056	bdl	bdl	bdl	bdl
Ho	0.418	0.257	0.135	0.080	0.043	0.028	bdl	bdl	0.011	bdl	bdl	bdl	bdl	bdl	bdl	0.045	0.031	bdl
Er	0.769	0.390	0.273	0.105	0.097	bdl	bdl	bdl	0.041	bdl	bdl	bdl	bdl	bdl	bdl	0.120	0.138	0.018
Tm	0.070	0.055	0.030	0.014	0.015	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.018	0.036	0.006
Yb	0.463	0.323	0.173	bdl	bdl	bdl	bdl	bdl	0.027	0.039	bdl	bdl	bdl	bdl	bdl	0.192	0.308	0.033
Lu	0.053	0.049	0.026	0.012	bdl	bdl	0.008	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.032	0.061	0.011
Hf	bdl	bdl	bdl	bdl	0.359	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.095	bdl	bdl
Ta	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Pb	16.4	16.6	17.4	17.0	15.9	16.2	15.3	15.9	13.1	13.5	15.8	19.3	22.1	27.8	2.17	bdl	bdl	0.083
Th	bdl	bdl	bdl	bdl	0.017	0.034	0.018	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
U	bdl	bdl	bdl	bdl	0.039	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.024	bdl	bdl

*bdl: below detection limit; Dol/Gt: magnesite in dolomite in garnet.

Tabel 3 Bulk composition used for pseudosection calculation and mineral assembalges from Fig. 6a

Sample	SiO$_2$	Al$_2$O$_3$	Na$_2$O	K$_2$O	FeO	Fe$_2$O$_3$	MgO	CaO	MnO	CO$_2$	H$_2$O
L0910	43.39	12.71	3.44	1.19	7.24	1.9	6.73	12.76	0.11	5.77	4.68

Field A:

A$_1$: amp omp grt phn chl arag law q f

A$_2$: amp omp grt phn chl dol arag law q f

A$_3$: amp omp grt phn chl dol arag law f

Field B:

B$_1$: amp omp grt phn chl dol law f

B$_2$: omp grt amp phn chl dol mag law f

B$_3$: omp grt amp phn dol mag law f

B$_4$: omp grt amp phn dol mag law f q

Field C:

C$_1$: omp grt phn dol mag law q f

C$_2$: omp grt phn dol mag law ep q f

C$_3$: omp grt phn dol mag ep q f

A: omp phn chl amp dol mag law rhc f

B: amp omp phn chl dol law arag rhc f

C: amp omp grt phn chl arag law ep q f

D: amp omp grt phn chl dol arag law ep q f

E: amp omp grt phn chl dol arag law ep f

F: amp omp grt phn chl arag ep q f

G: amp omp grt phn chl dol arag ep q f

H: amp omp grt phn chl dol arag ep f

I: amp omp grt phn dol law f

J: amp omp grt phn dol law ep f

K: amp omp grt phn dol law ep q f

L: amp omp grt phn dol mag law ep q f

M: amp omp grt phn dol mag ep q f

N: omp grt phn dol law q f

O: amp omp grt phn dol zoi q f
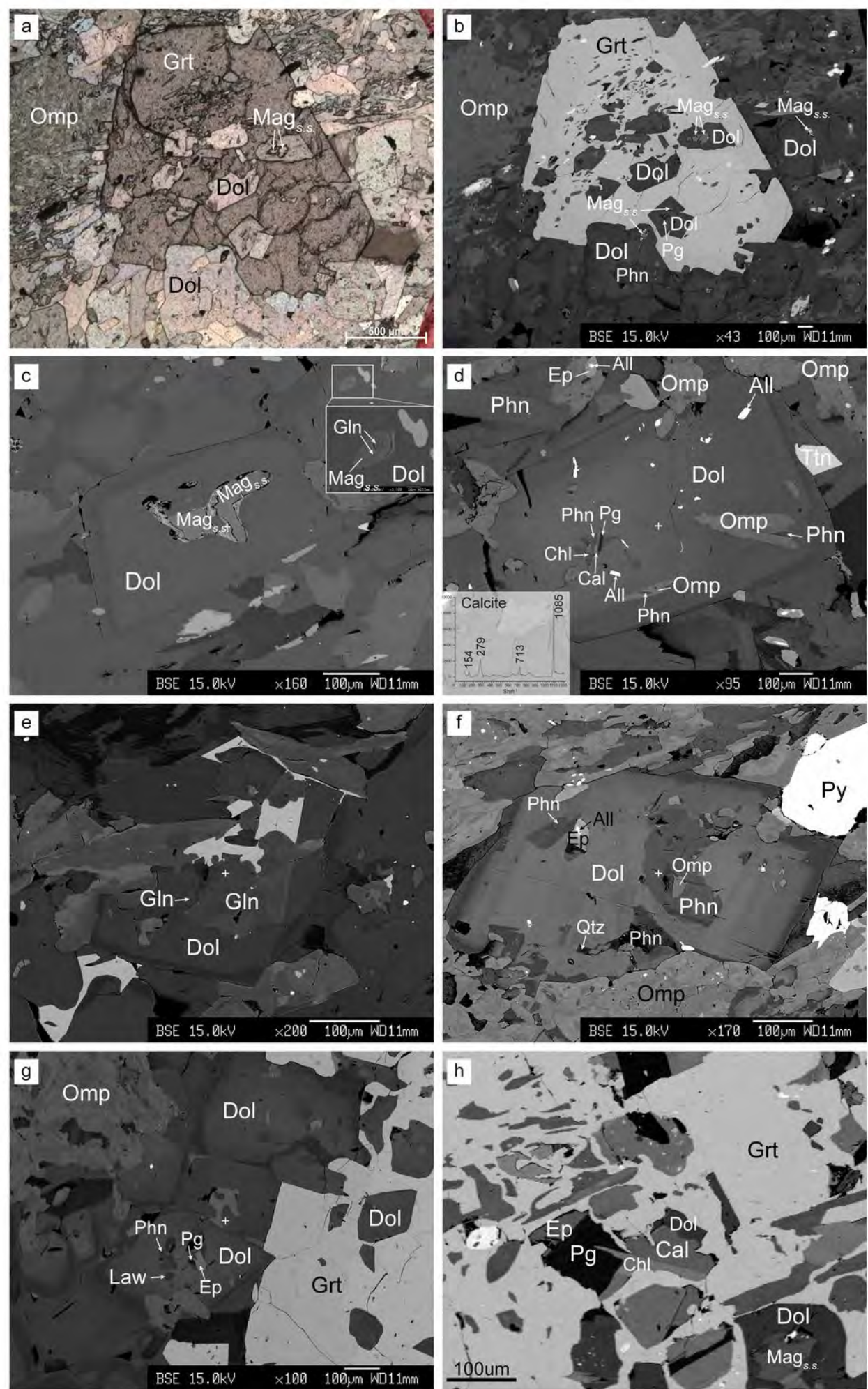
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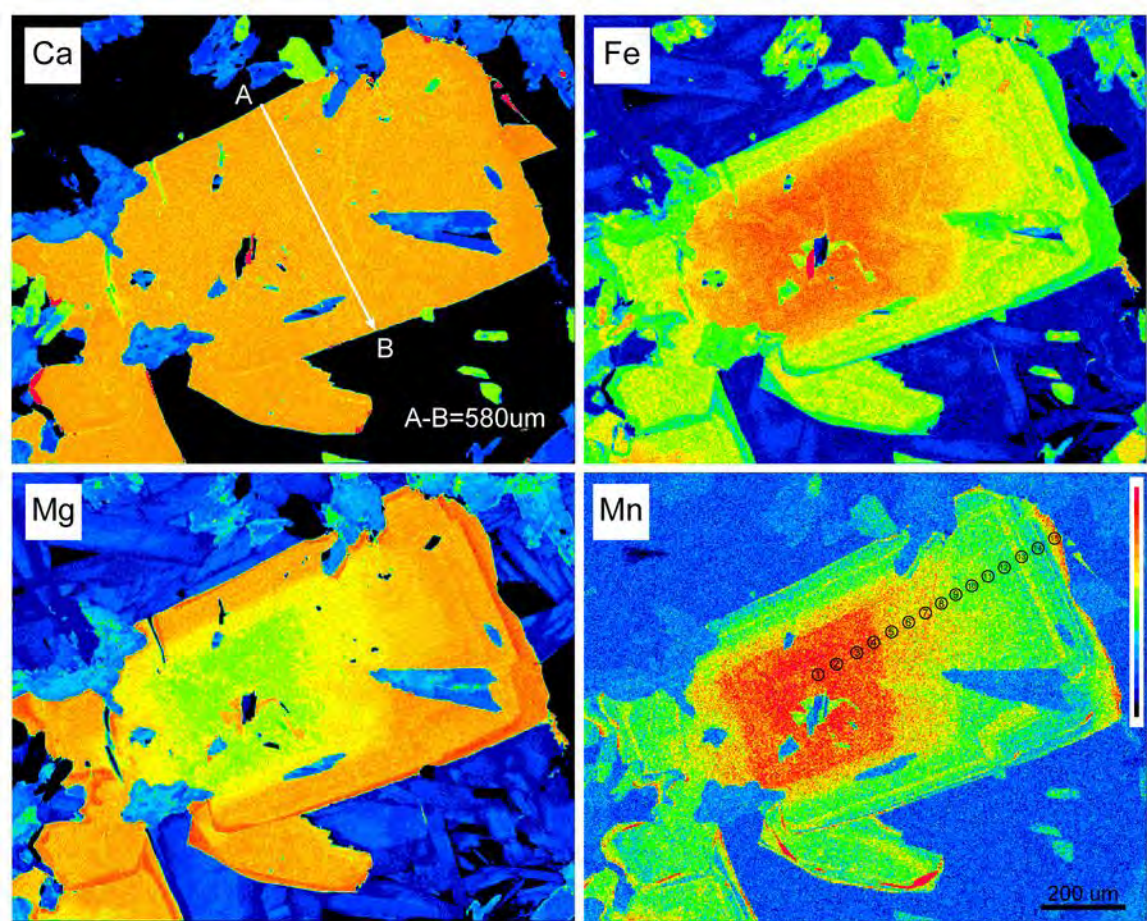
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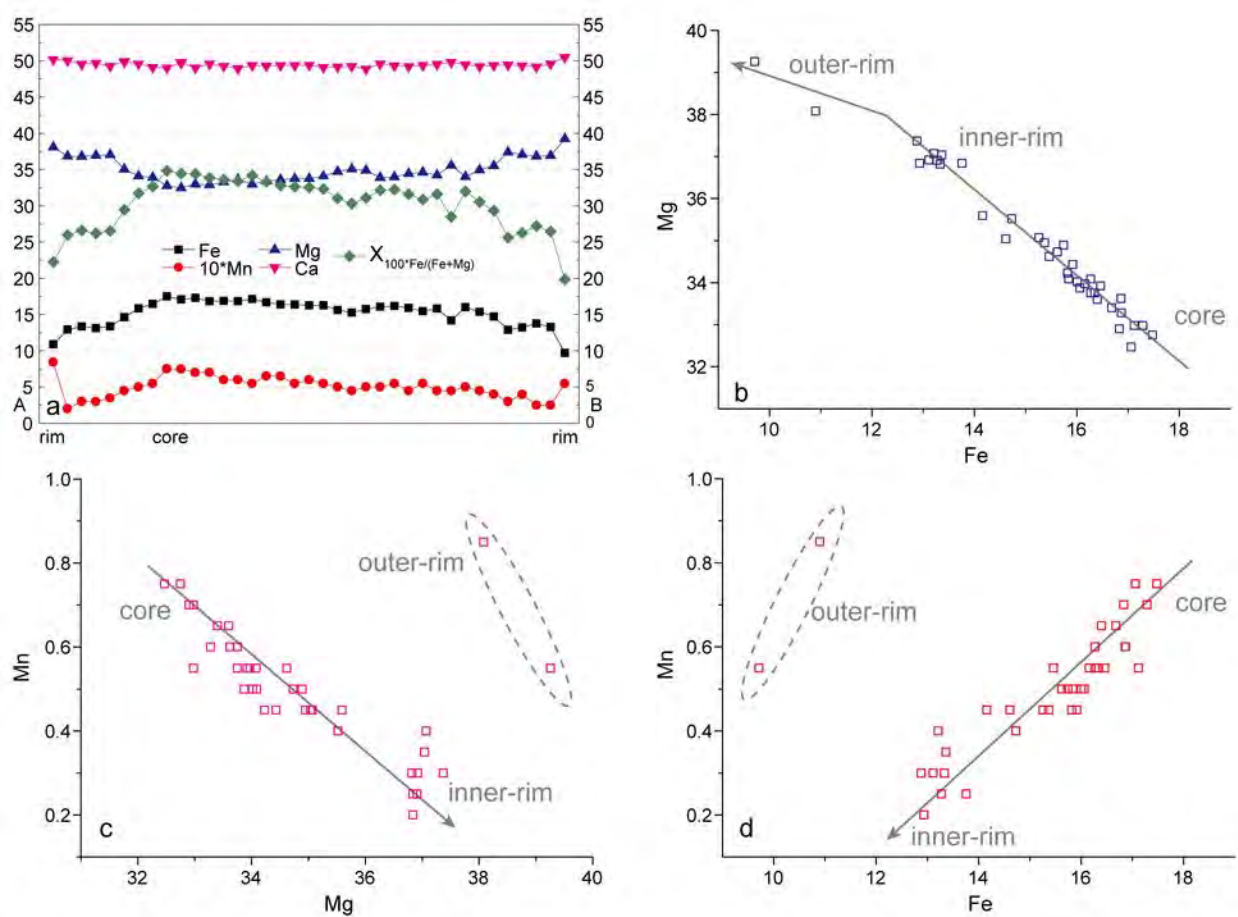
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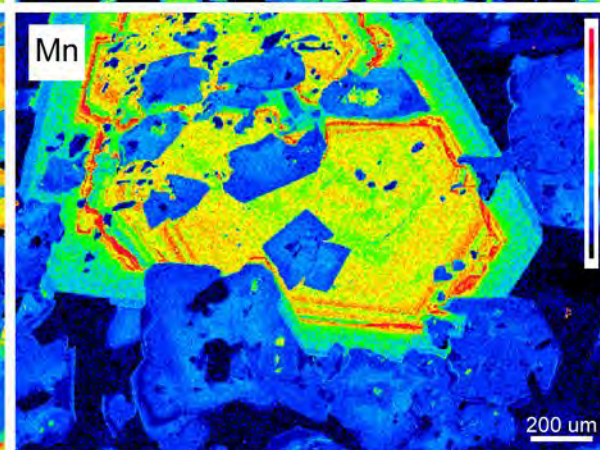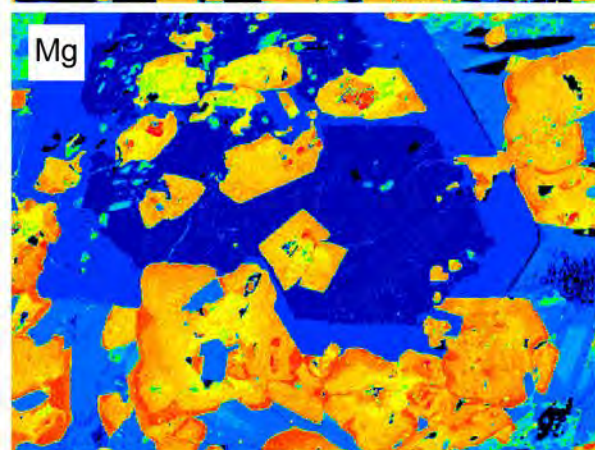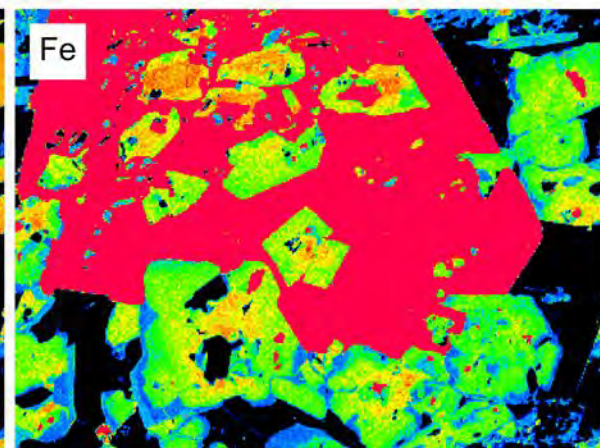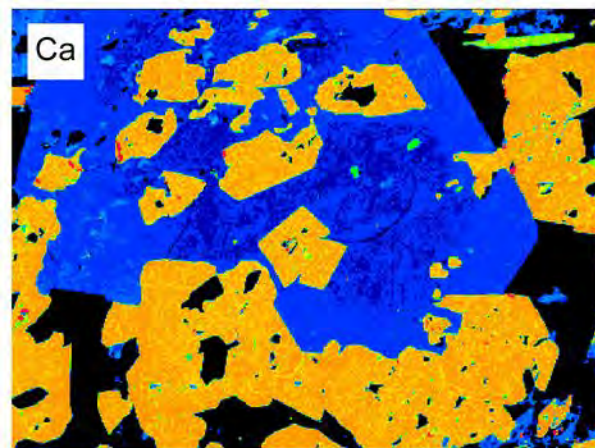
Figure 4

Figure 5

Figure 6