Dissolving dolomite in a stable UHP mineral assemblage: evidence from Cal-Dol marbles of the Dora-Maira Massif (Italian Western Alps).

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1 # Revision 1

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4 # (Italian Western Alps)

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15

16 **ABSTRACT**

17 In deep and cold subduction such as that experienced by the UH*P* Units of the Western Alps,

18 carbon dissolution is a relevant mechanism for carbon transfer from the slab into the mantle. The

19 UH*P* impure Cal-Dol-marbles from the Dora-Maira Massif are studied to investigate the poorly

20 known evolution of dolomite during deep subduction. Dolomite shows four stages of growth, from

21 pre-Alpine to early-retrograde Alpine, coupled with chemical variations and distinct included

22 mineral assemblages. To explain the evidence for growth and partial reabsorption of dolomite

23 through H*P* prograde, UH*P* peak, and UH*P* early-retrograde Alpine metamorphism, a chemically

24 simple marble (Cal, Dol, Di, Fo, and retrograde Atg, Tr, Mg-Chl) has been studied in detail.

25   Microstructural relationships, coupled with mineral chemistry, indicate the growth of the

26   assemblage dolomite+diopside+forsterite±aragonite during H*P* prograde, UH*P* peak, and UH*P*

27   early-retrograde evolution.

28   Mixed-volatile *P-T* projection modelled in the simple CaO-(FeO)-MgO-SiO$_2$-H$_2$O-CO$_2$ system and

29   *T/P-X*(CO$_2$) petrogenetic grids and pseudosections predict the prograde (1.7 GPa, 560°C) growth of

30   dolomite in equilibrium with diopside and forsterite through the breakdown of antigorite +

31   aragonite. In a H$_2$O-CO$_2$ saturated system, the subsequent H*P*-UH*P* evolution is predicted in the

32   Di+Fo+Dol+Arg stability field in equilibrium with a dominantly aqueous COH fluid

33   (0.0003<*X*(CO$_2$)<0.0008), whose composition is internally buffered by the equilibrium assemblage.

34   Thermodynamic modelling indicates that neither the consumption nor the growth of new dolomite

35   generations at UH*P* conditions can have been induced by metamorphic reactions. The abundant

36   primary H$_2$O + Cal + Dol + Cl-rich Tr + Cl-rich Tlc ± chloride fluid inclusions present in UH*P* Cpx

37   indicate that a dominantly aqueous, saline (salinity > 26.3 wt% of NaCl$_{eq}$) COH fluid, containing

38   Ca, Mg, and Si as dissolved cations was present during the growth of the UH*P* assemblage

39   Dol+Cpx+Ol+Arg.

40   The complex zoning of dolomite is therefore interpreted as due to protracted episodes of dissolution

41   and precipitation in saline aqueous fluids at H*P*/UH*P* conditions. Kinetics of dolomite dissolution in

42   aqueous fluids is poorly known, and experimental and thermodynamic data under H*P* conditions are

43   still lacking. Data on calcite indicate that dissolution at H*P* is enhanced by a prograde increase in

44   both *P* and *T*, by high salinity in aqueous fluids, and/or low pH conditions. In the studied marble,

45   the *P-T* path and the occurrence of free high-saline fluids represent favourable conditions i) for the

46   inferred dissolution-precipitation processes of the stable dolomite in a closed system; ii) for possible

47   migration of the dissolved carbonate, if the system would have been open during subduction.

48

49   **Keywords:** subduction, zoned dolomite, cathodoluminescence, micro-Raman spectroscopy,

50   thermodynamic modelling, COH fluid, dissolution-precipitation.

51

INTRODUCTION

53 In the long-term global carbon cycle, the flux of carbon released in the Earth's interior by

54 subduction is directly connected with that released from volcanic arcs and, ultimately, can

55 contribute to climate variability. The still poorly constrained nature and composition of the COH

56 fluids generated during deep (i.e., at ultra-high pressure conditions) subduction, such as their fate in

57 the Earth's interior, are responsible for the highly controversial estimations of carbon fluxes to the

58 exosphere (e.g., Kelemen and Manning, 2015). In this context, metamorphic evolution of

59 carbonates during subduction plays an important role, because they are relevant constituents of the

60 altered oceanic crust and of the sedimentary materials in convergent settings.

61 Thermodynamic modelling on natural samples and experimental data indicate that carbonates are

62 resistant to metamorphic decarbonation and to melting during relatively cold subduction, i.e. such

63 as that experienced by the Units of the Western Alps (e.g. Castelli, 1991; Ballévre and Lagabrielle,

64 1994; Molina and Poli, 2000; Kerrick and Connolly, 2001 a, b; Connolly, 2005; Dasgupta et al.,

65 2005; Gorman et al., 2006; Castelli et al., 2007; Poli et al., 2009; Mposkos et al., 2010), although

66 some exceptions from natural samples are reported (e.g., Cook-Kollars et al., 2014). Experiments

67 on (Ca, Fe, Mg)-carbonates indicate that they are stable at high pressure (e.g., Gorman et al., 2006;

68 Poli et al., 2009; Dasgupta and Hirschmann, 2010; Tumiati et al., 2013; Schmidt and Poli, 2014).

69 Experiments on a basaltic composition in the presence of a H_2O-CO_2 mixed fluid demonstrate that

70 calcite is stable at $P \leq 1.4$ GPa, dolomite at P between 1.4 and 1.8 GPa, and dolomite and magnesite

71 at $P \geq 1.8$ GPa (Molina and Poli, 2000). Experiments at high pressure show that dolomite can be

72 stable up to ca. 5 GPa and 600°C (e.g., Buob et al., 2006; Hammouda et al., 2011; Luth, 2001;

73 Martinez et al., 1996; Morlidge et al., 2006; Sato and Katsura, 2001). At higher P-T conditions,

74 dolomite breakdowns to produce magnesite + aragonite, and the natural occurrence of this mineral

75 assemblage has been considered as evidence for geothermic gradients near or below the "forbidden

76 zone" (i.e. < 5°C/km; e.g. Zhu and Ogasawara, 2002; Zhang et al., 2003; Proyer et al., 2013).

77 However equilibrium/disequilibrium microstructures between magnesite and aragonite and their Fe-

78 contents must be carefully considered (e.g., Smit et al., 2008; Korsakov et al., 2009; Proyer et al.,

79 2013; Li et al., 2014; Liu et al., 2015).

80 Although thermodynamic modelling and experimental studies suggest that carbonates are mostly

81 recycled into the mantle at subduction zones, increasing natural evidence testifies for a significant

82 mobility of COH fluids during subduction. During the prograde evolution or at peak *P-T* conditions,

83 fluid-rock interactions between COH fluids and surrounding rocks can occur either at a local-scale,

84 i.e. in a relatively closed system (e.g. Philippot and Selverstone 1991; Ishida et al., 2003; Frezzotti

85 et al., 2011; Gao et al., 2014), or in an open system, as testified by the occurrence of veins and

86 alteration zones within eclogite-facies rocks (e.g., Gao and Klemd, 2001; Ague and Nicolescu,

87 2014). Moreover, the wide occurrence of COH fluids during deep subduction is suggested by the

88 relatively common presence of carbonates, often associated with microdiamonds, as solids

89 precipitated in fluid inclusions and multiphase-solid inclusions in high pressure (HP) and ultra-high

90 pressure (UHP) crustal and mantle rocks from Dabie-Sulu (e.g., Fu et al., 2003; Ferrando et al.,

91 2005; Gao et al., 2014), Kokchetav (e.g., Dobrzhinetskaya et al., 2003; Hwang et al., 2006;

92 Korsakov and Hermann, 2006), Western Gneiss Region (e.g., Svensen et al., 1999; Carswell and

93 van Roermund, 2005), Moldanubian Zone (Naemura et al., 2009), Erzgebirge (e.g.,

94 Dobrzhinetskaya et al., 2007), Rhodope (Mposkos et al., 2009), Tauern Window (Selverstone et al.,

95 1992), Dora-Maira (e.g., Philippot et al., 1995; Ferrando et al., 2009), Monviso (Philippot and

96 Selverstone, 1991), Lago di Cignana (Frezzotti et al., 2011; for a review see Frezzotti and Ferrando,

97 2015). Whereas in deep and hot subduction regimes, such as that recorded by the Kokchetav

98 Massif, the possible melting of carbonates can generate carbonatitic liquids rich in CO_2 (e.g,

99 Korsakov and Hermann, 2006; Grassi and Schmidt, 2011; Gao et al., 2014; Poli, 2015), in deep and

100 cold subduction settings, such as the UHP Units of the Western Alps, the carbon fractionation in a

101 liquid phase can be induced by dissolution of carbonates in aqueous fluids released by the

102 breakdown of hydrous phases (e.g., Caciagli and Manning, 2003; Frezzotti et al., 2011, 2014;

4

103   Manning et al., 2013; Pan et al., 2013). Thermodynamic modelling in H_2O-CO_2 mixed volatile

104   systems indicates that these fluids are H_2O-dominated (e.g., Castelli, 1991; Wang and Liou, 1993;

105   Ballévre and Lagabrielle, 1994; Kato et al., 1997; Ogasawara et al., 1998; Omori et al., 1998;

106   Ogasawara and Aoki, 2005; Castelli et al., 2007; Proyer et al., 2008; Massonne, 2011; Droop, 2013;

107   Liu et al., 2015). Accordingly, Raman analyses of C species in UH*P* aqueous fluid inclusions in

108   oceanic metasediments from Lago di Cignana (Frezzotti et al., 2011; 2014) revealed the presence of

109   oxidized carbon dissolved as CO_3^{2-}(aq) and HCO_3^-(aq), along with hydrous and hydrated

110   carbonates and diamond, and no detectable CO_2. Recent experimental and theoretical researches on

111   dissolution of carbonates are in agreement with observations on natural samples (Manning et al.,

112   2013 and references therein). The spectroscopy experiments at 25-650 °C and 0.5-30 GPa

113   performed by Martinez et al. (2004), Sanchez-Valle et al. (2013) and Facq et al. (2014) reveal the

114   dominant presence of carbonate ions, similar to those found in the Lago di Cignana rocks, in UH*P*

115   aqueous fluids.

116   Among carbonates, dolomite from UH*P* rocks is the best candidate to investigate the poorly known

117   evolution of carbonates during cold subduction. In fact, experiments on dolomite, calcite and

118   magnesite at 700-800°C and 0.3 GPa (Davis et al., 2011) reveal that the constant rate of grain

119   growth for dolomite is three orders of magnitude lower than that of calcite and more than one order

120   lower than that of magnesite. This implies that zoning is a common feature in dolomite, making it

121   able to preserve evidence for its prograde-to-peak evolution (e.g., Li et al., 2014). Moreover, the

122   process of dolomite dissolution still remains unclear in both sedimentary and metamorphic

123   petrology. In fact, the thermodynamics of dolomite solubility in water are difficult to be

124   constrained, even at diagenetic conditions, because of its slow rate of dissolution and its

125   incongruent dissolution behaviour (e.g., Busenberg and Plummer, 1982; Hardie, 1987).

126   Polymetamorphic impure calcite-dolomite marbles from the well known UH*P* Brossasco-Isasca

127   Unit of the southern Dora-Maira Massif (Italian western Alps) (Fig. 1) are promising rocks to

128   investigate the H*P*-UH*P* dolomite evolution. In this paper, we describe zoned dolomite

129   porphyroclasts showing evidence for their destabilization and growth close to metamorphic peak *P-*

130   *T* conditions, and occurring in impure calcite-dolomite marbles belonging to different chemical

131   systems. To characterize the processes involved in the consumption/growth of dolomite, a detailed

132   microstructural study, coupled with mineral chemistry, thermodynamic modeling and fluid

133   inclusion study are performed on a sample referring to the simple $CaO-(FeO)-MgO-SiO_2-COH$

134   system. The data suggest dissolution-precipitation mechanisms, instead of metamorphic reactions,

135   to explain the dolomite evolution. To our knowledge, this is the first report of dolomite dissolution-

136   precipitation processes occurred in marbles from continental crust involved in cold subduction. Our

137   results suggest that in cold subduction settings, carbonate dissolution in aqueous fluids, rather than

138   metamorphic decarbonation, is the crucial process controlling the mobility of carbon in and from

139   the subducting plate.

140

141   GEOLOGICAL BACKGROUND AND FIELD DESCRIPTION

142   The Brossasco-Isasca Unit (BIU) is a small tectonic sheet of continental crust belonging to the

143   Southern Dora-Maira Massif (Compagnoni et al., 2012; Fig. 1a). Two lithostratigraphic complexes

144   have been distinguished in the BIU (Compagnoni et al., 1995). The "Monometamorphic Complex"

145   is derived from the Alpine tectonic and metamorphic reworking of Permian (275 Ma; Gebauer et

146   al., 1997) granitoids and consists of metagranitoid, augen-gneiss, fine-grained orthogneiss, garnet +

147   jadeite + kyanite + quartz granofels, and the Mg-metasomatic rocks (pyrope-bearing whiteschist) in

148   which natural coesite was discovered and studied for the first time (Chopin, 1984). The

149   "Polymetamorphic Complex" is derived from the Alpine reworking of a Variscan amphibolite-

150   facies metamorphic basement that locally experienced a low-*P* static recrystallisation related to the

151   intrusion of the Permian granitoids (Fig. 1b; Groppo et al., 2007a). This Complex mainly consists of

152   paraschists that include bodies of eclogites, marbles, and calc-silicate rocks.

153   The *P-T-t* Alpine evolution of the BIU has been constrained from different lithologies such as

154   whiteschist (Duchêne et al., 1997; Gebauer et al., 1997; Compagnoni and Hirajima, 2001; Hermann,

155   2003; Vaggelli et al., 2006; Ferrando et al., 2009; Gauthiez-Putallaz et al., 2016), marble (Ferraris et

156   al., 2005; Di Vincenzo et al., 2006; Castelli et al. 2007; Groppo et al., 2007a), eclogite (Di

157   Vincenzo et al., 2006; Groppo et al., 2007b), calc-silicate rocks (Rubatto and Hermann, 2001), and

158   orthogneiss (Di Vincenzo et al., 2006). Figure 1b reports the Variscan and Alpine evolution of the

159   BIU as inferred from all these data. The Alpine BIU evolution is characterized by: 1) a prograde

160   stage at ~1.6 GPa and ≤600 °C, recorded in relict metapelitic xenoliths partly metasomatized during

161   stage 2; 2) prograde dehydration reactions and local Mg-metasomatism along shear zones (i.e.,

162   subduction-related whiteschist genesis) at 1.7–2.1 GPa and 560–590 °C; 3) prograde dehydration

163   reactions, and local progressive Mg-metasomatism, with development of a (relict) prograde

164   foliation recorded in whiteschists and marbles, in the large *P-T* range of ~2.2-2.8 GPa and ~590-640

165   °C (i.e., up to the quartz-coesite transition) and dated at ~41-35 Ma; 4) local UH*P* prograde

166   dehydration reactions in whiteschists at 3.5-4.0 GPa and 700-730°C dated at ~ 35 Ma, and UH*P*

167   peak recorded by all studied lithologies at ~4.0–4.5 GPa and 730-750 °C and dated at ~35 Ma; 5) an

168   early, almost isothermal, decompression with development of the UH*P* main regional foliation,

169   locally observed in the BIU lithologies, at ~3.7-4.0 GPa and ~720-740°C; 6) a decompression

170   coupled with cooling recorded in marbles and whiteschists at ~3.0 GPa and ~700°C (i.e., still in the

171   coesite stability field); 7) a decompression coupled with cooling recorded in marbles, eclogites and

172   whiteschists at ~2.5-2.7 GPa and ~650-690°C (i.e., in the quartz stability field); 8) an almost

173   isothermal decompression recorded in marbles at ~2.0 GPa and ~640-660°C; 9) a further

174   decompression with moderate cooling recorded in marbles, eclogites, whiteschists and

175   orthogneisses at ~1.2-1.4 GPa and ~610-640°C; 10) a decompression coupled with cooling recorded

176   in calc-silicate rocks and marbles at ~0.7-1.0 GPa and ~530°C and dated at ~33 Ma; 11) a

177   decompression coupled with heating recorded in calc-silicate rocks and marbles at ~0.5 GPa and

178   ~550°C and dated at ~32 Ma, and a further cooling at greenschist facies conditions.

179   In the BIU, pure and impure calcite marbles, impure calcite-dolomite marbles, and carbonate-

180   silicate rocks are usually hosted within the paraschists of the "Polymetamorphic Complex" as

181   lenses, from a few metres to tens of metres long and from a few dm to several metres thick, that

182   locally contain thin discontinuous interlayers of micaschist and boudins of eclogite. The

183   polymetamorphic evolution of these marbles is usually described by variations in the silicate

184   mineral assemblages. Pre-Alpine minerals are mainly observed in calcite-dolomite marbles and

185   consist of HT minerals such as spinel and ilmenite (Groppo et al., 2007a). Prograde phengite has

186   been recognised in calcite marbles (Ferraris et al., 2005). UHP Na-clinopyroxene, garnet (or epidote

187    $s.l.$), phengite, and rutile (or titanite) are observed in calcite marbles (Ferraris et al., 2005; Castelli et

188   al., 2007) and in calc-silicate rocks (Rubatto and Hermann, 2001), whereas UHP corundum and

189   chlorite locally occur in calcite-dolomite marbles (Castelli et al., 2007). Retrograde garnet, epidote

190    $s.l.$, white mica, Mg-hornblende, diopside + plagioclase symplectites, biotite, titanite, quartz are

191   recognised in calcite marbles (Ferraris et al., 2005; Castelli et al., 2007) and in calc-silicate rocks

192   (Rubatto and Hermann, 2001), and chlorite, Na-margarite, högbomite, and ilmenite in calcite-

193   dolomite marbles (Castelli et al., 2007; Groppo et al., 2007a).

194   The studied samples have been collected from the largest marble lenses in the BIU, i.e. those of

195   Costa Monforte (Castelli et al., 2007) and Isasca (Fig. 1a), both characterized by a medium- to

196   coarse-grained fabric with local occurrence of mylonitic fabric within shear zones. These lenses

197   consists of impure calcite-dolomite marbles with scattered and lens-shaped silicates-rich domains,

198   from few centimetres to some decimetres in thickness (i.e., banded marbles), set parallel to the

199   early-retrograde UHP regional foliation (Fig. 1b) and characterized by distinct mineral

200   assemblages. The banded structure likely derives from primary differences in the marble's protolith.

201   Most of the impure calcite-dolomite marbles can be described in the complex Na_2O-K_2O-CaO-FeO-

202   MgO-Al_2O_3-SiO_2-COH (NKCFMAS-COH) system (i.e., white mica $\pm$ Cpx $\pm$ Zo $\pm$ Grt $\pm$ Amp $\pm$

203   Chl $\pm$ Qz calcite-dolomite marbles; mineral abbreviation according to Whitney and Evans, 2010) or

204   in the (Na_2O)-CaO-FeO-MgO-(Al_2O_3)-SiO_2-COH ((N)CFM(A)S-COH) system (i.e., Cpx $\pm$ Amp $\pm$

205   Chl calcite-dolomite marbles). On the contrary, Chl ± Atg ± Tr ± Ol ± Di calcite-dolomite marbles

206   referring to the CaO-(FeO)-MgO-SiO$_2$-COH (C(F)MS-COH) system only occur in minor volumes

207   (Table 1). Evidence for chemical interaction among the chemically distinct layers are lacking.

208

209   **METHODS**

210

211   The characterization of mineral assemblages, microstructures, mineral phase compositions and fluid

212   inclusions have been obtained combining optical, cathodoluminescence and back-scattered electron

213   microscope observations, WDS and SEM-EDS analyses, micro-Raman spectroscopy and micro-

214   XRF maps.

215

216   **Cathodoluminescence**

217   Cathodoluminescence images were collected at the Department of Earth Sciences (University of

218   Torino, Italy) with a microscope performed with CITL 8200 mk3 equipment. Operating conditions

219   were 17 kV and 400 mA. The luminescence of minerals, in particular of carbonates (e.g.,

220   Habermann et al., 1996, 1998), is suppressed by some major or trace elements (typically Fe, Sr) and

221   activated by others (typically Mn, Na, Ti, Sm, Dy, Tb). The Fe/Mn ratio, in particular, is more

222   important than their absolute concentrations (e.g., Jarc and Zupancic, 2009). Crystallographic

223   structure, reticular defects, and crystallographic orientation of minerals also influence their

224   luminescence (e.g., Schertl et al., 2004).

225

226   **Mineral chemistry**

227   Compositions of minerals in sample DM675 were obtained using a JEOL 8200 Superprobe (WDS)

228   at the Department of Earth Sciences, University of Milano (Italy). Acceleration voltage was set to

229   15 kV, beam current was 5 nA, beam diameter was 5 μm. Back-scattered electron images and

230   composition of minerals from the other samples were collected with a JEOL JSM 6310 scanning

231   electron microscope equipped with an Oxford Link ISIS EDS spectrometer and a Microspec WDS

232   spectrometer (for Na and F) at the University of Graz (Austria). Analytical conditions were 15 kV

233   accelerating voltage and 6 nA probe current for silicates and 2 nA for carbonates, respectively, with

234   a 1–2 μm diameter of the focused beam. In both cases, natural minerals were used as standards and

235   a $\rho\Phi Z$ routine was used for matrix correction. Mineral phase compositions are reported in Tables 2,

236   3 and Supplementary Table S1.

237   The solids within primary fluid inclusions in diopside (sample DM675) were analyzed with a

238   Cambridge Stereoscan 360 SEM equipped with an EDS Energy 200 and a Pentafet detector (Oxford

239   Instruments) at the Department of Earth Sciences, University of Torino. The operating conditions

240   were as follows: 50 s counting time and 15 kV accelerating voltage. SEM–EDS qualitative data

241   (spot size = 2 μm) were acquired and processed using the Microanalysis Suite Issue 12, INCA Suite

242   version 4.01.

243

244   **Micro-Raman spectroscopy**

245   Micro-Raman spectra and maps were acquired using the integrated micro/macro-Raman LABRAM

246   HRVIS (Horiba Jobin Yvon Instruments) of the Interdepartmental Center "G. Scansetti"

247   (Department of Earth Sciences, University of Torino, Italy), equipped with a computer-controlled,

248   automated X–Y mapping stage. Excitation lines at 532 nm (solid-state Nd laser and 80 mW of

249   emission power) were used, with Edge filter and a grating of 600 grooves/mm. Calibration was

250   performed using the 520.6 cm^{-1} Si band. Each spectrum was collected by 3-5 accumulations of 5-20

251   s and with a laser spot of 2 μm. The map of 16 μm x 16 μm, with steps of 0.5 μm and a laser spot of

252   2x2 μm, was acquired by one accumulation of 5 s, each step.

253

254   **Micro-X-ray fluorescence (μ-XRF) map**

255   The micro-XRF map of the whole thin section of sample DM675 were acquired using a μ-XRF

256   Eagle III-XPL spectrometer equipped with an EDS Si(Li) detector and with an Edax Vision32

10

257 microanalytical system (Department of Earth Sciences, University of Torino, Italy). The operating

258 conditions were as follows: 100 ms counting time, 40 kV accelerating voltage and a probe current

259 of 900 μA. A spatial resolution of about 65 μm in both x and y directions was used. Quantitative

260 modal percentages of each mineral were obtained by processing the μ-XRF maps with the software

261 program ''Petromod'' (Cossio et al. 2002).

262

263 **Phase diagrams computation**

264 Phase diagrams in the CaO-(FeO)-MgO-SiO$_2$–H$_2$O-CO$_2$ (C(F)MS–H$_2$O-CO$_2$) system were

265 calculated using Perple_X (version 6.7.2, Connolly 1990, 2009) and the thermodynamic dataset and

266 equation of state for H$_2$O-CO$_2$ fluid of Holland and Powell (1998, revised 2004). Being impossible

267 at this stage to model all the complexities of UHP COH fluids due to the presence of silica and

268 alkalis as dominant solutes at UHP conditions, as well as of dissolved carbon species, our

269 calculations are limited to binary H$_2$O-CO$_2$ fluid (see e.g. Castelli et al., 2007) (note the different

270 notations: C(F)MS-COH, used to describe the relevant mineral assemblages, and C(F)MS-H$_2$O-

271 CO$_2$, used for the thermodynamic modelling). This also implies that it is not possible, at this stage,

272 to model processes different from the "classical" metamorphic reactions using the conventional

273 thermodynamic modelling approach.

274 For the calculation of the P/T-X(CO$_2$) grid and mixed-volatile P-T projection in the CMS-H$_2$O-CO$_2$

275 system, the following solid end-members were considered: aragonite/calcite, brucite, dolomite,

276 diopside, forsterite, magnesite, quartz/coesite, talc and tremolite in addition to the binary H$_2$O-CO$_2$

277 fluid (Connolly and Trommsdorff, 1991).

278 For the calculation of the P/T-X(CO$_2$) pseudosection in the CFMS-H$_2$O-CO$_2$ system, the following

279 solid solution models were used: amphibole (ideal model for tremolite), clinopyroxene, olivine and

280 dolomite (Holland and Powell 1998), in addition to the binary H$_2$O-CO$_2$ fluid. Calcite/aragonite and

281 quartz/coesite were considered as pure end-members. The bulk rock composition of sample DM675

282 has been calculated by combining the mineral proportions obtained from the modal estimate of

11

283   micro-XRF map with mineral chemistry acquired at WDS. In addition, as the studied sample shows

284   a banded structure, the bulk composition has been calculated for the olivine-rich layer with the most

285   abundant zoned dolomite crystals. Calculation of the bulk composition has be obtained starting

286   from the vol% of each mineral and from their compositions, and considering the molar volume of

287   each phase.

288

289   **AN OVERVIEW OF THE IMPURE CAL-DOL MARBLES**

290   In this section, an overview, not necessarily exhaustive, of the microstructures and mineral

291   compositions essential for the comprehension of the complex tectono-metamorphic evolution of the

292   impure calcite-dolomite marbles is reported.

293   The sampled impure calcite-dolomite marbles show a granoblastic, polygonal to mortar,

294   microstructure. Locally, the early-retrograde UHP regional foliation (see Fig. 1b) is recorded and,

295   depending on the local bulk composition (i.e., NKCFMAS-COH, (N)CFM(A)S-COH, or C(F)MS-

296   COH systems; see above and Table 1), is mainly defined by the preferred orientation of phengite,

297   Mg-chlorite, clinopyroxene and/or by silicate-rich layers wrapping around porphyroblastic

298   dolomite, clinopyroxene and olivine, or garnet, and/or zoisite (Fig. 2a-b; Fig. 3a-b). (Mg-)calcite

299   occurs in the rock matrix as weakly-deformed, coarse-grained relics with irregular grain boundaries,

300   or as medium-grained neoblasts. Locally, it includes vermicular inclusions of dolomite.

301   Considering the prograde- to early-retrograde evolution, at least four metamorphic events can be

302   recognized based on distinct silicate mineral assemblages (Fig. 4), which depend on local bulk

303   composition: i) HT-LP pre-Alpine event characterized by Ti-rich (Ti = 0.06 a.p.f.u.) andradite-rich

304   garnet (Fe^{3+} = 0.02 a.p.f.u; Ca = 2.453 a.p.f.u.; Table 2; Fig. 2c-d), Fe-Na rich diopside with Ca-

305   tschermak component (Mg = 0.946-0.99 a.p.f.u., Al = 0.017-0.09 a.p.f.u., Fe$_{tot}$ = 0.02-0.042 a.p.f.u.,

306   Na = 0.006-0.010 a.p.f.u.), forsterite with relatively (i.e. compared to the other forsterite

307   generations) low Mg# [Mg/(Mg+Fe^{2+}) = 0.983)], pargasite, talc, ilmenite, and magnetite; ii) HP

308   Alpine prograde event (stages 2 or 3 in Fig. 1b) represented by Ti-Ca-poor (Ti = 0.01 a.p.f.u., Ca =

309   1.97 a.p.f.u.) almandine-rich garnet (Fe^{2+} = 0.23 a.p.f.u., Fig. 2d), Na-bearing diopside (Mg =

310   0.978-0.988 a.p.f.u., Al = 0.006 a.p.f.u., Fe_{tot} = 0.011-0.019 a.p.f.u., Na = 0.004-0.006 a.p.f.u.),

311   forsterite with high Mg# (0.994), talc, phengite, zoisite, and titanite; iii) UHP peak event (stage 4 in

312   Fig. 1b) recorded by Ti-Fe-poor (Ti = 0.01 a.p.f.u., Fe^{2+} = 0.21 a.p.f.u), grossular-rich (Ca = 2.07

313   a.p.f.u.) garnet (Fig, 2e), almost pure diopside (Mg = 0.987-1.010 a.p.f.u., Al $\leq$ 0.003 a.p.f.u., Fe_{tot} =

314   0.001-0.008 a.p.f.u., Na $\leq$ 0.001 a.p.f.u.), forsterite with high Mg# (0.993), phengite (Si = 3.53

315   a.p.f.u.), zoisite, and rutile; iv) UHP early-retrograde event locally developing the regional foliation

316   (stage 5 in Fig. 1b; Fig. 2a-b; Fig. 3a-b) and recorded by Na-bearing diopside (Mg = 0.991-1.000

317   a.p.f.u., Al $\leq$ 0.001 a.p.f.u., Fe_{tot} = 0.006-0.009 a.p.f.u., Na = 0.004 a.p.f.u., Fig. 2f), phengite,

318   forsterite with the highest Mg# (0.995), Mg-chlorite, Al-rich antigorite, phlogopite (Mg# = 0.92),

319   Na-bearing tremolite, Al-F-rich (Al = 0.18 a.p.f.u.; F = 0.106 a.p.f.u) titanite. The late-retrograde

320   undifferentiated events (stages 6-11 in Fig. 1b) are represented by Mg-chlorite, antigorite, Mg-

321   hornblende, tremolite variably enriched in Na-Al-Fe (Fig. 2f), Na-bearing diopside (Mg = 0.990-

322   0.995 a.p.f.u., Al = 0.001-0-003 a.p.f.u., Fe_{tot} = 0.002-0.011 a.p.f.u., Na = 0.002-0.003 a.p.f.u.),

323   forsterite, epidote *s.l.*, phlogopite, talc, and Al-F poor (Al = 0.10 a.p.f.u.; F = 0.065 a.p.f.u) titanite.

324   In all impure calcite-dolomite marble types, dolomite occurs as sub-rounded pre-kinematic

325   porphyroblasts (Fig. 2a-c, g-h; Fig. 3) with curved, irregular or lobed grain boundaries, and it shows

326   a more rigid behaviour than calcite. Under both SEM (back-scattered electron images, BSE; Figs.

327   2c-d, e, g) and cathodoluminescence (CL; Fig. 2h; Figs. 3a, c-d), dolomite usually shows distinct

328   stages of growth, coupled with chemical variations and distinct mineral inclusions depending on the

329   local bulk composition and *P-T* conditions. Dol I constitutes a dark-gray (BSE), light- to medium-

330   red (CL) relic inner core rich in Cal component and locally including pre-Alpine mineral

331   assemblage (Figs. 2c-e, g-h; Figs. 3a, d). Dol II constitutes a dark-gray (BSE), medium-to-light red

332   (CL) outer core poor in Cal component and replacing, or concentrically overgrowing, the inner core

333   and locally including HP mineral assemblage (Fig. 2c-d, g-h, Fig. 3a, c-d). Dol III constitutes a

334   medium-gray (BSE), dark-red (CL) inner rim, with intermediate Cal-component, locally including

13

335   the UHP mineral assemblage (Fig. 2e), and asymmetrically overgrowing the partly reabsorbed core

336   (Figs. 2c, e, g-h; Fig. 3). Dol IV constitutes a light-gray (BSE), poorly luminescent (CL) outer rim

337   poor in Cal component, locally including early-retrograde mineral assemblages (Fig. 2g) and

338   overgrowing the inner rim in sharp discontinuity and locally without preserving its crystallographic

339   orientation (Figs. 2c-e, g-h; Fig. 3).

340

341   **SIMPLIFYING THE PROBLEM: AN EXAMPLE FROM THE CAO-(FEO)-MGO-SIO$_2$-COH SYSTEM**

342   As evident from the previous section, the different local bulk compositions produce a large

343   variability in the silicate mineral assemblages referring to the same metamorphic stage. Their

344   correlation is nevertheless possible, comparing microstructural relationships (with respect to the

345   main foliation and/or to mineral inclusions) and/or trend of variation in mineral compositions, and

346   allows unambiguous interpretation of the prograde to early-retrograde evolution of dolomite (Fig.

347   4). The HP-UHP dolomite evolution can be more easily characterized and modelled in the

348   chemically-simple C(F)MS-COH system, well represented by the impure Cal-Dol marble sample

349   DM675 (Table 1).

350

351   **The Chl ± Tr ± Atg ± Ol ± Di calcite-dolomite marble**

352   Sample DM675 is representative of mm-banded marble whose phase assemblages can be modelled

353   in the C(F)MS-COH system; each layer contains different modal amounts of calcite, dolomite,

354   clinopyroxene, and olivine (Fig. 5). In particular, the sample consists of Mg-calcite, porphyroblasts

355   of dolomite (Figs. 6a-c), porphyroblastic and neoblastic diopside (Figs. 6b-d), porphyroblastic and

356   neoblastic forsterite (Figs. 6a-b, d), and very minor retrograde antigorite (Figs. 6a, c-d), tremolite

357   and Mg-chlorite (Fig. 4).

358   Different generations of dolomite, diopside and forsterite have been recognized on the basis of

359   microstructural evidence (optical and CL microscopy) and mineral composition. Although BSE

14

360   images do not reveal a strong chemical zoning, WDS analyses reveal minor, but systematic,

361   changes in mineral compositions among the different generations.

362   In the zoned **dolomite** porphyroblasts, the four generations previously described (Fig. 4) are clearly

363   recognizable only under cathodoluminescence (Figs. 6a–b). The relict pre-Alpine inner core (Dol I)

364   is characterized by high $CaCO_3$ ($Cal_{51.05-51.18}$), low $MgCO_3$ ($Mgs_{48.69}$) and relatively low $FeCO_3$

365   ($Sd_{0.08-0.17}$) components (Figs. 7a-b and Table 3). The prograde outer core (Dol II: $Cal_{49.94-}$

366    $_{50.13}Mgs_{49.72-49.92}Sd_{0.06-0.09}$), concentrically overgrowing Dol I, shows a decrease in $CaCO_3$ and

367    $FeCO_3$ and an increase in $MgCO_3$. The peak inner rim overgrows Dol II with sharp and irregular

368   contacts (Figs. 6a–b) and has variable intermediate compositions (Dol III: $Cal_{50.33-50.77}Mgs_{49.03-}$

369    $_{49.49}Sd_{0.11-0.19}$). Early-retrograde Dol IV in the inner rim also shows irregular, re-entrant and sharp

370   contacts and, locally, different crystallographic orientation. It shows compositions similar to Dol II

371   (Dol IV: $Cal_{49.97-50.07}Mgs_{49.80-49.81}Sd_{0.01-0.13}$). MnO is present in all dolomite generations and ranges

372   from 0.001 to 0.097 wt%. The Mn/Fe ratio in the different dolomite generations (Fig. 7c) seems

373   correlated to the CL color, being broadly in the range: 0.2-0.5 (Dol I: light red), 0.6-0.7 (Dol II:

374   bright yellow) and 0.05-0.5 (Dol III: light-to-medium red). Data for Dol IV (dark red) are more

375   ambiguous, being the Mn/Fe ratio more variable.

376   **Clinopyroxene** is always an almost pure diopside. It occurs both as porphyroblasts, with preferred

377   dimensional orientation that locally define the early-retrograde regional foliation, and stubby

378   neoblasts. Under CL both porphyroblasts and neoblasts show a relatively irregular zoning that

379   corresponds to slight chemical variations. Five generations of diopside are recognized (Figs. 6b-d;

380   7d). The pre-Alpine Cpx I occurs as very rare relict cores, brown under CL, within the

381   porphyroblasts. Cpx I is Fe-Na bearing in composition (Mg = 0.946 a.p.f.u., Al = 0.017 a.p.f.u.,

382   Fe_{tot} = 0.042 a.p.f.u., Na = 0.010 a.p.f.u.; Table 2 and Fig. 7d) and it is the only generation of

383   diopside with significant amount of the Ca-tschermak component. The H*P* prograde Cpx II,

384   constituting the red (CL) core of porphyroblasts (Fig. 6d), has higher Mg and lower Na and Fe

385   contents (Mg = 0.978-0.988 a.p.f.u., Al = 0.006 a.p.f.u., Fe_{tot} = 0.011-0.019 a.p.f.u., Na = 0.004-

386   0.006 a.p.f.u.) with respect to Cpx I. The peak Cpx III, from yellow-orange to yellow-green under

387   CL, constitutes the core of neoblasts and inhomogeneous portions in the core of porphyroblasts

388   (Fig. 6d). Cpx III is a pure diopside (Mg = 0.987-1.010 a.p.f.u., Al $\leq$ 0.003 a.p.f.u., Fe_{tot} = 0.001-

389   0.008 a.p.f.u., Na is below detection limit). Early-retrograde Cpx IV, yellow under CL, constitutes

390   the outer core of neoblasts and inhomogeneous portions in the rim of porphyroblasts (Fig. 6b, d). It

391   has Mg and Fe content similar to peak Cpx III, but it has slightly higher Na content (Mg = 0.991-

392   1.000 a.p.f.u., Al $\leq$ 0.001 a.p.f.u., Fe_{tot} = 0.006-0.009 a.p.f.u., Na = 0.004 a.p.f.u.). Retrograde light

393   blue (CL) Cpx V asymmetrically overgrows Cpx IV in sharp discontinuity (Fig. 6b, d) and shows

394   lower Na content (Mg = 0.990-0.995 a.p.f.u., Al = 0.001-0-003 a.p.f.u., Fe_{tot} = 0.002-0.011 a.p.f.u.,

395   Na = 0.002-0.003 a.p.f.u.).

396   Under CL, forsterite is dark-red (Fig. 6a-b, d) and, as expected for this chemical system, evidence

397   for chemical zoning is apparently lacking in BSE images. However, at least four possible

398   generations of olivine, forsteritic in composition, seems to be present in textural equilibrium with

399   different dolomite and diopside generations (Fig. 4). Pre-Alpine Ol I is present as very rare relics

400   with relatively low Mg# (0.983) compared to the other forsterite generations. Pre-Alpine Ol I occurs

401   as slightly bright (CL) portions in the core of the porphyroblasts. More commonly, porphyroblasts

402   are characterized by Mg# = 0.993-0.994, with the higher Mg# detected in the core (interpreted as

403   prograde Ol II; dark-red under CL; Fig. 6b) and lower Mg# detected in the rim (interpreted as

404   possible peak Ol III; darker-red under CL; Fig. 6b). The neoblasts in textural equilibrium with Cpx

405   IV (Fig. 6d) show the highest Mg# (0.995) and are interpreted as early-retrograde Ol IV.

406

407   **Thermodynamic modelling in the C(F)MS-H$_2$O-CO$_2$ system**

408   *P/T-X*(CO$_2$) petrogenetic grids and pseudosections (Fig. S1), and mixed-volatile *P-T* projection

409   (Fig. 8) have been modelled in the C(F)MS-H$_2$O-CO$_2$ system to predict the production vs.

410   consumption of dolomite through metamorphic reactions along the BIU prograde *P-T* path (Fig.

411   1b). More than 30 univariant and 20 invariant equilibria are modelled by the *P/T-X*(CO$_2$) grid (Fig.

412   S1a). Among them, only 8 univariant (i.e. curves 12-15, 17-18 and 26-27 in Fig. S1a) and two

413   invariant (i.e. points I1 and I13 in Fig. S1b) equilibria can be effectively "seen" by the studied

414   sample, as predicted by the P/T-$X(CO_2)$ pseudosection (Fig. S1b) calculated for the measured bulk

415   composition of sample DM675.

416   Invariant equilibria in the P/T-$X(CO_2)$ grid correspond to fluid-present univariant equilibria in the

417   P-T mixed-volatile projection of Fig. 8 (i.e. curves i1 to i19) (e.g. Baker et al., 1991; Carmichael,

418   1991; Connolly and Trommsdorff, 1991). This implies that the studied impure Cal-Dol marble

419   DM675 is sensitive to only two univariant equilibria (curves i1 and i13 in Fig. 8); both are Dol-

420   forming reactions. More in detail, the mixed-volatile P-T projection predicts that the first, and only,

421   prograde (1.7 GPa - 560°C) growth of dolomite in equilibrium with diopside and forsterite (i.e. the

422   observed assemblage Dol II + Cpx II + Ol II) occurred through the univariant reaction i1 (Fig. 8),

423   i.e through the breakdown of antigorite + aragonite (i.e., 2.0 Arg + 0.1 Atg → 1.0 Di + 1.4 Fo + 1.0

424   Dol + 3.1 $F_{0.0003}$, where F is the fluid with composition expressed as $X(CO_2)$]. In a H_2O-CO_2

425   saturated system, the subsequent HP-UHP prograde, peak and early-retrograde evolution of the

426   studied marble is entirely predicted in the Di + Fo + Dol + Arg stability field. Furthermore, along

427   the prograde and early-retrograde evolution, the composition of the fluid in equilibrium with this

428   mineral assemblage remains constant, because the P-T path is roughly parallel to the isopleths of

429   fluid composition (i.e. the red dotted lines in Fig. 8). This fluid is a dominantly aqueous H_2O-CO_2

430   fluid (0.0003<$X(CO_2)$<0.0008).

431   The observed microstructures combined with the results of phase diagram modelling strongly

432   suggest that the studied marble behaved as an internally buffered system during prograde and early-

433   retrograde evolution, i.e. the equilibrium mineral assemblage controlled the composition of the pore

434   fluid. Two evidences support this hypothesis: (i) the observed microstructures reflect the

435   isothermal/isobaric univariant assemblage Fo + Arg + Di + Dol (i.e. univariant equilibrium 15 in

436   Fig. S1a); for open system behaviour, isothermal/isobaric divariant assemblages would have been

437   instead observed (e.g. Trommsdorff, 1972; Hewitt, 1973; Kerrick, 1974; Rice & Ferry, 1982); (ii) if

438 significant fluid infiltration would have occurred (i.e. if the system was completely externally

439 buffered), either dolomite or olivine would have been completely consumed, depending on the

440 nature of the infiltrating fluid (i.e. either H_2O- or CO_2- rich; Fig. S1b).

441

442 **Fluid inclusion data**

443 Both UH*P* porphyroblastic and neoblastic Cpx III and IV include abundant primary multiphase

444 aqueous inclusions (Fig. 9). They are up to 10 μm long and 5 μm large, and show negative crystal

445 shape and crystallographic orientation. At room temperature the inclusions consist of H_2O (up to 40

446 vol% of the inclusion), locally biphase ($H_2O_L + H_2O_V$; Fig. 9b). Under the optical microscope they

447 include apparently homogenous and birefringent crystals (Fig. 9c), but SEM-EDS qualitative

448 analyses reveal that these solid phases consists of an aggregate of Ca±Mg-carbonates and Cl-rich

449 hydrous Ca- and Mg-silicates. Micro-Raman spectra on these minerals, although showing broad

450 peaks, allow to recognize the carbonates as Mg-calcite (with typical peaks at 1089, 284 and 714 cm^{-1}

451 ^{1}; Fig. 10a), and dolomite (characterized by peaks at 1098, 301, 177, 724 cm^{-1}). One of the silicates

452 results to be tremolite by the peaks at 676, 161, 126, 180, 224, 1063, 855, 303, 932, 417, 357 cm^{-1},

453 and by the OH stretching vibration at 3674 cm^{-1} (Fig. 10). The other silicate is talc, as testified by

454 the peaks at 197, 678, 506, 465, 368 cm^{-1} (Fig. 10b). The intense peak at 3676 cm^{-1} and the very

455 weak one at 3676 cm^{-1}, that are related to the OH stretching vibration of talc, arises from a large

456 band centred at about 3680 cm^{-1} which is indicative for the presence of molecular water in its

457 crystallographic structure. More rarely, a small colourless (at the optical microscope) cube that does

458 not produce Raman spectrum (i.e., a chloride) is also visible within the inclusions.

459 The Raman spectral image of a primary fluid inclusions (Fig. 11) allows to visualize the distribution

460 of the solid phases within the inclusions and to qualitatively estimate their volume. Note that the

461 aqueous fluid in the inclusion has no significant Raman signal in the investigated region, and thus

462 does not interfere with the measurements. Mg-calcite constitutes large crystals that occupy about

463 65% of the inclusion volume, in association with a single small (about 5 vol%) crystal of dolomite.

464 Talc rich in Cl (SEM-EDS data) occurs as small crystals (about 10 vol%) around Mg-calcite. The

465 tremolite distribution is impossible to be obtained because its Raman bands are too close to those of

466 the host diopside or, for the OH band, to that of talc. However, it should occupy about 10% of the

467 inclusion volume.

468

469 **DISCUSSION: PREDICTED THERMODYNAMIC STABILITY VS. OBSERVED UNSTABLE BEHAVIOUR OF**

470 **DOLOMITE**

471 The sharp and irregular contacts observed between Dol II and Dol III, and between Dol III and Dol

472 IV suggest the succession of several episodes of corrosion/consumption and growth for the different

473 generations of dolomite. At least three different processes might explain the dolomite consumption

474 and growth at HP/UHP conditions and will be discussed in the following.

475

476 **Dolomite evolution by metamorphic reactions**

477 Although often overlooked (see the dissertation in Poli, 2014), compositional complexities in

478 dolomite have been reported in a few recent papers and mostly interpreted as the product of

479 prograde metamorphic reactions. Li et al. (2014) demonstrate that UHP zoned dolomite can record

480 evidence of the prograde P-T evolution of mafic eclogites from Tianshan, and of their interactions

481 with coexisting fluids. These authors describe metamorphic dolomite with zoning organized in both

482 normal and oscillatory patterns (Shore and Fowler, 1996), and show that this zoning is produced by

483 consecutive prograde metamorphic reactions. A paper by Mposkos et al. (2006) on UHP dolomitic

484 marbles from Rhodope proposes two hypotheses to explain the UHP Ca-rich composition (X_{MgCO3}

485 $= 0.34 – 0.43$) observed at the dolomite rim or along cracks: i) it formed by high temperature (T >

486 850°C) metamorphic reaction involving the destabilization of Mg-calcite, to give aragonite and a

487 disordered dolomite able to incorporate high amounts of Ca (see also Franzolin et al., 2011); ii) it

488 formed by external influx of fluids leaching Mg from carbonates.

489   The irregular, re-entrant and sharp contacts observed in the zoned dolomite crystals investigated in

490   this study are very different from the dolomite zoning described by Li et al. (2014) or Mposkos et

491   al. (2006). Thermodynamic modelling in the C(F)MS-H_2O-CO_2 system (Figs. 8 and Fig. S1)

492   predicts a simple evolution for the BIU Cal-Dol marble and confirms that decarbonation reactions

493   do not occur during subduction, as also reported by previous studies (e.g., Molina and Poli, 2000;

494   Kerrick and Connolly, 2001 a, b; Castelli et al., 2007).

495   In particular, thermodynamic calculations predict the prograde growth of Dol II, in equilibrium with

496   Cpx II and Ol II, at 1.7 GPa and 560°C (i.e. at P-T conditions similar to those of stage 2; Fig. 1).

497   The Dol II -forming reaction involves the destabilization of aragonite coupled with antigorite

498   dehydration (univariant reaction i1 in Fig. 8; isobaric/isothermal invariant point I1 in Fig. S1a) and

499   releases a dominantly aqueous fluid with $0.0003 < X(CO_2) < 0.0008$, which remains within the system.

500   The observed equilibrium assemblage further suggests that the system was internally buffered

501   during the whole prograde-to-peak and early-retrograde evolution (see above), i.e. it evolved along

502   the isobaric/isothermal univariant equilibrium 15 (Fig. S1a) during most of the prograde and early-

503   retrograde evolution. Internal buffering of fluid composition can be achieved either (i) in a

504   completely closed system or, (ii) in cases of limited fluid infiltration, i.e. intermediate conditions

505   between a complete internal buffering behaviour and a complete external buffering behaviour (e.g.

506   Greenwood, 1975; Rice and Ferry, 1982; Ferry, 1983; Ague and Rye, 1999). (i) If buffering

507   occurred in a completely closed system, the progress of reaction 15 was virtually null, i.e. the

508   prograde HP-UHP evolution occurred in the Di + Fo + Dol + Arg stability field without involving

509   any mineral production or consumption. The prograde P-T trajectory, in fact, is parallel to the

510   compositional isopleths of the fluid (Fig. 8): this means that, in order to maintain the equilibrium

511   between the mineral assemblage and the fluid, the reaction should not proceed, otherwise the fluid

512   composition would be shifted toward CO_2-richer compositions. Therefore, complete internal

513   buffering cannot explain either the consumption of Dol II and the growth of peak Dol III during the

514   prograde-to-peak evolution, or the consumption of Dol III and the growth of Dol IV during the

515   peak-to-early-retrograde evolution. (ii) The infiltration of small amounts of a CO_2-rich fluid (i.e.

516   $X(CO_2)>0.0005$) or brines could have driven the isobaric/isothermal univariant reaction 15 (2 Fo +

517   4 Arg + $2CO_2 \rightarrow$ Di + 3 Dol), favouring the formation of dolomite and diopside at the expenses of

518   forsterite and aragonite (now Mg-calcite). Such a process could explain the formation of both peak

519   Dol III + Cpx III and early-retrograde Dol IV + Cpx IV; however, it cannot explain neither the

520   formation of Ol III and Ol IV (microstructurally in equilibrium with Dol III and Dol IV,

521   respectively), nor the corrosion/consumption of Dol II and Dol III. Alternatively, the infiltration of

522   a H_2O-rich fluid (i.e. $X(CO_2)<0.0005$) without dissolved salts could have driven the

523   isobaric/isothermal univariant reaction 15 in the reverse sense (Di + 3 Dol $\rightarrow$ 2 Fo + 4 Arg +

524   $2CO_2$), enhancing the formation of forsterite and aragonite (now Mg-calcite) at the expenses of

525   diopside and dolomite. This process can explain the partial consumption of Dol II during the

526   prograde-to-peak evolution, and of Dol III during the peak-to-early-retrograde evolution. However,

527   it is not able to explain the growth of peak Dol III and Ol III, and of early-retrograde Dol IV and Ol

528   IV.

529   This implies that thermodynamic modelling fails in explaining the complexity of dolomite zoning

530   observed in the studied marbles. In fact, neither the consumption nor the growth of the observed

531   mineral assemblages (Dol III + Cpx III + Ol III; Dol IV + Cpx IV + Ol IV) result to have been

532   induced by metamorphic reactions. Because the thermodynamic modelling approach is not able to

533   explain the observed microstructures, a different process should be envisaged other than the

534   metamorphic reaction process, to explain the observed zoning of the dolomite crystals.

535

536   **Dolomite evolution by "dynamic wetting" of migrating grain boundaries**

537   The irregular, re-entrant and sharp contacts observed in the different dolomite generations from the

538   BIU impure marbles are similar to those described for calcite, replacing former aragonite, in Arg-

539   Dol-bearing calc-schists from Lago di Cignana (Reinecke et al., 2000), and interpreted as due to

540   lattice diffusion and interfacial mass transport linked with a heterogeneous distribution of fluid

541   ("dynamic wetting" of migrating grain boundaries; Reinecke et al., 2000). In the BIU marble, the

542   dolomite zoning cannot be ascribed only to this process because the presence of abundant,

543   crystallographically-oriented, primary multiphase (mainly silicates and carbonates + liquid)

544   aqueous inclusions in UHP diopside coexisting with dolomite indicates migration of carbonate-

545   bearing brines at least at the sample scale (i.e., well interconnected fluid films). Moreover, fluid

546   inclusions dropped from a fluid-filled moving grain boundary should be rounded and distributed

547   along the annealed grain-boundaries (e.g., Roedder, 1984; Craw and Norris, 1993; Schmatz and

548   Urai, 2010), whereas in the studied sample they are evenly distributed.

549

550   **Dolomite evolution by dissolution-precipitation processes**

551   A further process able to explain the observed microstructures in the studied BIU marbles is

552   dissolution-precipitation in aqueous fluids. The kinetics of dolomite dissolution is poorly known.

553   Experimental and thermodynamic studies on dolomite dissolution are commonly performed to

554   reproduce sedimentary conditions (e.g., Plummer and Busenberg, 1982). Experiments on

555   dissolution rates of dolomite at 25°C indicate that dissolved Ca is a strong inhibitor of dolomite

556   dissolution above neutral pH, whereas dissolved Mg has no effect on the dissolution rate

557   (Pokrovsky and Schott, 2001).

558   Experimental and theoretical studies performed on carbonate dissolution at high P-T conditions are

559   rare, and mainly focused on $CaCO_3$ (e.g., Fein and Walther, 1989; Newton and Manning, 2002;

560   Caciagli and Manning, 2003; Martinez et al., 2004; Dolejš and Manning, 2010; Manning et al.,

561   2013; Pan et al., 2013; Sanchez-Valle, 2013; Facq et al., 2014). Experimental data on calcite

562   dissolution during subduction suggest that the process is enhanced by: 1) the increase of both P and

563   T along a subduction geothermal gradient (Doleiš and Manning, 2010); 2) the presence of a saline

564   water (e.g., Newton and Manning, 2002), and in particular the presence of NO^{3-}, Cl^-, SO_4^{2-} (in order

565   of increasing dissolution power; e.g., King and Putnis, 2013); 3) the decrease of pH (e.g., Manning

566   et al., 2013). At least two of these three factors enhancing carbonate dissolution-precipitation

567   processes occurred in the studied impure calcite-dolomite marbles: (1) they experienced a prograde

568   increase in both P and T; (2) the fluid phase present at UHP conditions was a saline COH fluid.

569   From fluid inclusion study, the mineral phases within the inclusions (Mg-calcite + dolomite +

570   tremolite + talc) result to be the hydrous counterpart of the UHP mineral assemblage observed in

571   the studied sample. These minerals cannot be considered as incidentally trapped together with the

572   fluid inclusion because: i) they are present in all inclusions, and ii) both the relatively-broad Raman

573   peaks of minerals and the presence of molecular water in the crystallographic structure of talc (Fig.

574   10) indicate that they are poorly crystalline, and this is a typical feature of solids precipitated from

575   an aqueous fluid phase. In addition, the systematic occurrence of Cl in these hydrous minerals, and

576   the local occurrence of a small chloride within the fluid inclusions, indicate the presence of a saline

577   (fluid salinity > 26.3 wt% of NaCl$_{eq}$) aqueous solution in the inclusions. Thus, fluid inclusion data

578   indicate that the fluid phase present during the UHP evolution of the studied marble was a

579   dominantly aqueous, saline COH fluid, containing Ca, Mg, and Si as dissolved cations. These data

580   are in agreement with the thermodynamic modelling that predicts very low CO_2 content in the UHP

581   fluid phase. This COH fluid could have enhanced dissolution processes at UHP conditions,

582   explaining the irregular, re-entrant and sharp contacts observed in the zoned dolomite crystals.

583   The complex zoning of dolomite, diopside and forsterite could be therefore explained by protracted

584   episodes of dissolution and precipitation at HP/UHP conditions. More specifically, the following

585   dolomite evolution can be tentatively proposed:

586   (i) **growth of Dol II**: Dol II, concentrically overgrowing the pre-Alpine Dol I, formed through a

587   prograde metamorphic reaction involving the destabilization of aragonite and the dehydration of

588   antigorite (see previous discussion and Fig. 8). This reaction occurred at 1.7 GPa and 560°C

589   (i.e. at P-T conditions similar to those of stage 2 in Fig. 1b);

590   (ii) **consumption of Dol II**: during the subsequent increase in P-T conditions (from stage 2 to stage

591   4 in Fig. 1b), the brine previously produced by antigorite dehydration and still present in the

592   nearly closed system became able to dissolve Dol II, other that the metastable aragonite. In this

593   case the dissolution process could have been enhanced by the increase in both P and T

594   conditions;

595   (iii) **growth of peak Dol III**: the precipitation of peak Dol III (stage 4 in Fig. 1b) might have been

596   favoured by the attainment of over-saturation conditions of the fluid . The mechanism(s) for the

597   over-saturation at UHP peak still remain unclear, although it can be excluded that over-

598   saturation was induced by the decrease in fluid salinity, because of the nearly-closed behaviour

599   of the system. Previous thermodynamic studies on calcite solubility in aqueous fluids at HP

600   conditions (Dolejs and Manning, 2010) and pH measures on pure H_2O and on COH fluids in

601   equilibrium with a pelite up to 900°C and 3 GPa (Galvez et al., 2015) were not able to predict

602   the attainment of the fluid over-saturation conditions required for carbonates precipitation

603   observed in the Dora-Maira sample. It is worth noting that, in the models of Galvez et al.

604   (2015), the UHP fluids are enriched in Si, Na, K, and Al, whilst in the studied marble the fluid

605   is a COH brine containing Ca, Mg, and Si. The presence of Ca and Mg and the lack of alkalies

606   as dissolved cations could have had a role, still unexplored, in the pH variations and, then, could

607   have possibly promoted the attainment of fluid over-saturation conditions and the consequent

608   precipitation of carbonates;

609   (iv)**consumption of Dol III**: although the system is no more in a subduction regime but in a very-

610   early decompressional evolution (from stage 4 to stage 5 in Fig. 1b), the residual fluid, having

611   lost part of its dissolved charge, is again a highly-reactive brine able to dissolve carbonates. In

612   particular, further dissolution can be facilitated by the increasing under-saturation of the

613   interfacial solution (Putnis and John, 2010; King and Putnis, 2013).

614   (v) **growth of Dol IV**: the subsequent precipitation of UHP Dol IV, might have been due again to

615   the attainment of fluid over-saturation conditions with respect to carbonates. In this case, fluid

616   over-saturation is probably caused by the abrupt P and T decrease, maybe coupled with the

617   increase in pH, during early exhumation (stage 5 in Fig. 1b).

618   Summing up, these dissolution-precipitation events likely continued during the whole prograde- to

619   early-retrograde evolution, as far as the *P-T* path remained within the dolomite + diopside stability

620   field.

621

622   **IMPLICATIONS**

623   Cathodoluminescence observations allowed to recognise a complex zoning pattern in dolomite, with

624   at least four growth shells. The irregular, re-entrant and sharp contacts between each growth shell

625   suggest a complex dolomite evolution, characterized by several episodes of dolomite consumption

626   and growth.

627   According to the thermodynamic modelling results, only the H*P* prograde growth of Dol II is due to

628   metamorphic reactions. On the contrary, the subsequent growth of UH*P* Dol III and Dol IV cannot

629   be induced by isochemical metamorphic reactions. Based on present data, the UH*P* growth of Dol

630   III and Dol IV, as well as the consumption of Dol II and Dol III, are interpreted as due to several

631   dissolution-precipitation episodes occurred in the presence of saline aqueous fluids. The BIU *P-T*

632   path and the occurrence of free high-saline fluids rich in Ca, Mg, Si represent favourable conditions

633   for: i) the inferred dissolution-precipitation processes of the stable dolomite in a nearly closed

634   system; ii) the possible migration of the dissolved carbonates, if the system would have been open

635   during subduction.

636   To our knowledge, this study presents the first evidence for UH*P* dissolution of dolomite in natural

637   samples. Therefore, it represents a contribution to the understanding of the H*P*-UH*P* evolution of

638   carbonates and to the understanding of the difference in solubility among dolomite and aragonite.

639   Concerning this second point, in fact, the presence of both calcite and dolomite in primary fluid

640   inclusions, with calcite volumetrically more abundant than dolomite (Fig. 11), suggests that: i) both

641   aragonite and dolomite are dissolved at H*P*/UH*P* condition, ii) aragonite seems to have a higher

642   solubility with respect to dolomite, and/or, iii) the $CaCO_3$–component of dolomite has, maybe, a

643 higher solubility than its $MgCO_3$-component (i.e., incongruent dissolution of dolomite; Busenberg

644 and Plummer, 1982).

645 Finally, the data reported in this study refer to a very simple chemical system [C(F)MS-COH], and

646 can therefore represent a useful starting point for: i) further experiments on dolomite dissolution at

647 HP-UHP conditions, which so far are still lacking, and ii) further studies on carbon production and

648 sequestration in ultramafic systems (i.e. the same C(F)MS-COH system).

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980

981   **FIGURE CAPTIONS**

982   **Figure 1: (a)** Simplified geological map of the coesite-bearing Brossasco-Isasca Unit (modified

983   from Compagnoni et al., 2004 and Castelli et al., 2007). Undifferentiated units: graphite-rich schists

984   and metaclastics of the epidote-blueschist facies "Pinerolo Unit"; "San Chiaffredo Unit" and

985   "Rocca Solei Unit", with pre-Alpine basement rocks overprinted by Alpine quartz-eclogite facies

986   metamorphism. The white stars show the two locations of the studied marbles. The inset shows the

987   location of the Southern Dora-Maira Massif within a simplified tectonic sketch-map of the Western

988   Alps. Helvetic-Dauphinois domain: MB, Mont Blanc-Aiguilles-Rouges. Penninic domain: SB,

989   Grand St. Bernard Zone; MR, Monte Rosa; GP, Gran Paradiso; DM, Dora-Maira; V, Valosio; PZ,

990   Piemonte zone of calcschists with meta-ophiolites. Austroalpine Domain: DB, Dent Blanche nappe;

991   ME, Monte Emilius klippe; SZ, Sesia-Lanzo zone; SA, Southern Alps; EU, Embrunais-Ubaye

992   flysch nappe; PF, Penninic thrust front; CL, Canavese line. **(b)** Variscan and Alpine *P-T(-t)* paths of

993   the Brossasco-Isasca Unit inferred from previous studies (see for comparison Castelli et al., 2014).

994   Open circles labelled 1 to 11 represent the Alpine metamorphic stages inferred from different

995   lithologies (whiteschist, marble, eclogite, calc-silicate rocks, orthogneiss) discussed in the text. Data

996   of stage 1 are inferred from Compagnoni and Hirajima (2001) and Ferrando et al. (2009); those of

997   stage 2 from Ferrando et al. (2009); those of stage 3 from Ferraris et al. (2005), Di Vincenzo et al.

998   (2006), Ferrando et al. (2009), Gauthiez-Putallaz et al (2016); those of stage 4 from Gebauer et al.

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1000   (2016); those of stage 5 from Rubatto and Hermann (2001), Hermann (2003), Ferraris et al. (2005);

1001   Di Vincenzo et al. (2006), Castelli et al. (2007), Groppo et al. (2007b), Ferrando et al. (2009); those

1002   of stage 6 from Hermann (2003), Ferraris et al. (2005), Di Vincenzo et al. (2006); those of stage 7

1003   from Hermann (2003), Di Vincenzo et al. (2006), Castelli et al. (2007), Groppo et al. (2007b); those

1004   of stage 8 from Ferraris et al. (2005), Di Vincenzo et al. (2006), Castelli et al. (2007), Groppo et al.

1005   (2007b); those of stage 9 from Hermann (2003), Di Vincenzo et al. (2006), Castelli et al. (2007),

1006   Groppo et al. (2007b); those of stage 10 from Rubatto and Hermann (2001), Di Vincenzo et al.

1007   (2006), Castelli et al. (2007); those of stage 11 from Rubatto and Hermann (2001), Ferraris et al.

1008   (2005), Di Vincenzo et al. (2006), Castelli et al. (2007).

1009   **Figure 2:** Representative microstructures of calcite-dolomite marbles referring to the (N)CFM(A)S-

1010   COH (a) and NKCFMAS-COH (b-h) systems. **(a)** Amphibole and chlorite poorly defines an early-

1011   retrograde UH*P* regional foliation. Porphyroblasts of stretched dolomite are also evident. Sample

1012   DM1657, crossed polarized light (XPL). **(b)** Porphyroclastic Na-diopside, including prograde

1013   phengite, and dolomite are wrapped around by the early-retrograde UH*P* regional foliation defined

1014   by phengite and neoblastic Na-diopside. Sample DM1649, XPL. **(c)** Back scattered (BSE) image of

1015   a zoned dolomite with a dark-grey inner core (Dol I), including pre-Alpine andraditic garnet and

1016   diopside with Ca-tschermak component, overgrown by a dark-gray outer core (Dol II) and a

1017   medium-gray inner rim (Dol III). A light-gray outer rim (Dol IV) overgrows previous dolomite

1018   generations. Sample ADM17, back scattered image (BSE). **(d)** Dark-grey Dol II outer core with

1019   inclusions of zoned garnet. The pre-Alpine andradite-rich core is rimmed by the H*P* prograde

1020   almanidine-rich rim. Both of them includes calcite. The medium-gray inner rim (Dol III) and the

42

1021   light-gray outer rim (Dol IV) of dolomite are also recognizable. Sample ADM17, BSE. **(e)**

1022   Medium-gray Dol III inner rim with an inclusion of UH*P* grossular-rich garnet. The picture also

1023   shows the dark-grey outer core (Dol II) and the light-grey outher rim (Dol IV) of dolomite. Sample

1024   DM1636, BSE. **f)** Relict of neoblastic early-retrograde UH*P* Na-bearing diopside partly replaced by

1025   late-retrograde tremolite. Sample DM1631, XPL. **(g)** BSE image of zoned dolomite porphyroblasts

1026   showing relict dark-gray inner core (Dol I) concentrically overgrown by dark-gray H*P* Dol II outer

1027   core. The medium-grey UH*P* inner rim (Dol III) overgrows the partly reabsorbed core. The light-

1028   grey early retrograde outer rim (Dol IV), in equilibrium with tremolite, overgrows the previous,

1029   partly reabsorbed, dolomite generations. Inset not in scale. Sample ADM17. **(h)**

1030   Cathodoluminescence (CL) image of zoned dolomite porphyroblasts in which the light-red Dol I,

1031   the medium-red Dol II, the dark-red Dol III and the poorly luminescent Dol IV generations show

1032   the same microstructural relationships observed in Figs. 2c, d,e, g. Inset not in scale. Sample

1033   DM1657.

1034   **Figure 3:** Representative microstructures of calcite-dolomite marbles referring to the C(F)MS-COH

1035   system as recognized in CL and BSE. **(a)** The foliation is defined by not-luminescent Mg-chlorite

1036   that wraps around dolomite porphyroclasts characterized by four stages of growth. Inset not in

1037   scale. Sample DM1638, CL. **(b)** Dolomite porphyroclast wrapped around by flakes of Mg- chlorite;

1038   both are cut by rare antigorite. DM1638, BSE **(c)** Calcite-dolomite marble with a granoblastic

1039   structure. The porphyroclastic dolomite shows three stages of growth and not-luminescent Ca-

1040   amphiboles are also present. Sample DM1657, CL. **(d)** A dolomite porphyroclast is characterized

1041   by four stages of growth. Not-luminescent Mg-chlorite locally defines the main foliation. Sample

1042   DM1170, CL.

1043   **Figure 4:** Metamorphic evolution of the impure calcite-dolomite marbles from the BIU; mineral

1044   assemblages referring to the (N)CFM(A)S-COH and NKCFMAS-COH systems are reported in dark

1045   gray, those referring to the C(F)MS-COH system are reported in light gray.

Figure 5: Major elements µ-XRF map of the whole thin section from sample DM675. The marble

shows a banded fabric: each layer contains different modal amounts of calcite, dolomite,

clinopyroxene, and olivine in textural equilibrium. The white dashed box refers to the olivine-rich

level that was considered for the estimate of the bulk composition to be used in the pseudosection

modelling.

Figure 6: Representative microstructures from the chemically simple sample DM675 (C(F)MS-

COH system), as recognized in cathodoluminescence (CL) and SEM (BSE). **(a)** The foliation is

defined by the preferred dimensional orientation of zoned dolomite. Porphyroblastic forsterite is

partly retrogressed to antigorite along cracks. CL. **b)** Neoblastic forsterite and yellow Cpx IV are

included in Dol IV. Yellow Cpx IV, locally rimed by light-blue Cpx V, growths around

porphiroblastic forsterite. CL. **(c)** Porphyroblastic dolomite includes Cpx III in the core (Dol III)

and Cpx IV in the rim (Dol IV). BSE. **(d)** Diopside occurs as zoned porphyroblasts, showing

dimensional preferred orientation along the regional foliation, and stubby zoned neoblasts.

Porphyroblastic forsterite partly retrogressed to antigorite is also present. CL

Figure 7 (a-c) Dolomite composition plotted in the $CaCO_3$ *vs* $MgCO_3$ **(a)**, $FeCO_3$ **(b)**, and

MnO/FeO **(c)** diagrams. **(d)** Clinopyroxene composition plotted in the Mg *vs* Na diagram. WDS

data from sample DM675.

Figure 8: Mixed-volatile *P-T* projection calculated in the system $CMS-H_2O-CO_2$. The univariant

reactions "seen" by the studied sample DM675 and relevant for the prograde *P-T* path of the BIU

(blue dotted line; see Fig. 1b) are reported in black, whereas the others (unlabeled) are reported in

grey (see also Fig. S1). Large black dots are invariant points for the relevant reactions. The yellow

field is the stability field of the Arg + Dol + Di + Fo + *F* assemblage, i.e. the assemblage observed

in sample DM675. The studied marble is sensitive to only two Dol-forming univariant reactions,

which are reported in red (*i*1 and *i*13). Fluid composition varies along each fluid-present univariant

curve. Dotted red lines are isopleths of fluid (*F*) composition (XCO_2) in the Arg + Dol + Di + Fo +

F stability field; the small red dots indicate the variation in fluid composition.

1072 **Figure 9:** Microphotographs showing primary fluid inclusions in diopside. **(a)** Primary fluid

1073 inclusions containing high birefringent solids are included in both porphyroclastic and neoblastic

1074 Cpx III. Sample DM675, XPL. **(b)** Detail of Cpx III including a primary fluid inclusion that

1075 consists of an aggregate of calcite + dolomite + tremolite + talc and an aqueous fluid phase (liquid

1076 and vapour). Sample DM675, PPL. **(c)** Detail of Cpx III including primary fluid inclusions that

1077 consists mainly of an aggregate of high birefringent solids (calcite + dolomite + tremolite + talc).

1078 Sample DM675, XPL.

1079 **Figure 10:** Raman spectra of solids within primary multiphase aqueous inclusions in diopside.

1080 Sample DM675. **(a)** Raman spectrum of mixed Mg-calcite + tremolite + host diopside. The broad

1081 peaks related to the minerals in the inclusion indicate their poor crystallinity. **(b)** Raman spectrum

1082 of mixed talc + tremolite + host diopside. The 3676 cm^{-1} peak, related to the OH bonds of talc,

1083 arises from a large band, suggesting the presence of molecular water in the crystallographic

1084 structure. The peak related to OH bonds of tremolite (see Fig. 9a) is not visible because of the very

1085 low intensity of the mineral in this site.

1086 **Figure 11: (a)** Photomicrograph of the mapped primary multiphase aqueous inclusion; the mapped

1087 area is 16 x 16 μm. Sample DM 675, XPL. **(b-d)** Raman spectral images, respectively, of Mg-

1088 calcite (1089 cm^{-1}), talc (190 cm^{-1}), and dolomite (303 cm^{-1}) distribution in the fluid inclusion. The

1089 color intensity of the daughter minerals (from black to white) reflects the increase in the intensity of

1090 the Raman band.

1091 **Table 1**: samples of impure calcite-dolomite marbles referring to the C(F)M(A)S-COH,

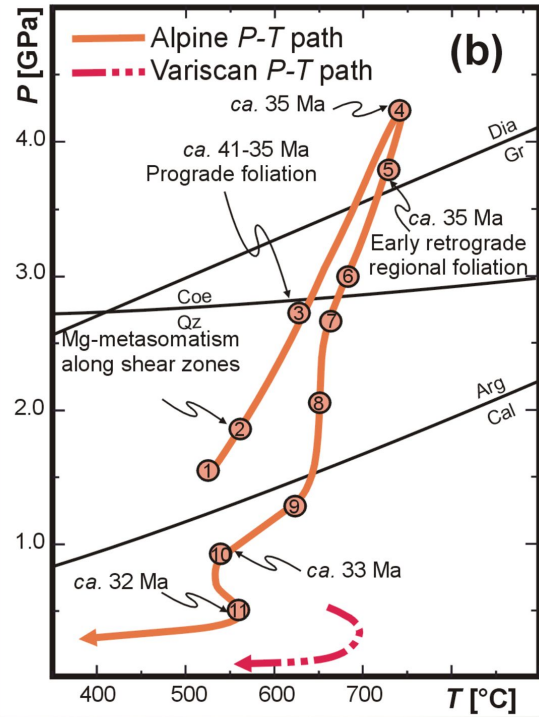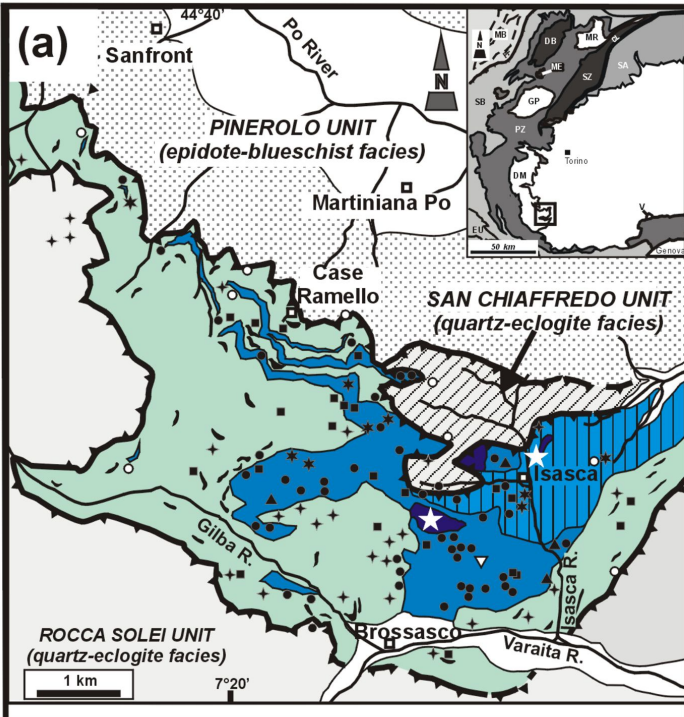1092 (N)CFM(A)S-COH, and NKCFMAS-COH systems. Wm = white mica

1093 **Table 2**: representative chemical composition of silicates from the impure calcite-dolomite marbles.

1094 EDS-WDS* = WDS data for Na and F; Fe$_2$O$_3$* = calculated; "-" not measured; b.d.l. = below

1095 detection limit; Mg# = Mg/(Mg+Fe^{2+})

1096 **Table 3**: representative chemical composition of dolomite from sample DM675. b.d.l. = below

1097 detection limit

1098   **Figure supp mat 1: (a)** P/T-$X(CO_2)$ phase diagram section in the system CMS-H_2O-CO_2,

1099   calculated for the prograde P-T path of the BIU (Fig. 1b). Product assemblages on the right side of

1100   reactions; the isobaric/isothermal univariant reactions "seen" by the studied sample DM675 are

1101   reported in red. Qz/Coe-bearing equilibria are not numbered. Large black points are

1102   isobaric/isothermal invariant points; the fluid-present isobaric/isothermal invariant points

1103   correspond to univariant curves in the P-T mixed volatile projection of Fig. 7. **(b)** P/T-$X(CO_2)$

1104   pseudosection calculated for sample DM675 (bulk composition in mol%) in the system CFMS-

1105 H_2O-CO_2 for the prograde P-T path of the BIU. White (i.e. 5 mineral phases), light-grey (4 mineral

1106   phases) and dark-grey (3 mineral phases) fields are di-, tri- and quadri-variant fields, respectively.

1107   The narrow isobaric/isothermal 3-phases fields correspond to the isobaric/isothermal univariant

1108   reactions in (a). The stable assemblage Ol + Cpx + Dol + Arg is modelled by the narrow 4-phases

1109   field labelled in red.

1110   **Table supp mat 1:** chemical composition of silicates from the impure calcite-dolomite marbles.

1111   EDS-WDS* = WDS data for Na and F; Fe_2O_3* = calculated; "-" = not measured; b.d.l. = below

1112   detection limit.

1113

(a) Sanfront · 44°40' · Po River · N

PINEROLO UNIT
(epidote-blueschist facies)

Martiniana Po

Case Ramello

SAN CHIAFFREDO UNIT
(quartz-eclogite facies)

Isasca

Gilba R.

Isasca R.

ROCCA SOLEI UNIT
(quartz-eclogite facies)

Brossasco

Varaita R.

1 km · 7°20'

50 km · Torino · Genova

(b)

— Alpine *P-T* path
—·—· Variscan *P-T* path

P [GPa]

ca. 35 Ma — 4

ca. 41-35 Ma
Prograde foliation — 3

ca. 35 Ma
Early retrograde
regional foliation — 6

Coe
Qz

Mg-metasomatism
along shear zones — 2

5

7

8

Dia
Gr

Arg
Cal

1

9

ca. 32 Ma · 10 · *ca.* 33 Ma

11

T [°C]

400 · 500 · 600 · 700

BROSSASCO-ISASCA UNIT (coesite-eclogite facies)

Polymetamorphic Complex

- Paraschists with Coe-eclogite and marbles
- Main marble lenses
- Phengite-rich gneiss

Monometamorphic Complex

- Augen gneiss with pyrope-bearing whiteschist layers

+ relict Permian granitoid
▽ relict regionally metamorphosed Variscan paraschist
▲ relict thermally metamorphosed Variscan paraschist
✶ small marble lenses
● fresh eclogite
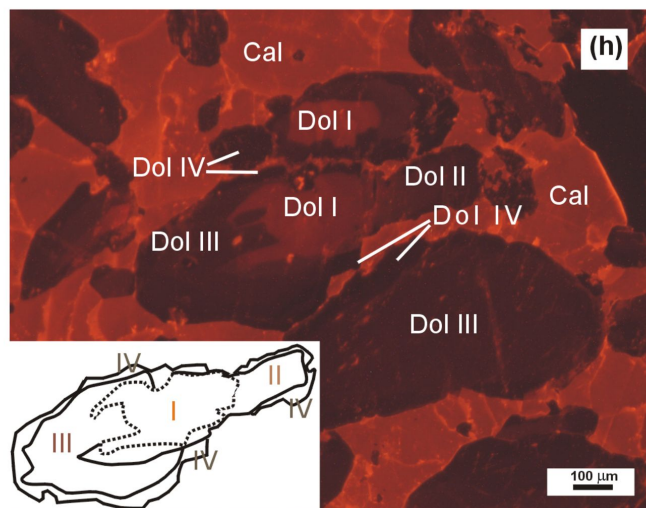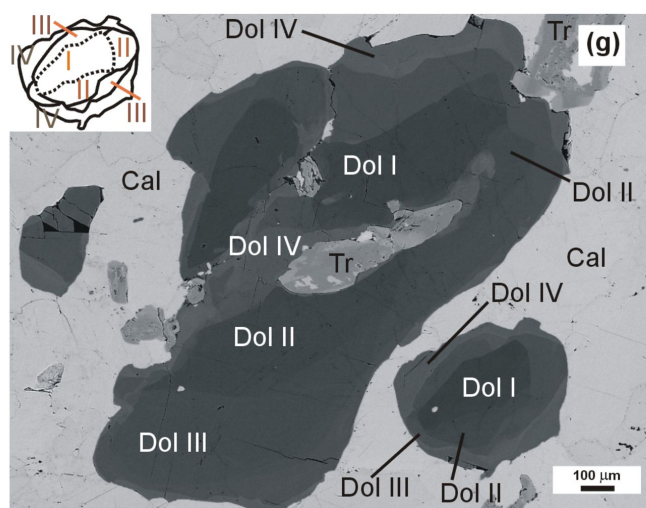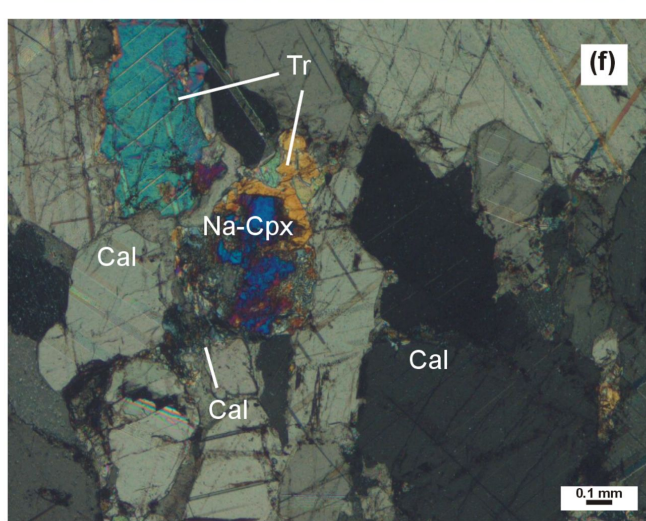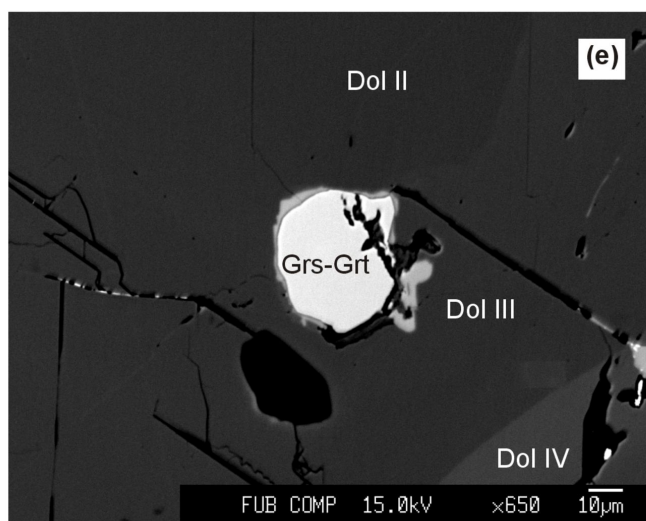○ retrogressed eclogite
■ Ky + Jd assemblages

Figure 1

Figure 2

Figure 3

	Pre-Alpine Assemblage	Alpine assemblage			
		Prograde	Peak	Early retrograde S_r	Late retrograde
Cal/Arg					
Dol	Cal-rich Dol I	Cal-poor Dol II	Cal-interm Dol III	Cal-poorer Dol IV	
Di	Ca-tschermak Cpx I	Na-bearing Cpx II	pure Di Cpx III	Na-bearing Cpx IV	Na-bearing Cpx V
Fo	low Fo Ol I	high Fo Ol II	high Fo Ol III	highest Fo Ol IV	
Grt	Adr-rich	Alm-rich	Grs-rich		
Amp	Al-rich Prg			Na-Al-Fe-Tr	Tr/Mg-Hbl / Tr
Qz/Coe					
Ilm					
Mag					
Tlc					
Ph					
Atg			Al-rich		
Ep s.l.	Zo	Zo			
Ttn	Al-F-poor			Al-F-rich	Al-F-poor
Rt					
Chl				Mg-Chl	Fe-richer
Phl					

Figure 4

	Cal	Dol	Cpx	Ol
vol%	77.0	1.5	6.5	15.0

0.5 cm

Figure 5

Figure 6

F i g u r e   7

(i1) Atg + Arg = Di + Fo + Dol + F
(i7) Atg + Dol = Di + Fo + Mag + F
(i8) Atg + Mag = Fo + Tlc + F
(i10) Atg + Dol + Tr = Di + Mag + F

(i11) Atg + Dol + Tlc = Mag + Tr + F
(i13) Cal + Tr + Atg = Di + Dol + F
(i15) Dol + Tlc = Di + Mag + Coe + F
(i19) Arg + Tr = Di + Dol + Qz + F
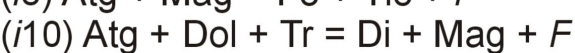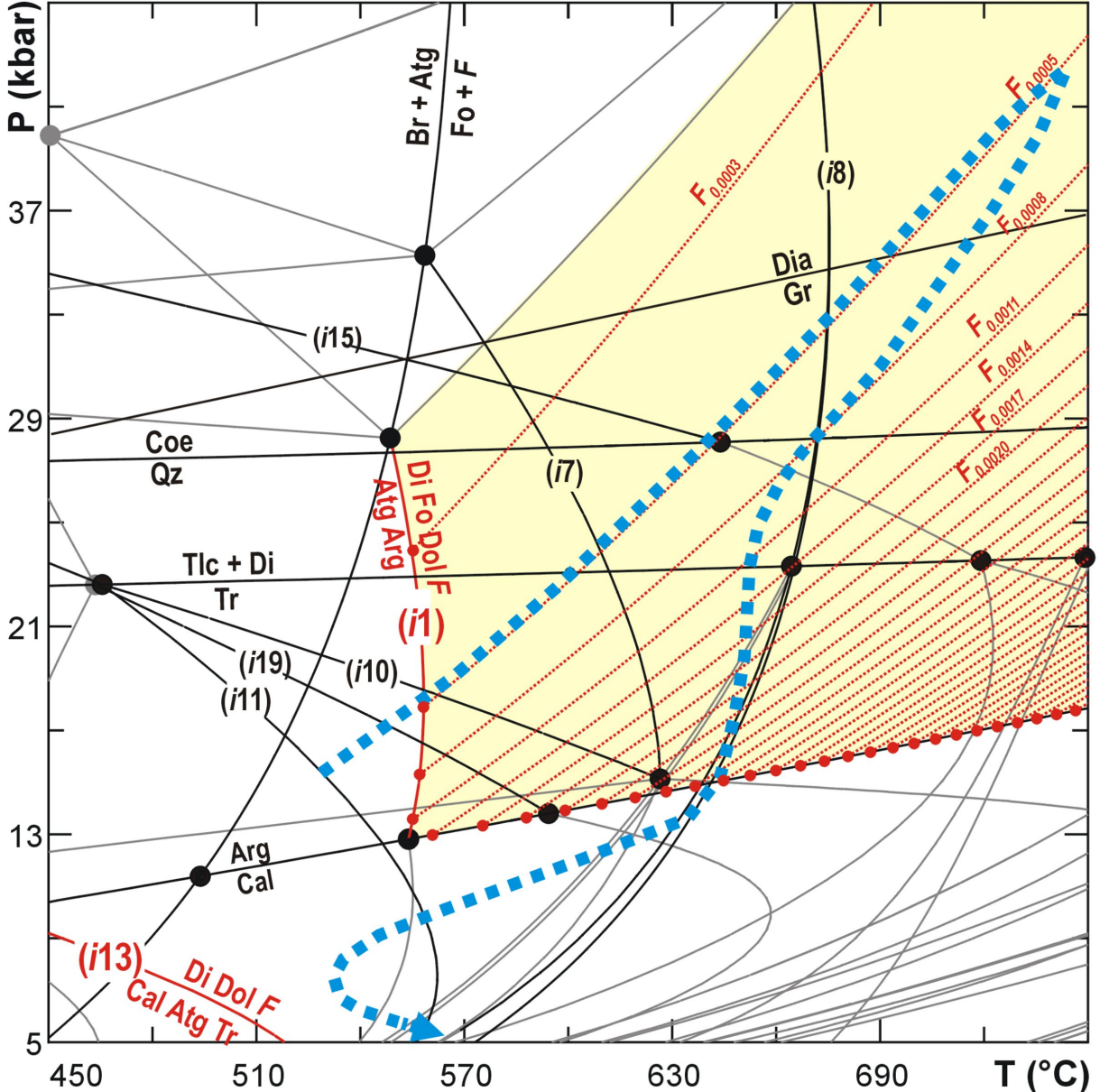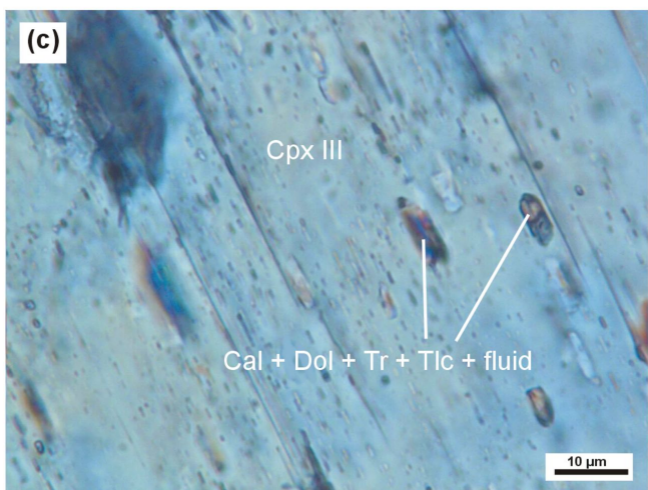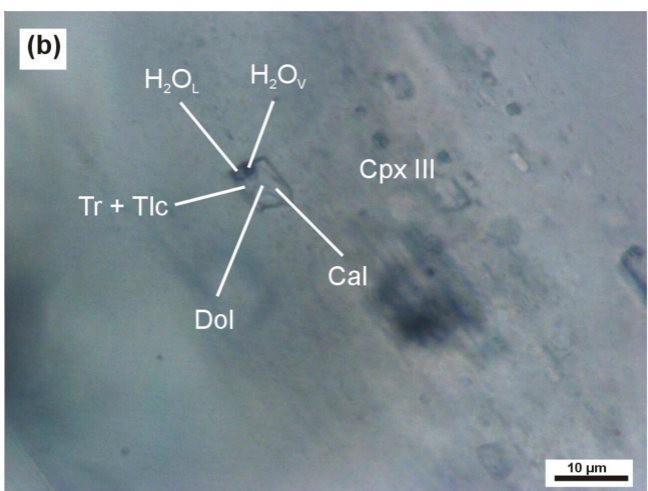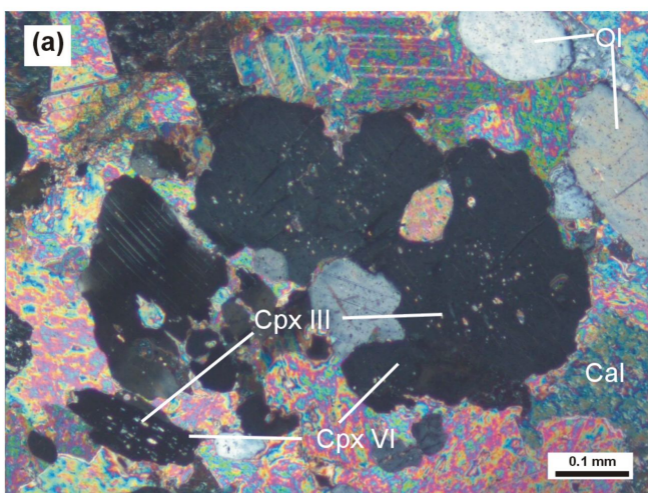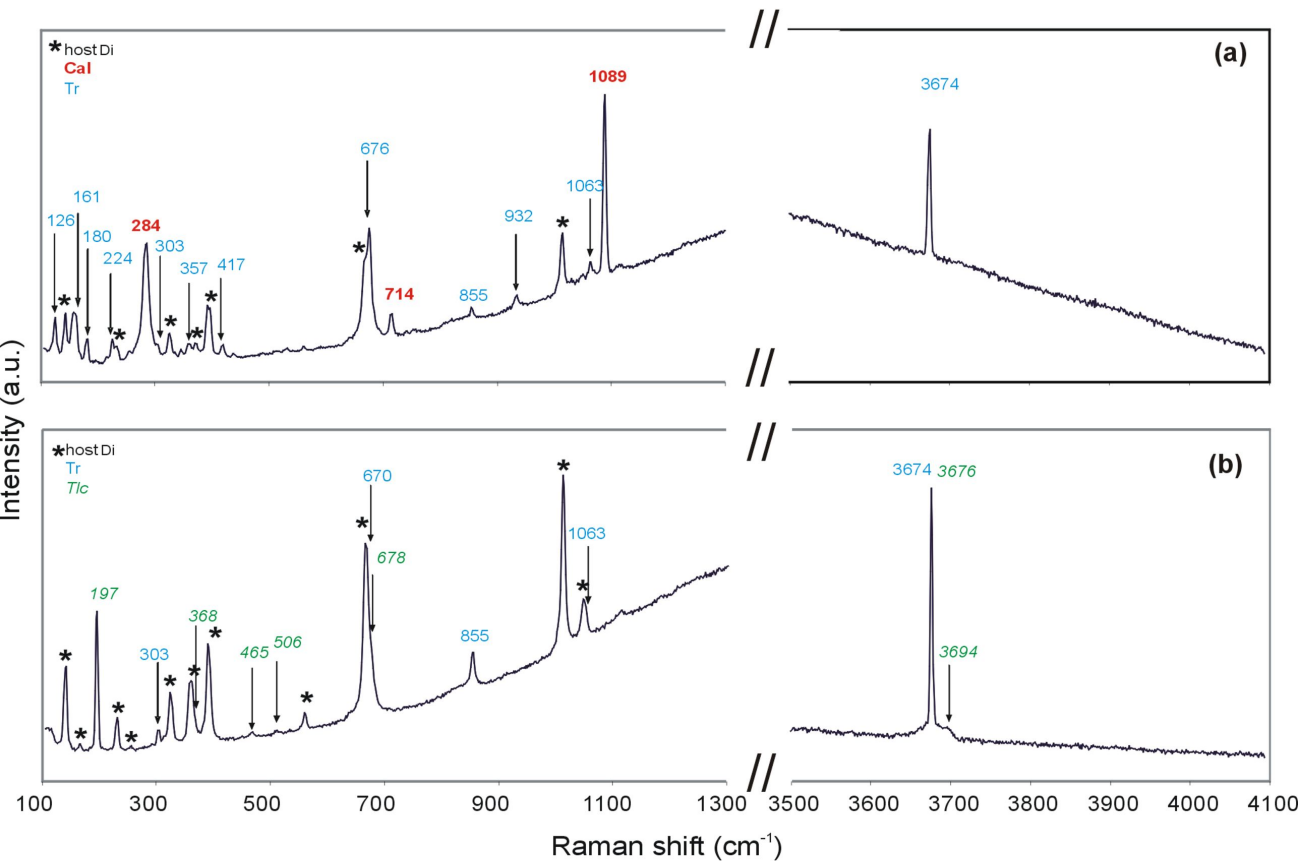
Figure 8

Figure 9

Figure 10
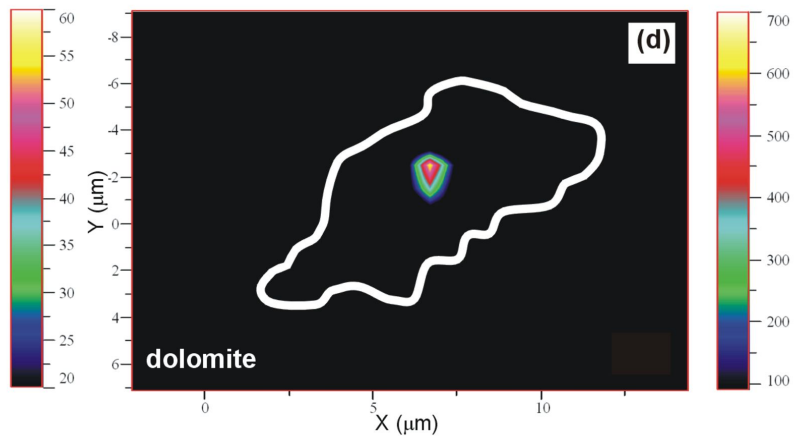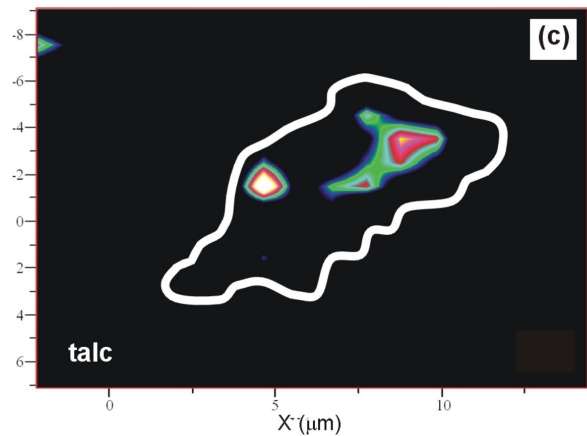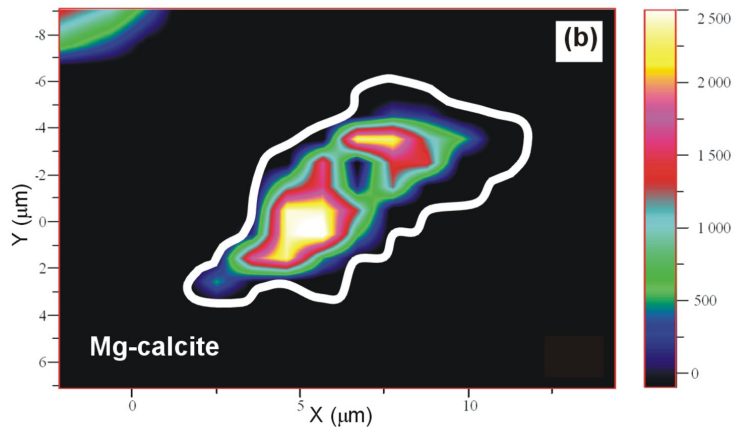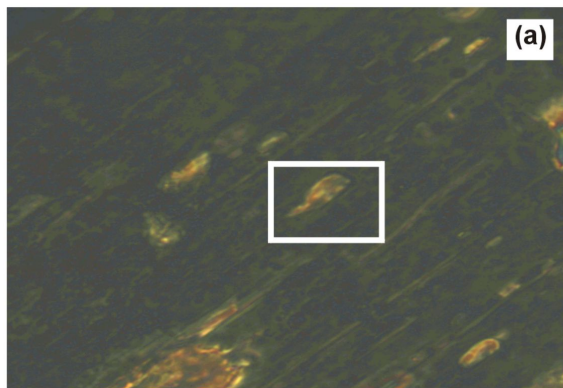
Figure 11

Table 1: list of the studied samples

	Sample	Lithology	Main forming minerals	Locality
	DM675 (layer)	Atg-Ol-Cpx-rich calcite-dolomite marble	Dol, Cc, Atg, Ol, Cpx, Chl	Costa Monforte
	DM675 (layer)	Ol-Atg-Chl-Amp-rich calcite-dolomite marble	Dol, Cc, Ol, Atg, Chl, Amp	Costa Monforte
C(F)M(A)S-COH system	DM675 (layer)	Ol-Cpx-Atg-Chl-Amp-rich calcite-dolomite marble	Dol, Cc, Ol, Cpx, Atg, Chl, Amp	Costa Monforte
	DM1170 (layer)	Chl-rich calcite-dolomite marble	Dol, Cc, Chl, Rt	Costa Monforte
	DM1170 (layer)	Atg-Chl-rich calcite-dolomite marble	Dol, Cc, Atg, Chl, Amp	Costa Monforte
	DM1638 (layer)	Chl-Cpx-rich calcite-dolomite marble	Dol, Cc, Chl, Cpx, Amp	Isasca
	DM1638 (layer)	Atg-Chl-rich calcite-dolomite marble	Dol, Cc, Atg, Chl, Amp	Isasca
(N)CFM(A)S-COH system	DM1631	Cpx-Amp-rich calcite-dolomite marble	Dol, Cc, Cpx, Amp	Costa Monforte
	DM1649 (layer)	Cpx-Chl-rich calcite-dolomite marble	Dol, Cc, Cpx, Chl, Amp	Isasca
	DM1657 (layer)	Amp-Chl-rich calcite-dolomite marble	Dol, Cc, Amp, Chl	Costa Monforte
NKCFMAS-COH system	DM1636	Wm-Amp-Chl-rich calcite-dolomite marble		Costa Monforte
	DM1649 (layer)	Wm-rich calcite-dolomite marble	Dol, Cc, Wm	Isasca
	DM1649 (layer)	Cpx-Zo-Wm-Ttn-rich calcite-dolomite marble	Dol, Cc, Cpx, Zo, Wm, Amp, Ttn	Isasca
	DM1649 (layer)	Cpx-Wm-Qz-rich calcite-dolomite marble	Dol, Cc, Cpx, Wm, Qz, Amp, Ep, Ttn	Isasca
	DM1657 (layer)	Wm-Amp-Chl-Cpx-rich calcite-dolomite marble	Dol, Cc, Wm, Amp, Chl, Cpx	Costa Monforte
	ADM17	Wm-Amp-Chl-Grt-Cpx-rich calcite-dolomite marble	Dol, Cc, Wm, Amp, Chl, Grt, Cpx, Qz, Chl, Ep	Costa Monforte

Table 2: representative chemical composition of silicates from the impure calcite-dolomite marbles

Sample	DM1636	DM1636	DM675	DM675	DM1636	DM675	DM675	DM675	DM675
Metam. stage	pre-Alpine	pre-Alpine	pre-Alpine	pre-Alpine	prograde	prograde	prograde	prograde	prograde
Location	Dol inner c	Dol inner c			Dol outer c				
Mineral	Grt	Cpx I	Cpx I	Ol I	Grt	Cpx II	Cpx II	Ol II	Ol II
No.	grtN11a	cpxN15b	29-28	29-20	grtN7b	25-3	22b-40	25-1	25-36
Anal. technique	EDS-WDS*	EDS-WDS*	WDS	WDS	EDS-WDS*	WDS	WDS	WDS	WDS
SiO_2	39.22	53.83	55.63	42.60	40.93	55.04	55.86	42.35	41.69
TiO_2	1.04	0.24	b.d.l.	b.d.l.	0.15	b.d.l.	b.d.l.	0.00	0.00
Cr_2O_3	b.d.l.	b.d.l.	b.d.l.	0.06	b.d.l.	b.d.l.	b.d.l.	0.01	0.06
Al_2O_3	21.90	2.06	0.41	b.d.l.	23.31	0.14	0.14	0.00	0.01
Fe_2O_3*					0.71				
FeO	3.16	0.62	1.38	1.37	3.79		0.35	0.62	0.64
MnO	0.23	b.d.l.	0.07	0.10	0.21	0.03	0.01	0.01	0.02
MgO	3.28	18.53	17.67	56.68	6.91	18.23	18.51	57.86	57.66
NiO	-	-	0.09	0.03	-	b.d.l.	b.d.l.	b.d.l.	b.d.l.
CaO	30.36	24.93	25.49	0.10	25.17	26.17	25.76	0.01	b.d.l.
Na_2O	b.d.l.	0.09	0.15	b.d.l.	b.d.l.	0.05	0.08	0.01	0.01
K_2O	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.01	b.d.l.	0.01	b.d.l.
F	b.d.l.	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	b.d.l.	-	-
Total	99.19	100.29	100.89	100.94	100.47	100.38	100.71	100.88	100.09
Si	2.96	1.93	1.999	0.995	3.00	1.982	2.001	0.984	0.975
Ti	0.06	0.01			0.01			0.000	0.000
Cr				0.001				0.000	0.001
Al	1.95	0.09	0.017		2.01	0.006	0.006	0.000	0.000
Fe^{3+}	0.02	0.02			0.00	0.019	0.000	0.000	0.000
Fe^{2+}	0.18	0.00	0.042	0.027	0.23	0.000	0.011	0.012	0.013
Mn	0.02		0.002	0.002	0.01	0.001	0.000	0.000	
Mg	0.37	0.99	0.946	1.973	0.75	0.978	0.988	2.003	2.010
Ni	-	-	0.003	0.001	-				
Ca	2.45	0.96	0.981	0.003	1.97	1.010	0.989	0.000	0.000
Na		0.006	0.010			0.004	0.006	0.001	0.001
K						0.001		0.000	
F								-	-
Mg#			0.983					0.994	0.994

Notes: EDS-WDS* = WDS data for Na and F; Fe_2O_3* = calculated; "-" = not measured; b.d.l. = below detection limit; Mg# = $Mg/(Mg+Fe^{2+})$;

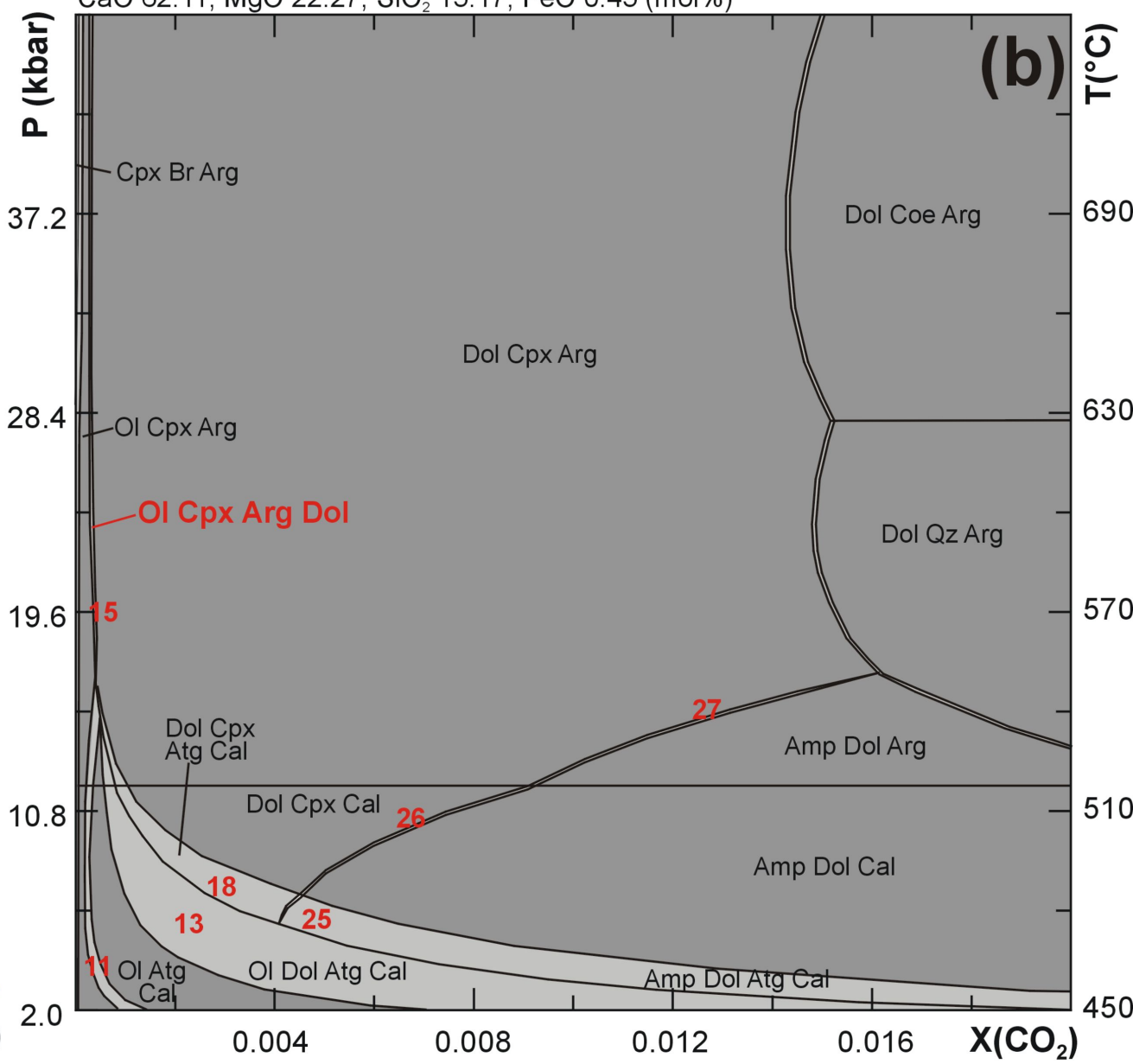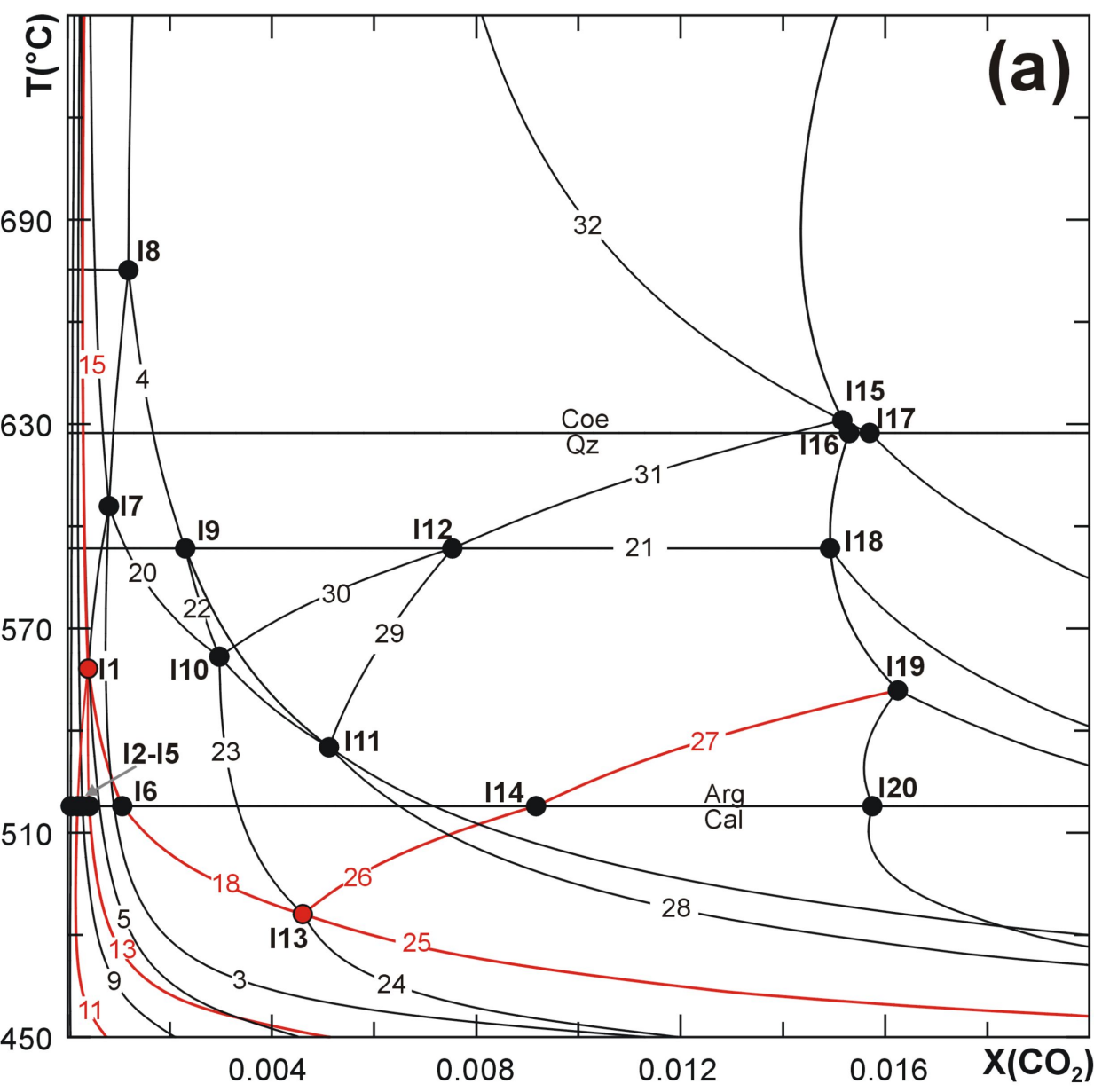**Table 2: representative chemical composition of silicates from the impure calcite-dolomite marbles (continue)**

Sample	DM1636	DM1636	DM675	DM675	DM675	DM675	DM675	DM675	ADM17	DM675	DM675	DM675
Metam. stage	peak	peak	peak	peak	peak	peak	early retrograde	early retrograde	early retrograde	early retrograde	late retrograde	late retrograde
Location	Dol inner r	Dol inner r							Dol outer r			
Mineral	Grt	Phg	Cpx III	Cpx III	Ol III	Ol III	Cpx IV	Cpx IV	Phl	Ol IV	Cpx V	Cpx V
No.	grtN1b	Nphe2	25-5	22b-38	25-2	25-37	22-10	22x-24	67phl1_in_dol	18-34	29-30	22b-39
Anal. technique	EDS-WDS*	EDS-WDS*	WDS	WDS	WDS	WDS	WDS	WDS	EDS-WDS*	WDS	WDS	WDS
SiO_2	40.29	53.58	55.77	55.87	42.21	42.53	55.93	55.58	41.14	42.54	55.70	56.20
TiO_2	0.25	0.49	b.d.l.	0.03	0.02	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.01	0.03
Cr_2O_3	b.d.l.	b.d.l.	0.04	b.d.l.	0.09	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Al_2O_3	22.64	23.38	0.02	0.01	b.d.l.	b.d.l.	b.d.l.	0.02	13.34	b.d.l.	0.06	0.04
Fe_2O_3*							0.02				0.08	
FeO	3.44	0.26	0.12	0.16	0.56	0.55	0.18	0.27	3.79	0.45	b.d.l.	0.14
MnO	0.33	b.d.l.	0.01	0.01	0.03	b.d.l.	b.d.l.	0.02	b.d.l.	b.d.l.	0.02	0.03
MgO	6.20	6.65	18.47	18.70	57.38	58.04	18.57	18.57	25.85	58.10	18.64	18.63
NiO	-	-	b.d.l.	b.d.l.	0.01	0.07	0.07	0.00	-	0.01	0.03	b.d.l.
CaO	25.97	b.d.l.	26.05	25.85	0.05	0.04	25.97	25.25	0.24	0.04	26.13	25.73
Na_2O	b.d.l.	0.06	b.d.l.	b.d.l.	0.01	b.d.l.	0.05	0.06	0.04	b.d.l.	0.03	0.04
K_2O	b.d.l.	11.64	0.01	b.d.l.	b.d.l.	b.d.l.	0.01	0.04	10.89	0.03	b.d.l.	b.d.l.
F	b.d.l.	b.d.l.	b.d.l.	b.d.l.	-	-	b.d.l.	b.d.l.	0.86	-	b.d.l.	b.d.l.
Total	99.12	96.05	100.49	100.63	100.36	101.30	100.80	99.81	96.15	101.17	100.70	100.84
Si	3.00	3.53	2.003	2.002	0.986	0.984	2.002	2.008	2.92	0.985	1.994	2.010
Ti	0.01	0.02		0.001	0.000	0.001					0.000	0.001
Cr			0.001		0.002	0.001						
Al	1.99	1.82	0.001	0.000				0.001	1.12		0.003	0.002
Fe^{3+}							0.001				0.002	
Fe^{2+}	0.21	0.01	0.004	0.005	0.011	0.011	0.005	0.008	0.23	0.009		0.004
Mn	0.02	0.00	0.000	0.000	0.001	0.000		0.001			0.001	0.001
Mg	0.69	0.65	0.989	0.999	1.998	2.002	0.991	1.000	2.74	2.005	0.995	0.993
Ni	-	-			0.000	0.001	0.002	0.000	-	0.000	0.001	
Ca	2.07		1.002	0.993	0.001	0.001	0.996	0.977	0.02	0.001	1.002	0.986
Na		0.007			0.001	0.000	0.004	0.004	0.005		0.002	0.003
K		0.98	0.001				0.001	0.002	0.99	0.001		
F					-	-			0.192	-		
Mg#					0.993	0.993			0.92	0.995		

Notes: EDS-WDS* = WDS data for Na and F; Fe_2O_3* = calculated; "-" = not measured; b.d.l. = below detection limit; Mg# = $Mg/(Mg+Fe^{2+})$;

Table 3: representative chemical composition of dolomite from sample DM675

Sample	DM675	DM675	DM675	DM675	DM675	DM675	DM675	DM675	DM675	DM675	DM675	DM675	DM675
Metam. stage	pre-Alpine	pre-Alpine	prograde	prograde	peak	peak	peak	peak	peak	peak	peak	early retrograde	early retrograde
Location	Dol inner c	Dol inner c	Dol outer c	Dol outer c	Dol inner r	Dol inner r	Dol inner r	Dol inner r	Dol inner r	Dol inner r	Dol inner r	Dol outer r	Dol outer r
No.	DM675-18-17	DM675-18-18	DM675-18-16	DM675-29-31	DM675-25-7	DM675-18-15	DM675-25-8	DM675-18-14	DM675-29-23	DM675-29-32	DM675-18-35	DM675-25-6	DM675-29-33
Anal. technique	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS
SiO_2	0.039	0.001	0.008	0.025	b.d.l.	b.d.l.	0.009	b.d.l.	0.025	0.029	0.003	0.012	b.d.l.
TiO_2	b.d.l.	0.002	b.d.l.	0.025	b.d.l.	b.d.l.	0.008	b.d.l.	0.041	b.d.l.	0.025	0.002	0.029
NiO	b.d.l.	0.065	0.080	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.052	b.d.l.	0.079	0.077	0.161	0.149
Cr_2O_3	0.016	0.036	0.077	b.d.l.	0.082	0.037	0.046	b.d.l.	b.d.l.	0.176	0.014	0.018	0.034
Al_2O_3	0.009	0.056	0.025	b.d.l.	0.015	0.000	b.d.l.	b.d.l.	0.038	b.d.l.	0.025	b.d.l.	0.058
FeO	0.183	0.212	0.048	0.070	0.135	0.083	0.121	0.091	0.146	0.149	0.111	0.091	0.098
MnO	0.033	0.097	0.034	0.042	0.003	0.059	0.033	0.040	0.002	0.060	0.001	0.056	0.001
MgO	21.671	21.422	21.837	21.638	21.555	21.804	21.754	21.621	21.190	21.754	21.688	22.185	21.887
CaO	29.802	30.250	30.390	30.348	31.048	30.852	31.034	30.656	30.418	31.188	30.838	30.964	30.614
Na_2O	0.023	b.d.l.	b.d.l.	0.044	b.d.l.	b.d.l.	0.037	0.005	b.d.l.	0.061	b.d.l.	0.029	0.038
K_2O	0.032	b.d.l.	0.031	0.007	b.d.l.	0.023	0.014	0.018	b.d.l.	0.004	0.031	0.031	0.008
SrO	0.102	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.103	0.044	0.044	b.d.l.
BaO	b.d.l.	b.d.l.	0.046	b.d.l.	0.044	b.d.l.	0.070	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
ZrO_2	0.043	0.103	0.061	b.d.l.	b.d.l.	0.005	0.020	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.076
P_2O_5	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.077	b.d.l.	b.d.l.	0.044	0.077	b.d.l.	0.045	0.088	0.022
Cl	0.008	0.007	b.d.l.	0.009	b.d.l.	b.d.l.	0.014	0.004	b.d.l.	b.d.l.	b.d.l.	0.024	0.007
CO_2	47.602	48.186	47.876	47.577	48.049	48.125	48.284	47.800	47.180	48.565	48.069	48.802	48.183
Tot	100.105	101.351	100.514	99.785	101.007	100.986	101.443	100.333	99.118	102.169	100.969	102.508	101.204
O=Cl	2.184	2.042	0.000	2.666	0.000	0.000	3.886	1.248	0.000	0.000	0.000	6.835	1.900
Total	97.921	99.309	100.514	97.119	101.007	100.986	97.558	99.085	99.118	102.169	100.969	95.673	99.304
$CaCO_3$	51.05	51.18	49.94	50.13	50.77	50.33	50.51	50.39	50.69	50.57	50.46	49.97	50.07
$MgCO_3$	48.69	48.69	49.92	49.72	49.03	49.49	49.25	49.44	49.12	49.07	49.36	49.81	49.80
$MnCO_3$	0.00	0.05	0.04	0.05	0.00	0.08	0.04	0.05	0.00	0.08	0.00	0.07	0.00
$FeCO_3$	0.17	0.08	0.06	0.09	0.17	0.11	0.15	0.12	0.19	0.19	0.14	0.11	0.13
$SrCO_3$	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.04	0.04	0.00
$BaCO_3$	0.00	0.00	0.03	0.00	0.03	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00

Notes: b.d.l. = below detection limit

Figure S1

Table supp mat 1: chemical composition of silicates from the impure calcite-dolomite marbles

Sample	DM675	DM675	DM675	DM675	DM675	DM675	DM675	DM675	ADM17
Metam. stage	peak	peak	peak	peak	peak	peak	early retrograde	early retrograde	early retrograde
Mineral	Cpx III	Cpx III	Cpx III	Cpx III	Cpx III	Cpx III	Cpx IV	Cpx IV	Al-rich Ttn
No.	22-9	22b-12	22b-13	22x-25	22x-26	22x-27	22-11	22b-42	tit1
Anal. technique	WDS	WDS	WDS	WDS	WDS	WDS	WDS	WDS	EDS-WDS*
SiO2	55.77	55.17	55.74	55.41	55.77	55.77	55.65	55.28	30.79
TiO2	b.d.l.	0.02	b.d.l.	b.d.l.	0.06	b.d.l.	b.d.l.	b.d.l.	33.74
Cr2O3	0.04	0.01	b.d.l.	0.05	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Al2O3	0.02	b.d.l.	b.d.l.	0.06	0.01	b.d.l.	b.d.l.	0.01	4.564
Fe2O3*		0.24	0.16				0.24	0.21	
FeO	0.12	0.00	0.00	0.27	0.23	0.18	0.00	0.08	b.d.l.
MnO	0.01	0.05	0.07	b.d.l.	0.07	0.03	b.d.l.	0.03	b.d.l.
MgO	18.47	18.59	18.79	18.21	18.61	18.86	18.63	18.41	b.d.l.
NiO	b.d.l.	0.06	b.d.l.	b.d.l.	0.02	0.09	b.d.l.	b.d.l.	-
CaO	26.05	25.88	25.83	25.25	25.80	25.36	26.14	25.68	28.12
Na2O	b.d.l.	0.02	b.d.l.	0.02	0.02	0.01	0.06	0.06	b.d.l.
K2O	0.01	b.d.l.	0.01	b.d.l.	b.d.l.	0.02	0.01	b.d.l.	b.d.l.
F	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.01
Total	100.49	100.04	100.60	99.27	100.61	100.32	100.73	99.76	98.22
Si	2.003	1.989	1.998	2.015	2.000	2.004	1.992	1.999	1.02
Ti		0.001			0.002				0.84
Cr	0.001	0.000		0.001	0.001				
Al	0.001			0.003	0.000			0.000	0.18
Fe3		0.007	0.004				0.007	0.006	
Fe2	0.004	0.000	0.000	0.008	0.007	0.005	0.000	0.003	
Mn	0.000	0.002	0.002	0.000	0.002	0.001		0.001	
Mg	0.989	0.999	1.004	0.987	0.995	1.010	0.994	0.992	
Ni		0.002			0.001	0.003			-
Ca	1.002	1.000	0.992	0.984	0.991	0.976	1.003	0.995	1.00
Na		0.001		0.001	0.001	0.001	0.004	0.004	
K	0.001		0.001			0.001	0.001		
F									0.106

Notes: EDS-WDS* = WDS data for Na and F; $Fe_2O_3^*$ = calculated; "-" = not measured; b.d.l. = below detection limit

Table supp mat 1: chemical composition of silicates from the impure calcite-dolomite marbles (continue)

Sample	DM675	DM675	ADM17	DM1636	ADM17	ADM17	ADM17
Metam. stage	late retrograde	late retrograde	late retrograde	late retrograde	late retrograde	late retrograde	late retrograde
Mineral	Cpx V	Cpx V	Al-poorTtn	Tlc	Mg-Hbl	Tr	Tr
No.	29-29	22b-41	tit2	tlcX	39tre1	3tre2	39tre2
Anal. technique	WDS	WDS	EDS-WDS*	EDS-WDS*	EDS-WDS*	EDS-WDS*	EDS-WDS*
SiO2	55.22	55.80	30.50	62.06	54.46	56.62	56.80
TiO2	0.03	b.d.l.	36.55	b.d.l.	0.294	b.d.l.	b.d.l.
Cr2O3	b.d.l.	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Al2O3	0.05	0.03	2.49	b.d.l.	6.234	2.095	1.63
Fe2O3*	0.39						
FeO	0.00	0.18	0.35	1.50	3.32	3.22	3.56
MnO	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
MgO	18.50	18.53	b.d.l.	30.65	20.22	22.34	21.76
NiO	0.15	b.d.l.	-	-	-	-	-
CaO	25.75	26.01	27.66	2.03	11.39	12.96	12.18
Na2O	0.03	0.03	b.d.l.	0.08	1.52	0.44	0.55
K2O	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.19	b.d.l.	0.09
F	b.d.l.	b.d.l.	0.62	0.21	0.239	0.219	0.135
Total	100.16	100.60	98.18	96.53	97.87	97.89	96.71
Si	1.990	2.001	1.01	3.939	7.47	7.76	7.88
Ti	0.001		0.91		0.03		
Cr		0.001					
Al	0.002	0.001	0.10		1.01	0.34	0.27
Fe3	0.011		0.01		0.19	0.16	0.06
Fe2	0.000	0.005	0.00	0.08	0.19	0.21	0.35
Mn	0.001						
Mg	0.994	0.990		2.9	4.13	4.56	4.50
Ni	0.004		-	-	-	-	-
Ca	0.995	0.999	0.99	0.138	1.67	1.90	1.81
Na	0.002	0.002		0.010	0.404	0.117	0.148
K					0.03		0.02
F			0.065	0.042	0.104	0.095	0.059