Melting relations in the system $FeCO_3$-$MgCO_3$ and thermodynamic modeling of Fe-Mg carbonate melts

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ABSTRACT

To constrain the thermodynamics and melting relations of the siderite-magnesite ($FeCO_3$-$MgCO_3$) system, 27 piston cylinder experiments were conducted at 3.5 GPa and 1170-1575 °C. Fe-rich compositions were also investigated with 13 multi anvil experiments at 10, 13.6 and 20 GPa, 1500-1890 °C. At 3.5 GPa, the solid solution siderite-magnesite coexisting with melt over a compositional range of X_{Mg} (=$Mg/(Mg+Fe_{tot})$) = 0.38-1.0, while at ≥10 GPa solid solution appears to be complete. At 3.5 GPa the system is pseudo-binary because of the limited stability of siderite or liquid $FeCO_3$, Fe-rich carbonates decomposing at subsolidus conditions to magnetite-magnesioferrite solid solution, graphite and CO_2. Similar reactions also occur with liquid $FeCO_3$ resulting in melt species with ferric iron components, but the decomposition of the liquid decreases in importance with pressure.

25   At 3.5 GPa the metastable melting temperature of pure siderite is located at 1264 °C whereas

26   pure magnesite melts at 1629 °C. The melting loop is non-ideal on the Fe-side where the

27   dissociation reaction resulting in Fe^{3+} in the melt depresses melting temperatures and causes a

28   minimum. Over the pressure range of 3.5-20 GPa, this minimum is 20-35 °C lower than the

29   (metastable) siderite melting temperature. By merging all present and previous experimental

30   data, standard state (298.15 K, 1 bar) thermoydynamic properties of the magnesite melt

31   ($MgCO_3L$) end-member are calculated and the properties of $(Fe,Mg)CO_3$-melt fit by a regular

32   solution model with an interaction parameter of -7600 J/mol. The solution model reproduces

33   the asymmetric melting loop and predicts the thermal minimum at 1240 °C near the siderite

34   side at $X_{Mg}=0.2$ (3.5 GPa). The solution model is applicable to pressures reaching to the

35   bottom of the upper mantle and allows calculation of phase relations in the $FeO-MgO-O_2-C$

36   system.

1. Introduction

40   The stability of carbonates against decarbonation and melting is of considerable interest for

41   understanding the global carbon cycle (Dasgupta and Hirschmann 2010). Carbon solubilities

42   in mantle silicates are low, typically a few ppm and at most 10-20 ppm (Keppler et al. 2003,

43   Shcheka et al. 2006, Panero and Kabbes 2008). Hence, carbon is likely to be stored in a

44   separate phase either oxidized as carbonate(s), carbonated fluids (as documented e.g. in

45   inclusions in diamonds; Wang et al. 1996, Stachel et al. 2000, Klein-BenDavid et al. 2009) or

46   melts or in reduced phases such as diamonds, carbides or Fe-C alloys (Boulard et al. 2012).

47   Computed phase equilibria on sediment bulk compositions and metabasalts as well as phase

48   equilibria experiments on carbonated sediments, basaltic eclogites and peridotites suggest that

49   Ca-Mg-Fe carbonates remain stable beyond arc-depths and enter the deeper parts of the

50 mantle with higher melting temperatures than typical modern subduction geotherms (Wallace

51 and Green 1988, Falloon and Green 1989, Yaxley and Green 1994, Molina and Poli 2000,

52 Kerrick and Connolly 2001, 2001b, Dasgupta et al. 2004, Yaxley and Brey 2004, Dasgupta

53 and Hirschmann 2006, Poli et al. 2009, Mann and Schmidt 2015). At depth greater than 4-5

54 GPa, experiments indicate that magnesite ($MgCO_3$) is the most stable carbonate (Biellmann et

55 al. 1993, Fiquet et al. 2002, Isshiki et al. 2004). In general, carbonates tend to have high X_{Mg}

56 values compared to coexisting Fe-Mg silicates; typical compositional ranges for peridotites

57 are $X_{Mg}^{magnesite-siderite}$ of 0.93-0.99 (Brey et al. 2008, Brey et al. 2009, Ghosh et al. 2009), for

58 metabasalts 0.67-0.82 (Dasgupta et al. 2004, Yaxley and Brey 2004, Dasgupta et al. 2005), for

59 metapelites 0.3-0.8 (Thomsen and Schmidt 2008, Grassi and Schmidt 2011) and 0.2-0.9 in

60 carbonatites (Buckley and Woolley 1990). Hence, there is ample reason to investigate the Fe-

61 rich side of the magnesite-siderite binary experimentally and to develop a thermodynamic

62 model for the solid and liquid solutions in this system.

63   At the extreme Fe-rich end, natural siderite is generally associated with ankerite

64 ($Ca,Fe)CO_3$ in sedimentary banded iron formations (BIFs; Klein 2005, Kholodov and

65 Butuzova 2008). Before the rise of oxygen ~2.3 Ga ago, BIFs and anoxic shales were not only

66 platform sediments but also abundant on deep ocean floors (Beukes and Gutzmer 2008), but

67 most of the deep deposits have disappeared from the Earth surface via subduction (Polat et al.

68 2002, Dobson and Brodholt 2005). High pressure devolatilization and melting in such Fe-rich

69 systems are poorly understood and experimental investigation of the $MgCO_3$-$FeCO_3$ system is

70 required to understand the fate of subducted C-bearing BIFs. Siderite also occurs in

71 hydrothermal veins, in extraterrestrial materials such as on Mars (Morris et al. 2010), in the

72 Martian meteorite ALH84001 (Eiler et al. 2002) and in altered igneous rocks.

73   The melting of pure siderite is stable above 6.8 GPa (Tao et al. 2013, Kang et al. 2015), the

74 melting of pure magnesite above 2.5 GPa (Irving and Wyllie 1975). At lower pressures

75 magnesite simply decomposes to $MgO+CO_2$ while siderite decomposition involves a redox

76   reaction to magnetite and graphite. Due to the discordance of the graphite-CO_2 (CCO) oxygen

77   buffer with the common Fe-buffers (iron-wustite, wustite-magnetite, and magnetite-hematite),

78   wustite+CO_2 only become stable at temperatures higher than siderite stability (Fig. 1).

79   Experimental studies on the subsolidus phase relations in the $MgCO_3$-$FeCO_3$ system at 0.2-

80   0.4 GPa, 350-550 °C (Rosenberg 1967), at 1.5 GPa, 600-800 °C (Goldsmith et al. 1962) and

81   at 3.5 GPa, 900-1100 °C (Franzolin et al. 2011) prove that there is continuous solid solution

82   between siderite and magnesite. Subsolidus phase relations were then thermodynamically

83   modeled within the ternary Ca-Mg-Fe carbonate system at high pressures (Davidson 1994,

84   Franzolin et al. 2011, Holland and Powell 2011). The binary $MgCO_3$-$FeCO_3$ has recently been

85   studied at 6 GPa and 900-1700 °C (Shatskiy et al. 2015a), where results suggest minor

86   incongruent melting of Mg-Fe-carbonate to form oxide-carbonate liquids coexisting with CO_2

87   fluid. Phase equilibria studies, in particular on compositions near Fe-endmembers are

88   complicated by the fact that at conditions above the iron-wustite buffer, some of the ferrous

89   iron always oxidizes to ferric iron.

90   This study defines the melting loop of the $MgCO_3$-$FeCO_3$ binary at 3.5 GPa, 1170-1575 °C,

91   filling a decisive gap on the melting behavior of iron-bearing carbonates at mantle conditions.

92   In addition, we present experimental data constraining the Fe-rich side of this binary at 10,

93   13.6, and 20 GPa. Based on the experimental data we fit the thermodynamic solution model

94   for Mg-Fe carbonate melts considering the influence of fO_2 and redox reactions of iron-

95   bearing phases. This melt model provides the first approximation for the prediction of Mg-Fe

96   carbonate melting relations at pressure.

97   **2. Experimental and analytical methods**

98   *2.1 Starting materials*

99   Starting materials were prepared from natural magnesite with an X_{Mg} of 0.989 from

100   Obersdorf (Philipp 1998), synthetic magnesite (99.9% $MgCO_3$ powder from Alfa-Aesar) and

101   synthetic siderite. Starting materials for piston cylinder experiments were mixtures of natural

102   magnesite and synthetic siderite, while synthetic magnesite was used in the multi-anvil

103   experiments. Magnesite was dried at 220 °C for ~16 h and then stored at 110 °C. Siderite was

104   synthesized from iron oxalate, sealed into gold capsules of 5.4 mm outer diameter, at 350 °C

105   and 200 MPa in an externally heated cold seal vessel run for 6 days (French 1971). The

106   synthetic siderite had a gray-white, slightly brownish color. Each newly synthesized siderite

107   batch was analyzed by scanning electron microscope and X-ray diffraction, which did yield

108   pure siderite. Siderite was stored at ambient temperature in an evacuated glass desiccator to

109   slow oxidation, but with time develops a more intensive brown color due to oxidation. Storing

110   siderite at e.g. 110 °C in a vacuum oven to prevent hydration led to more rapid oxidation.

111   Drying siderite is not suitable as it starts to oxidize at 110 °C, hence our starting materials

112   may have contained small amounts of moisture. To minimize absorbed H_2O and oxidation,

113   siderite was synthesized repeatedly as required and experiments were done in less than 2

114   months after synthesis. Magnesite and siderite were mixed under alcohol and after drying, the

115   starting mixtures (Table 1) were stored in a glass dessicator under vacuum.

116   *2.2 Experimental methods*

117   High pressure experiments were conducted in an end-loaded piston cylinder at 3.5 GPa and

118   in a 1000 ton Walker-type multi-anvil at 10, 13.6 and 20 GPa. Piston cylinder experiments

119   were run with Teflon foil-talc-pyrex-graphite-MgO assemblies. To avoid Fe-loss to metal

120   capsules and prevent the consequent oxidation of the sample, inner graphite capsules were

121   inserted into 3 mm O.D. Pt capsules, which were welded shut. Run temperatures were

122   controlled by Eurotherm controllers within ± 2 °C, using B-type ($Pt_{94}Rh_6/Pt_{70}Rh_{30}$)

123   thermocouples. The assembly was gradually decompressed after quenching the experiments

124   by turning off the heating power.

125   Multi-anvil experiments were performed employing tungsten carbide cubes with truncation

126   edge lengths of 11, 8 and 3.5 mm in combination with prefabricated Cr_2O_3-doped MgO-

127   octahedra of 18, 14 and 10 mm edge length (18/11 assembly for 10 GPa, 14/8 for 13.6 GPa

128   and 10/3.5 for 20 GPa). Assemblies were composed of stepped (18/11, 14/8) or straight

129   (10/3.5) $LaCrO_3$ heaters, ZrO_2 sleeves, internal MgO spacers and an molybdenum end ring

130   and disc. The starting materials were loaded directly into $Au_{80}Pd_{20}$ capsules stacked in the

131   central part of the furnace assembly. The 18/11 and 14/8 assemblies contained axial

132   thermocouples while the 10/3.5 assembly has a thermocouple running across the center of the

133   furnace (Stewart et al. 2006). Temperature was controlled using a B-type ($Pt_{94}Rh_6/Pt_{70}Rh_{30}$)

134   thermocouple for 10 and 13.6 GPa or C-type ($W_{95}Re_5$-$W_{74}Re_{26}$) for 20 GPa. Typical thermal

135   gradients across a capsule are 15-25 °C in 18/11 and 14/8 assemblies. Temperature gradients

136   within the 10/3.5 assembly are 30-50 °C over the capsule length of 1.2 mm. Quenching was

137   done by turning off the heating power and was followed by pressure unloading for about 15-

138   20 h.

139   *2.3 Analytical techniques*

140   Capsules were mounted longitudinally in epoxy resin and polished to the center. The open

141   capsules were repeatedly impregnated in low-viscosity resin to avoid mechanical loss of the

142   exposed phases. Experimental charges were analyzed with a JEOL JXA8200 electron

143   microprobe (EPMA) to determine phase compositions. Hematite (Fe_2O_3) and periclase (MgO)

144   have been used as standards for Fe and Mg. The quenched melt was measured at 15 kV

145   acceleration voltage and 6 nA with a beam diameter of 15-20 μm to minimize beam damage.

146   Counting times were 30 s on the peak and 15 s on the background. Note that melt pools with

147   small melt fractions interstitial to grain boundaries were extremely difficult to measure,

148   especially with a defocused electron beam, and contamination by adjacent mineral phases

149   during the measurement could not always be excluded. In such cases we used an SEM-EDX

150 that allows acquisition using polygonal area measurements. CO_2 contents of carbonate melts

151 were estimated by difference of the totals to 100. These estimates were within a few percent

152 of the expected stoichiometric value with respect to $(Mg,Fe^{2+})CO_3$. Nevertheless, the

153 quenched melt may contain holes or disperse graphite, thus influencing analytical totals.

154 Secondly, the carbonate melts probably contain a small ferric component, and thirdly they

155 may dissolve molecular CO_2, both leading to CO_2-values different from those of

156 $(Mg,Fe^{2+})CO_3$. Calculated CO_2-concentrations were only used to plot liquid compositions in

157 FeO-MgO-CO_2 projected from graphite.

158 High resolution back-scattered electron (BSE) images were obtained from a Jeol JSM

159 6390LA scanning electron microscope to study textural relationships between phases. Micro-

160 Raman spectroscopy (Horiba Jobin Yvon LabRam HR 800) was employed to identify the

161 nature of the oxide phases (spinel group vs magnesiowustite). After analysis all samples were

162 stored in a desiccator.

163 **3. Experimental results**

164 Altogether, 40 successful experiments were performed on 6 different bulk compositions at

165 3.5, 10, 13.6 and 20 GPa, and at temperatures between 1170 and 1890 °C. All experimental

166 run conditions, phase assemblages and their molar compositions are presented in Table 1.

167 Distinctive textural features of the experimental charges at subsolidus and melting conditions

168 at 3.5 GPa and at higher pressure are shown in Figs. 2 and 3.

169 *3.1 Equilibration and run textures*

170 For the supersolidus experiments, 5-20 minutes runtime were sufficient to attain textural

171 equilibrium. Enhanced by high temperatures and the presence of a liquid phase, equilibrium is

172 evidenced by triple junctions, homogenous phase compositions, completely reacted starting

173 materials and pronounced grain growth of subsolidus carbonates. In general, equilibrium

174 carbonates form discrete large polyhedral grains. The onset of partial melting in experiments

7

175   is detected using textural criteria. Mostly, the liquid migrates and collects in the warmer zone

176   of the capsule. At low melt fractions, interstitial melt pools along grain edges (Fig. 2d) or

177   concentration of melt along capsule walls are observed (Fig. 2b, c). The carbonate melts are

178   not quenchable, quench phases from the liquid consist of dendritic aggregates of carbonates

179   (Carb-q, Fig. 2b, c, d, f) intergrown with iron oxides. Where large enough, these quench

180   oxides have been identified by Raman spectroscopy as magnetite (Mt-q), indicating that the

181   melt contains a minor ferric component.

182   For the subsolidus experiments, textural and compositional equilibrium was more difficult

183   to reach, generally requiring $\geq$1-2 h runtime. Disequilibrium was indicated by irregular grain

184   shapes Fig. 2a), magnesite-rich mineral cores and compositionally zoned carbonates. The only

185   result that is used from the subsolidus experiments are the carbonate compositions, assuming

186   that the measured carbonate compositions are (meta)stable at run condition.

187   Bubbles indicating gas- or fluid-saturation were rarely observed (Figs. 2, 3), also not in the

188   capsules where considerable equilibrium magnetite formed through reaction (1). In the

189   subsolidus runs, this may indicate that the copious amounts of CO_2 resulting from reaction (1)

190   were contained in the porosity of the graphite capsule, in supersolidus experiments all of the

191   CO_2 may be dissolved in the melt. The latter is also indicated by the coexistence of three Fe-

192   Mg phases + graphite, the phase rule only allowing for four phases in this system. Regarding

193   oxygen fugacity, the graphite-CO_2 buffer hence represents only an upper limit, supersolidus

194   experiments with all CO_2 dissolved in the melt may have a reduced CO_2-activity and hence an

195   oxygen fugacity slightly below CCO.

196

197   *3.2 Auto-redox dissociation, decarbonation and metastable equilibrium*

198   All textural and chemical features of the melting experiments in Pt-C double capsules at

199   3.5 GPa indicate equilibrium, however, this equilibrium is at least in part metastable.

200   Metastable equilibria can be experimentally investigated at appropriate run durations,

201 profiting of transition phases governed by intermediate steps of minima in the free energy

202 surface, according to the Ostwald step rule (see Putnis, 1992). Metastable equilibrium melting

203 of mullite has been extensively investigated in the system $Al_2O_3 - SiO_2$ at room pressure (see

204 Pask, 1996 for a review), and of muscovite in the system $K_2O\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$ (Rubie and

205 Brearley, 1990; Brearley and Rubie, 1990) at 0.1 GPa, revealing that metastable liquids can

206 persist over geologic timescales.

207 The range of compositions on the join magnesite-siderite for which metastable melting

208 occurs cannot be predicted a priori; as a consequence run durations were optimized following

209 a trial and error procedure. Initial run times were 24 hours, but had to be shortened to 5-20

210 min in order to minimize auto-redox dissociation of the siderite component:

211 $$6\,FeCO_3 = 2\,Fe_3O_4 + 1\,C + 5\,CO_2 \tag{1}$$
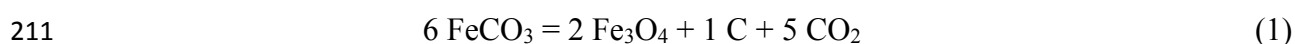
212 (French 1971, Weidner 1972, Koziol 2004, Tao et al. 2013, Kang et al. 2015). This reaction

213 progresses slowly with time, shifting the composition of the coexisting solid and liquid

214 carbonate phases towards the Mg-side. At least part of the resulting ferric iron and probably

215 most of the CO_2 are dissolved in the melt. Our results indicate that supersolidus experiments

216 equilibrate almost instantly (5-20 minutes) while subsolidus experiments result in polygonal

217 textures with 120° triple junction after 1-2 hours. However, run durations of 1-2 hours in the

218 supersolidus led to extensive redox-dissociation in Fe-rich compositions rendering the choice

219 of the optimal run duration difficult. Experiments directly run in $Au_{80}Pd_{20}$ capsules resulted in

220 minor Fe^0-loss causing a slightly stronger net oxidation of the charge.

221 *3.3 The siderite-magnesite join at 3.5 GPa*

222 The most critical compositions of run products at 3.5 GPa (Table 1) are depicted in 10

223 isothermal triangular sections (Fig. 4) saturated in graphite. The compositions of the

224 experimental carbonate liquid and solid pairs are shown in an isobaric T-X diagram (Fig. 5) of

225 the siderite-magnesite join. Unfortunately, this system is generally characterized by either the

226 auto redox dissociation (1) of the siderite component and/or the simple decarbonation reaction

227 of siderite-magnesite solid solution:

228 $$1 \text{ [siderite-magnesite]}_{ss} = 1 \text{ [wustite-periclase]}_{ss} + 1 \text{ } CO_2. \qquad (2)$$
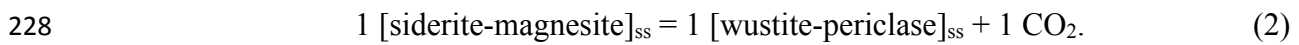
229 The oxide phases are composed of large and idiomorphic grains (up to ~100 μm),

230 identified as magnetite-magnesioferrite solid solution $((Mg,Fe^{2+})Fe^{3+}_2O_4)$ or magnesiowustite

231 $((Mg,Fe^{2+})O)$. As argued below, the experiments are most likely not on the CCO (C-CO-CO_2)

232 oxygen fugacity buffer, lending support to the hypothesis that the CO_2 produced by reactions

233 (1) and (2) may completely dissolve in the melt.

234 The textures and compositions of the experimental run products were used to define the

235 liquidus and solidus phase boundaries between carbonate liquid (Liq) and solid (Carb$_{ss}$). Bulk

236 and phase compositions are expressed on a molar basis i.e. $X_{Mg} = Mg/(Fe_{tot}+Mg)$ (Table 1).

237 Subsolidus phase assemblages change considerably at different bulk X_{Mg}. The amount of

238 magnetite-magnesioferrite solid solution (Mt$_{ss}$) in the run products increases with Fe content

239 in the bulk. At temperatures of 1170-1230 °C and bulk X_{Mg} of 0.1-0.15, crystal aggregates are

240 dominantly composed of Mt$_{ss}$ and little carbonate (Fig. 2a). Some of the initial experiments

241 (e.g. L-7 and L-8) exhibit large almost unreacted magnesite (X_{Mg} of ~0.94-0.98) grains up to

242 ~180 μm; in subsequent experiments, care was taken to grind the starting materials to <10 μm

243 grain size. Experiments with Pt-C double capsules do not inhibit completely the auto-redox

244 dissociation (1) and decarbonation reaction (2) of the siderite component, even with short run

245 times (5 min, Fig. 2d, e, f). Experimental products at subsolidus conditions with bulk

246 X_{Mg}=0.2-0.4 have Carb$_{ss}$ and Mt$_{ss}$. At higher bulk X_{Mg} the run products had magnesiowustite

247 (Mwu$_{ss}$) as the dominant oxide phase, its abundance generally increasing with run duration

248 (Fig. 2c) and temperature. Subsolidus phase assemblages with a bulk X_{Mg} of 0.75 appear at

249 temperatures up to ~1380 °C. These experimental charges contain mostly crystal aggregates

250 of (Fe,Mg)CO_3 and very minor oxide phases, either Mt$_{ss}$ or Mwu$_{ss}$ or both.

251   Solid phase assemblages do not invariably include oxide phases, e.g. where first partial

252   melting of carbonates occurs at 1250 °C with bulk X_{Mg} of 0.2, crystals consist essentially of

253    $Carb_{ss}$ (Fig. 2b). Carbonate melt is recognized by dendritic intergrowth of carbonate and oxide

254   quench fractions. The measured melt compositions range from X_{Mg} = 0.212 to 0.826.

255   Experiments with a higher bulk X_{Mg} of 0.75 show the onset of partial melting from ~1400 °C

256   upwards, these experimental charges are characterized by some minor unavoidable Mt_{ss} (Fig.

257   2d). Complete melting is obtained at 1575 °C (Fig. 2f).

258   *3.4 The Fe-rich side of the $MgCO_3$-$FeCO_3$ join at 10 – 20 GPa*

259   Additional melting experiments were performed with the starting compositions

260    $Mg_{0.1}Fe_{0.9}CO_3$ and $Mg_{0.15}Fe_{0.85}CO_3$, to define the Fe-rich side of the siderite-magnesite join at

261   10, 13.6 and 20 GPa. Textural features of experimental charges and compositions of run

262   products are summarized in Figs. 3 and 6, experimental data of the pure siderite component

263   are from Kang et al. (2015).

264   The experimental charges from 10-20 GPa are mostly partially molten at temperatures

265   from 1500 to 1890 °C, at 1550 °C one experiment (SM-05) contains only polygonal carbonate

266   crystals, indicating subsolidus conditions. Similar to the experiments at 3.5 GPa, Mg-bearing

267   siderite melt forms a dendritic texture composed of carbonate quench commonly accompanied

268   with small Fe-rich oxide quench phases (Fig. 3d). In some experiments melt is a more

269   homogenous carbonate quench showing only minor or no oxide quench (Fig. 3b, c).

270   The near-solidus experiments are characterized by wide melting intervals spanning 170 °C

271   at 10 GPa, 100 °C at 13.6 GPa and 320 °C at 20 GPa, but over most of these intervals, melt

272   proportions are small and do not exceed 5-15 vol% (Fig. 3b). We explain the appearance of a

273   small melt fraction, increasing little with temperature over a large temperature interval by

274   either absorbed water in the starting material or H_2O resulting from hydrogen diffusion

275   through the capsule wall during the experiment. We hence interpret the solidus of the dry

276   system to occur when large amounts (>30%) of melt appear, in particular as the Fe-rich bulk

277   compositions melt almost congruently. In comparison to the experiments at 3.5 GPa, charges

278   do not contain equilibrium Fe-spinel (Mt_{ss}) or magnesiowustite (Mwu_{ss}), but only a quench of

279   Fe-oxides (magnetite) interstitial to the dendritic quench of carbonates. At all pressure

280   condition, the compositions of the carbonates and coexisting melt phases are located towards

281   the Fe-rich side (Fig. 6). One experiment (SM-04, 1670 °C, 10 GPa) appears to be

282   inconsistent with all other experiments, the reason for this remains unclear.

283   **4. Thermodynamics of carbonate melts in the system $FeCO_3$-$MgCO_3$**

284   To derive a simple thermodynamic model for carbonate melts from our experiments we

285   assume that the melt can be described as a binary mixture between magnesite and siderite

286   endmember compositions, i.e., we neglect the Fe^{3+} component and dissolved CO_2 in the melt.

287   We adopt the van Laar model (Holland and Powell 2003) of Franzolin et al. (2011) for fully

288   disordered solid carbonate, which gives the partial molar gibbs energy of magnesite and

289   siderite as

290
$$g_i = g_i^0 + R * T * \ln(X_i) + R * T * \ln(\gamma_i) \tag{3}$$

291   where g_i^0 is the molar gibbs energy of the pure endmember, X_i its mol fraction in the solution,

292   and the activity coefficient

293
$$\ln(\gamma_i) = \frac{2*\alpha_i*(X_j*\alpha_j)^2}{(\alpha_i+\alpha_j)*(\alpha_i*X_i+\alpha_j*X_j)^2} * W_{sol} \tag{4}$$

294   with α_{mag} = 1 J/mol, α_{sid} = 0.01 J/mol + 0.000666 J/mol * T, and W_{sol} = 10000 J/mol. For

295   the liquid we assume a regular solution model, such that

296
$$R * T * \ln(\gamma_i) = (1 - X_i)^2 * W_{liq} \tag{5}$$

297   where W_{liq} is an interaction parameter to be determined by analysis of the experimental

298   results (Supplementary material). More complex, both subregular and assymetric formulations

299 for the liquid resulted in models that predicted implausible phase relations. The unknown

300 interaction parameter W_{liq} was calculated as the average of the values obtained by solving

$$g_{mag} = g_{magL}$$

$$g_{sid} = g_{sidL}$$

301 at the experimentally determined solidus conditions at 3.5 GPa and results to -7600 J/mol. For

302 these calculations, the thermodynamic properties of the endmembers siderite (Table 2) and

303 siderite melt (FeCO₃L) are taken from Kang et al. (2015). The caloric properties G_0 and S_0 of

304 magnesite were adopted from (Holland and Powell 2011), whereas the volumetric data (V_0, α_0,

305 K_0 and K') are from Merlini et al. (2016). Note that the volume data of Merlini et al. (2016)

306 are consistent with those on siderite and magnesite by Litasov et al. (2008, 2013). The

307 endmember data for magnesite liquid (MgCO₃L) were derived from the congruent melting

308 curve of magnesite. At pressures below 4 GPa, melting of magnesite is observed at ~1585 °C,

309 3 GPa and at 1610 °C, 3.6 GPa (Irving and Wyllie 1975). At higher pressures the melting

310 temperature of MgCO₃ is located at ~1910 °C, 8 GPa and 2090 °C, 15 GPa (Katsura and Ito

311 1990). Based on these four experimental brackets, we adopt the following melting curve for

312 pure magnesite

313 $$T_m(°C) = 1292.85 + 103.82 * P - 3.38 * P^2 \qquad (P \text{ in GPa}).$$

314 It is assumed that the temperature dependence of the thermal expansion (α_T) and bulk

315 modulus (K_T) of all endmembers are adequately represented by the empirical relations

316 $$\alpha_T = \alpha_0 * \left(1 - \frac{10}{\sqrt{T}}\right) \qquad (6)$$

317 $$K_T = K_0 \left(1 - 1.5 * 10^{-4}(T - 298.15)\right) \qquad (7)$$

318 given by Holland and Powell (1998) and volumes are computed from the Murnaghan equation

319 of state

320 $$V(T,P) = V(T,P_r) * \left[1 - K' * \frac{P}{\{K'*P + K(T,P_r)\}}\right]^{\frac{1}{K'}}. \qquad (8)$$

321   The heat capacity of magnesite is adjusted at high temperatures (>2000 K) such that C_P

322   converges to the Dulong-Petit limit

$$C_P = 3 * R * n + \alpha_T^2 * V_T * K_T * T \qquad (9)$$

324   where R is the gas constant and n the number of atoms in the substance of interest. The C_P of

325   magnesite at low temperatures (< 800 K) was computed from Holland and Powell (2011). The

326   total heat capacity range $C_P(T)$ is then fitted adopting the following polynomial (Holland and

327   Powell 1998)

$$C_P = a + b * T + \frac{c}{T^2} + \frac{d}{\sqrt{T}} \ . \qquad (10)$$

329   The equilibrium condition, $G^{MgCO3} = G^{MgCO3L}$ on the melting curve was then used to solve for

330     $H_0, S_0, V_0, \alpha_0,$ and K_0 of MgCO₃L. The pressure derivative of the bulk modulus K' for the melt

331   is set to the same value as for the solid, i.e. K'(melt) = K'(solid) = 5. The thermodynamic data

332   of all end-members are presented in Table 2.

333   **5. Discussion**

334   *5.1 The siderite-magnesite melting loop and pure siderite melting*

335   The experimental data and the calculated melting loop in the FeCO₃-MgCO₃ system at 3.5

336   GPa are illustrated in Fig. 5. At 3.5 GPa, only considering the binary siderite-magnesite solid

337   and liquid solutions, our model predicts an asymmetric melting loop (grey field) with both the

338   solid and melt side having a negative deviation from ideal behavior and a thermal minimum at

339   X_{Mg} of 0.2 and ~1240 °C. The exact location and temperature of this minimum is a result of

340   the thermodynamic analysis of the binary. Experiments at 1250 °C provide melt and a melting

341   loop that is still 0.2 X_{Mg}-units wide. Thermodynamic analysis of the pure siderite melting

342   curve from 6 to 20 GPa (Kang et al. 2015) permits calculating the metastable[1] melting curve

343   of siderite to 1264 °C at 3.5 GPa. This result is slightly above the temperature condition

344   where melt in the binary has been observed, suggesting a minimum. At 3.5 GPa, this

---

[1] with respect to magnetite+graphite+CO₂

345 minimum may lie within the uncertainties of the experiments and thermodynamic calculations,

346 nevertheless, at 10 GPa experiments have been run with two directly adjacent capsules: one

347 with pure siderite (pS-02, Kang et al. 2015) and one with a bulk X_{Mg}=0.15 (SM-02). In this

348 single experiment, with both capsules arranged symmetrically at the hotspot, the pure siderite

349 capsule remained unmolten, while the capsule with a bulk X_{Mg} of 0.15 showed 10-15% melt,

350 a clear indication of a minimum.

351   A non-ideal melting loop contrasts the diagram as drawn by Shatskiy et al. (2015a) who

352 show an ideal melting loop, based on a few experiments at relatively Fe-rich bulk

353 compositions (X_{Mg}= 0.07-0.35) at 1600-1700 °C at 6 GPa. In comparison to our work,

354 Shatskiy et al. (2015a) used natural siderite containing 6 mol% $MnCO_3$ and 7 mol% $MgCO_3$,

355 which may account for some difference in melting temperature. However, Shatskiy et al.

356 (2015a) propose stable melting of siderite at 6 GPa at a temperature slightly below 1600 °C

357 and observe complete melting of their $Fe_{0.87}Mn_{0.06}Mg_{0.07}CO_3$ composition at 1700 °C. This is

358 in wild contrast to the experimental data of Tao et al. (2013) and Kang et al. (2015), which

359 show siderite to be stable to 1400 °C but completely decomposed to magnetite+graphite+CO_2

360 at 1450 °C, 6 GPa. Note that above 1450 °C magnetite+graphite+CO_2 form a melt rich in

361 carbonate components. The data of Tao et al. (2013) and Kang et al. (2015) also indicate that

362 direct melting of siderite only occurs above 6 GPa (6.8 GPa in Kang et al. 2015). The

363 metastable pure siderite melting temperature at 6 GPa, as extrapolated from higher pressures,

364 is 1410 °C (Kang et al. 2015). This discrepancy was discussed by Shatskiy et al. (2015a)

365 aiming at experimental artefacts such as Fe-loss to the capsule but ignoring the autoredox-

366 decomposition of siderite. It remains unexplained why Tao et al. (2013) and Kang et al. (2015)

367 observe this redox decomposition while Shatskiy et al. (2015a) do not. Further, if the melting

368 temperature of pure siderite at 6 GPa would be almost 1600 °C instead of 1410 °C, as

369 suggested by Shatskiy et al. (2015a), then at 3.5 GPa the pure siderite melting temperature

370   would have to be considerably higher and the un-ideality and minimum of the system even

371   more pronounced.

372   At higher pressures of 10-20 GPa (Fig. 6) our experiments only constrain the behavior of

373   Fe-rich bulk compositions. Our melt model, which does not contain a pressure dependent non-

374   ideal term, indicates a flat minimum topology with melting temperatures from 1580 to

375   1840 °C, at X_{Mg} increasing from 0.2 to 0.28 with pressure. The calculated melting loop (based

376   solely on thermodynamic analysis of the experiments at 3.5 GPa) is in sufficient agreement

377   with the large scale melting (30-100%) observed in the experiments at 10-20 GPa, the small

378   melt fractions observed at lower temperatures being interpreted as hydrous melting caused by

379   moisture contamination of the starting material or H-gain though capsule wall diffusion (Fig.

380   6, diamonds).

381   *5.2 The pseudo-binary nature of FeCO$_3$-MgCO$_3$*

382   Experiments in the Fe-Mg-C-O$_2$ system at 3.5 GPa show that siderite decomposition

383   through the auto-redox dissociation reaction (1) or decarbonation of the siderite-magnesite

384   solid solution (Sid-Mag$_{ss}$) according to reaction (2) interfere with the carbonate melting

385   reaction in the MgO-FeO-CO$_2$-system. For that reason, the simple binary FeCO$_3$-MgCO$_3$ has

386   in reality the system components MgCO$_3$-FeCO$_3$-CO$_2$-Fe$_2$O$_3$, and is hence a pseudo-binary.

387   However, as long as the carbonate solid and melt are equilibrated, additional phases do not

388   influence this melting equilibrium and its thermodynamic analysis. The decomposition of the

389   siderite component hampers the determination of the melting loop:

390   (i)   In the experiments, the formation of Fe-rich oxides through reaction (1) or (2)

391   shifts the bulk carbonate composition away from the siderite side towards MgCO$_3$

392   and experiments targeted at the melting loop often result in solid carbonate or melt

393   coexisting with oxides but not in the desired coexisting solid and liquid carbonate.

16

394		Obviously, when abundant low X_{Mg} iron oxides form (Table 1), the carbonate
395		phases alone do not mass balance the bulk composition anymore.
396	(ii)	Secondly, further problems arise from the reaction products of reactions (1) and
397		(2): both reactions produce CO_2; this CO_2 was not observed as gas bubbles and is
398		likely to be dissolved in the carbonate melt.
399	(iii)	Moreover, carbonate liquids do not exclusively quench to carbonates, but into a
400		mixture of carbonate and ferric iron containing oxides clearly visible in BSE
401		images (Fig. 2b, c, d, f) and sometimes identifiable as magnetite by Raman
402		spectroscopy. These textures are consistent with the results of Shatskiy et al.
403		(2015a, b; Figs. 2e, f, h and Fig. 1j, respectively), who observe a quench phase
404		from the liquid that is much brighter in BSE images than siderite.

405 To provide a first order assessment of the effect of non-stoichiometric melting, carbonate

406 phase equilibria were calculated in the system MgO-FeO-O-C including magnetite-

407 magnesioferrite and magnesiowustite solid solutions in addition to the carbonate models (Figs.

408 7-9). Graphite-saturated phase relations for this system are presented in 5 isothermal

409 triangular chemographic sections calculated for 1200 to 1675 °C at 3.5 GPa (Fig. 7). The

410 graphite-only saturation condition allows for three coexisting Fe-Mg-phases, as observed in

411 many experiments, in this case CO_2-saturation cannot occur and the carbonate melt would be

412 the only liquid phase.

413 The same MgO-FeO join is projected from C and CO_2 such that f_{O2} is constrained to the C-

414 CO-CO_2 (CCO) buffer into a T-X diagram (Fig. 8). These phase equilibria calculations

415 confirm the experimental observations (Fig. 4) that siderite-rich carbonate phases become

416 unstable at 3.5 GPa and will always transform into ferric components forming Mt_{ss} below

417 ~1500 °C at the Fe side of this pseudo-binary. Above ~1500 °C the computation predicts

418 stability fields for magnesiowustite coexisting with the carbonate liquid field towards the Mg

419 side along the FeO-MgO join projected through O_2 and C, as it is depicted in the

17

420 chemographic triangles in Fig. 7. In the experiments we used inner graphite capsules, but fluid

421 vapor bubbles of CO_2 were not observed at 3.5 GPa, hence, the experimental f_{O2} may well be

422 below CCO.

423   A calculation at 1400 °C, 3.5 GPa in $\log(f_{O2})$ vs. X_{Mg} space, expanded around CCO,

424 suggests that small variations in f_{O2} below CCO would have a large effect on the

425 magnesiowustite composition and on liquid compositions (Fig. 9), but would cause little or

426 marginal differences in the Mt_{ss} stability. The computed phase diagram also shows that below

427 an fO_2 of CCO-0.4 the stability range of Fe-Mg carbonates decreases distinctively towards the

428 Mg side along the FeO-MgO join. The carbonate melt compositions are not located on the

429 same binary of the solid carbonates, analogous to the diopside-anorthite-albite system, where

430 liquids are expected to be on a cotectic; see Fig. 10.25 in Philpotts (1990). Our two

431 component thermodynamic melt model includes hence a deviation of the melt composition

432 from the simple binary, a situation not much different from many solid solutions, where pure

433 ferrous endmembers do not exist but always contain some ferric iron (e.g. biotite, staurolite,

434 saphirine, talc).

435

6. Concluding remarks

437   In this study we present experiments on the $FeCO_3$-$MgCO_3$ join at 3.5-20 GPa, which

438 allow depicting the melting loop in T-X diagrams. The melting loop is asymmetrical and has a

439 thermal minimum at Fe-rich bulk compositions. A regular solution model is adequate to

440 represent these phase relations over the pressure-temperature range of our observations.

441 Interpretation of the system at Fe-rich compositions is complicated by problems of Fe^{2+}-

442 oxidation and excess CO_2 dissolved in the melt. For the melting of basaltic and peridotitic

443 bulk compositions a liquid Fe-carbonate endmember is needed to calculate phase relations,

444 although the dominant carbonate melt components are the Mg and Ca ones. For carbonated

445   pelites, partial carbonate melts may reach down to X_{Mg} = 0.24 (Grassi and Schmidt 2011), at

446   the extreme banded iron formations may produce almost pure siderite melts.

447

454

455   **Figure captions**

456   **Fig.1** Schreinemaker analysis of the melting relations of siderite and magnesite at their

457   lowest melting pressures. The MgO-CO_2 system (a) behaves as a true binary and has a simple

458   topology, but phase relations describing siderite melting require 3 system components (FeO-

459   C-O_2), opening up a magnetite+graphite field (b). Wustite only becomes stable at higher

460   temperatures than siderite stability, a consequence of the discordance between the CCO buffer

461   and the Fe-O buffers (see insert). The topology of the FO-C-CO_2 system is drawn for two

462   options: in black and blue reactions for a siderite melt with stoichiometric siderite

463   composition, in black and red for siderite melt with a minor ferric component and dissolved

464   CO_2. Approximate pressures and/or temperatures are indicated, for magnesite as determined

465   by Irvine and Wyllie (1975), for siderite as determined by Tao et al. (2013) and Kang et al.

466   (2015). Phase abbreviations in text, figures and tables are: Wu = wustite; $Carb_{ss}$ = siderite-

467   magnesite solid solution; Mt_{ss} = magnetite-magnesioferrite solid solution; Gph = graphite; Liq

468   = carbonate melt (containing Fe-oxide quench phases); Mwu_{ss} = wustite-periclase solid

469   solution; Mag_{rem} = magnesite remnant stemming from starting material; Carb-q = carbonate

quench; Mt-q = magnetite quench; $MgCO_3L$ = magnesite liquid; $FeCO_3L$ = siderite liquid;

Sid = siderite; Mag = magnesite; Mt = magnetite; Per = periclase;

Fig. 2 Back-scattered electron (BSE) images of typical run products at 3.5 GPa showing subsolidus, near-solidus and supersolidus conditions. (**a**) Carbonates at subsolidus conditions with substantial decomposition to magnetite solid solution. Note that the bulk X_{Mg} is 0.1 but the resulting carbonate has X_{Mg}=0.61. (**b**) Partial melting of carbonates to dendritic carbonate melt consisting of carbonate quench and iron oxide fractions. Some melt infiltrates the innermost part of the graphite capsule (bottom of image). (**c**) Stable Fe-Mg-carbonates coexisting with carbonate melt and some wustite. (**d**) Carbonate melt coexisting with crystal carbonates; quenched carbonate melts are interstitial to the rounded carbonate grains. (**e**) At subsolidus conditions discrete carbonates appear with minor Mt_{ss} at low run times. (**f**) Supersolidus condition, carbonates are completely molten with an intergrowth of carbonate and magnetite quench.

Fig. 3 BSE images of run products at 10-20 GPa. (**a**) Monomineralic stable siderite assemblage in gold-palladium capsule at 10 GPa, 1500 °C from Kang et al. (2015). (**b**) Low degree of partial melting of Mg-bearing siderite with the starting composition $Mg_{0.15}Fe_{0.85}CO_3$ at 10 GPa, 1500 °C. A similar amount of melt persists over a temperature range of 30-200 °C and is interpreted as melting caused by small amounts of H_2O present in the capsule (see text). (**c**) Coexistence of siderite-magnesite solid solution with Fe-Mg carbonate melt at 13.6 GPa, 1700 °C. (**d**) Melting of Fe-Mg carbonates at 20 GPa, 1860 °C. Abbreviations as in Fig. 1

Fig. 4 Triangular isothermal sections of the most critical experimental runs showing compositions of run products in the $FeO-MgO-O_2$ system projected through graphite from 1575 to 1200 °C at 3.5 GPa. Note that melt compositions in e) and f) exhibit large standard

496 deviations (see also Fig. 5 and Table 1). Coexisting phases within each experiment were

497 connected by solid tie-lines. Symbol or tie-line labels indicate experiment number, see also

498 Table 1. Abbreviations as in Fig. 1

499

500 **Fig. 5** Isobaric T-X diagram in the simple $FeCO_3$-$MgCO_3$ binary at 3.5 GPa, depicting

501 experimental data of stable carbonate solid and liquid pairs with the calculated melting loop

502 employed by Perple_X 6.6.9 (Connolly 2009). The pure siderite melting temperature is

503 calculated from Kang et al. (2015), note that this melting temperature is metastable. The pure

504 magnesite melting temperature is after Irving and Wyllie (1975) and calculated for the pure

505 magnesite melting curve. Standard thermodynamic properties for the end-members siderite

506 and $FeCO_3L$ are adopted from Kang et al. (2015). Thermodynamic data for magnesite and

507 $MgCO_3L$ are from Merlini et al. (2016) and this study. We used our melt solution model

508 termed LIQ(NK) combined with the solid solution model for ternary Ca-Mg-Fe carbonates

509 termed dis(EF) from Franzolin et al. (2010). Dashed lines represent tie lines between

510 coexisting solid and liquid pairs. Thin solid lines display error bars in terms of standard

511 deviation. The symbols and error bars of experiments at 1250 °C are not superimposed for

512 clarity. Note that the Fe-rich side at $X_{Mg}<0.25$ is metastable with respect to magnetite+

513 CO_2+graphite. The position of the minimum is calculated from the fit of the loop to the

514 experimental data (see text). Abbreviations as in Fig. 1

515

516 **Fig. 6** Isobaric T-X sections of the Fe-rich side of the $FeCO_3$-$MgCO_3$ join at 10, 13.6 and

517 20 GPa. Experimental compositions of coexisting carbonate solid (filled symbols) and liquid

518 (open symbols) pairs are from this study, pure siderite experiments are from Kang et al.

519 (2015). Half-filled symbols illustrate partial melting. Blue diamonds indicate experiments

520 with <15% melt, interpreted as melting in the presence of minor H_2O unavoidable in this kind

521 of starting material. The melting loops including a minimum were calculated employing

522 Perple_X 6.6.9 (Connolly 2009). Note that the liquid solution model is entirely based on data

523 at 3.5 GPa. The small deviation between the calculated loop and the experimental data at high

524 pressure does not warrant an unideal pressure-term in the liquid solution model. The

525 thermodynamic data of all end-members are the same as in Fig. 5. Horizontal solid lines are

526 error bars in terms of standard deviation. Abbreviations as in Fig. 1

527

528 **Fig. 7** Calculated chemographic diagrams in the $FeO-MgO-O_2$ ternary saturated in graphite,

529 showing stable phase assemblages in isothermal sections from 1200 to 1675 °C employing

530 Perple_X 6.6.9 (Connolly 2009). For these calculations we included the ideal solid solution

531 models for magnetite-magnesioferrite (MF) and for periclase-wustite (P) from Perple_X in

532 addition to the carbonate models. Initial melting appears between 1200 and 1300 °C, see text.

533 White triangles suggest 3-phase fields where the phases at their corner points are stable with

534 each other. Grey fields represent two-phase fields between opposing mineral assemblages.

535 Solid solutions are indicated by bold lines. Abbreviations as in Fig. 1

536

537 **Fig. 8** Calculated isobaric *T-X* diagram along the FeO-MgO join projected through CCO,

538 i.e. saturated in CO_2 fluid and graphite at 3.5 GPa employing Perple_X 6.6.9 (Connolly 2009).

539 The solution models used in this computation are the same as in Fig. 6. CO_2 is chosen as the

540 independent saturated fluid component and O_2 as the saturated or buffered component. The

541 fluid EoS is X(O) GCOH-fluid hybrid-EoS from Connolly and Cesare (1993). Carbonates are

542 unstable near the siderite side where magnetite-magnesioferrite solid solution forms.

543 Thermodynamic properties of wustite, periclase, magnetite and magnesioferrite are from

544 Holland and Powell (2011). The thermodynamic data set of Fe-Mg carbonates and their melts

545 are the same as described in Fig. 4. Abbreviations as in Fig. 1

546

547   **Fig. 9** Calculated phase relations in $\log(f_{O2})$ vs. $X_{Mg}=Mg/(Fe_{tot}+Mg)$ expanded around the

548   CCO buffer at 1400 °C, 3.5 GPa portraying that small variations in f_{O2} have large effects on

549   magnesiowustite and on carbonate liquid compositions. As the experiments are most probably

550   below CCO the phase equilibria computation is in good agreement with the experimental

551   observations of Mwu_{ss} compositions deviating to higher X_{Mg} due to the change of f_{O2}. This

552   effect is prominently important, since carbonates become unstable to very low f_{O2} towards the

553   Mg side of this pseudo-binary. Note that the stability boundaries of the carbonate liquid and

554   solid field would slightly extended at higher fO_2 due to the ferric iron component in the melt.

555   The solution models used are the same as in Figs. 7 & 8.

556

557   **Appendix**

558   Thermodynamic modeling is used to determine the general shape of the stability fields and the

559   relations between the different phases occurring in the system. Furthermore, it allows

560   subsequent comparison between calculated and experimentally determined stability data. In

561   Earth sciences, thermodynamic melt models have been offered for granitic (Holland and

562   Powell 2001, Gualda et al. 2012) and basaltic silicate melts (Ghiorso and Sack 1995). In the

563   following section, we use our experimental data to develop a thermodynamic model for

564   carbonate melts within the $FeCO_3$-$MgCO_3$ system valid to 20 GPa.

565   The thermodynamic properties of the two liquid endmembers $FeCO_3L$ and $MgCO_3L$

566   constitute the basis of the solution model of carbonate liquids along the $FeCO_3$-$MgCO_3$ join.

567   The Gibbs energy of such a solution phase contains two terms in addition to the pure

568   mechanical mixing:

569     $$G_{sol} = G^{mech} + G^{conf} + G^{ex}$$

570   The molar Gibbs energy of a solution G_{sol} may hence be further formulated as

23

$$G_{sol} = \sum_{i=1}^{n} X_i G_i^0 + RT \sum_{i=1}^{n} X_i ln X_i + RT \sum_{i=1}^{n} X_i ln\gamma_i \, .$$

571   The first term is the energy arising from mechanically mixing of the endmembers and the

572   second term corresponds to the configurational entropy. The third term accounts for unideal

573   energetic effects caused by distortions of the atomic structure (e.g., strain) through mixing and

574   is the (excess) Gibbs energy of mixing G^{ex}.

575   At equilibrium, the chemical potentials of the components in the system (or their partial molar

576   Gibbs energies) are required to be equal in coexisting phases, i.e. in the melt and crystal. If μ

577   is the partial molar Gibbs energy, the following equations are valid for coexisting carbonatite

578   crystals and melts:

579    $$\mu_{Sid}^{S} = \mu_{Sid}^{L}$$

580    $$\mu_{Mag}^{S} = \mu_{Mag}^{L}$$

581   where S and L are the solid and liquid phases; Sid = siderite and Mag = magnesite.

582   The excess term of the solid phase is modeled with the Van Laar parameters α and one

583   interaction parameter W (in J/mol) based on the work of Franzolin et al. (2010). The activity

584   coefficient term $RTln\gamma_i$ of the solid phase is defined as

585    $$RTln\gamma_i = \frac{2\alpha_i}{\alpha_i + \alpha_j} \varphi_j^2 W_{ij}$$

586   (Holland and Powell 2003) where

587    $$\varphi_i = \frac{p_i \alpha_i}{\sum_{j=1}^{n} p_j \alpha_j} \, .$$

588   The proportion p is equal to the mole fraction since there are no order-disorder phenomena in

589   this system.

590   The excess term of the melt phase was modeled according to the symmetrical regular

591 (Hildebrand 1929) and macroscopic (asymmetrical) subregular formalism (Hardy 1953) with

592 one (W) or two (W_{12}, W_{21}) different Margules interaction parameters. The latter describe the

593 asymmetric activity-composition relationship in Fe-Mg-carbonate melts.

594   For a n component system, the excess Gibbs energy of an asymmetric, subregular solution

595 can be written in general terms as

596
$$G^{ex} = \sum_{i}^{n} \sum_{<j}^{n} X_i X_j (X_j w_{ij} + X_i w_{ji})$$

597 The activity coefficients of the two end-members in a subregular solution are given as

598
$$RT ln\gamma_{sid} = (1 - X_{sid}) X_{mag} [w_{sm} + 2(w_{ms} - w_{sm}) X_{sid}]$$

599
$$RT ln\gamma_{mag} = X_{sid} (1 - X_{mag}) [w_{ms} + 2(w_{sm} - w_{ms}) X_{mag}]$$

600 For $w_{12}=w_{21}$, these equations reduce to the expressions for a regular solution, i.e. the

601 interaction parameters are composition independent. For a regular binary solution with the

602 endmembers 1 and 2, G^{ex} is given by

603
$$G^{ex} = X_1 X_2 w_{12}$$

604 where $X_1 + X_2 = 1$ and only one of the two composition variables is independent. After

605 choosing X_2 as the independent variable i.e. $X \equiv X_2$, the activity terms can be expressed as

606
$$RT ln\gamma_{sid} = X^2 w_{sm}$$

607
$$RT ln\gamma_{mag} = (1 - X)^2 w_{sm}.$$

608   We tested both models for the excess term of the liquid by solving equations 11 and 12 at

609 each experimental data point. Comparison of the results yielded similar interaction parameters

610 and no significant improvement of the fit for the subregular model. We hence use the regular

611 model with only one parameter.

612 The interaction parameters w_{ij} can be further decomposed into enthalpic (w_{ij}^H), entropic (w_{ij}^S)

613 and volumetric terms (w_{ij}^V) aaccording to

614
$$w = w^H + w^S T + w^V P .$$

615 Introducing a temperature dependence to the interaction parameter w_S has not let to a better fit

616 of the experiments, but to an unreasonable extrapolation in temperature producing new phase

617 fields at high temperatures. So far, a pressure dependence of the interaction parameter,

618 applicable up to 20 GPa, is not needed since the location of the minimum with pressure fits

619 sufficiently with the (interpreted) melting temperatures on the Fe-rich side of the binary.

620 Nevertheless, we calculated the enthalpic terms w_{Sid}^H and w_{Mag}^H from the experimentally

621 determined phase diagram at 3.5 GPa and average them to $W_{MgFe} = W_{FeMg} = -7600$ J/mol (Table

622 2). The resultant energetic parameter is negative, maintaining a convex downward melting

623 loop with a minimum near the siderite side.

624

625

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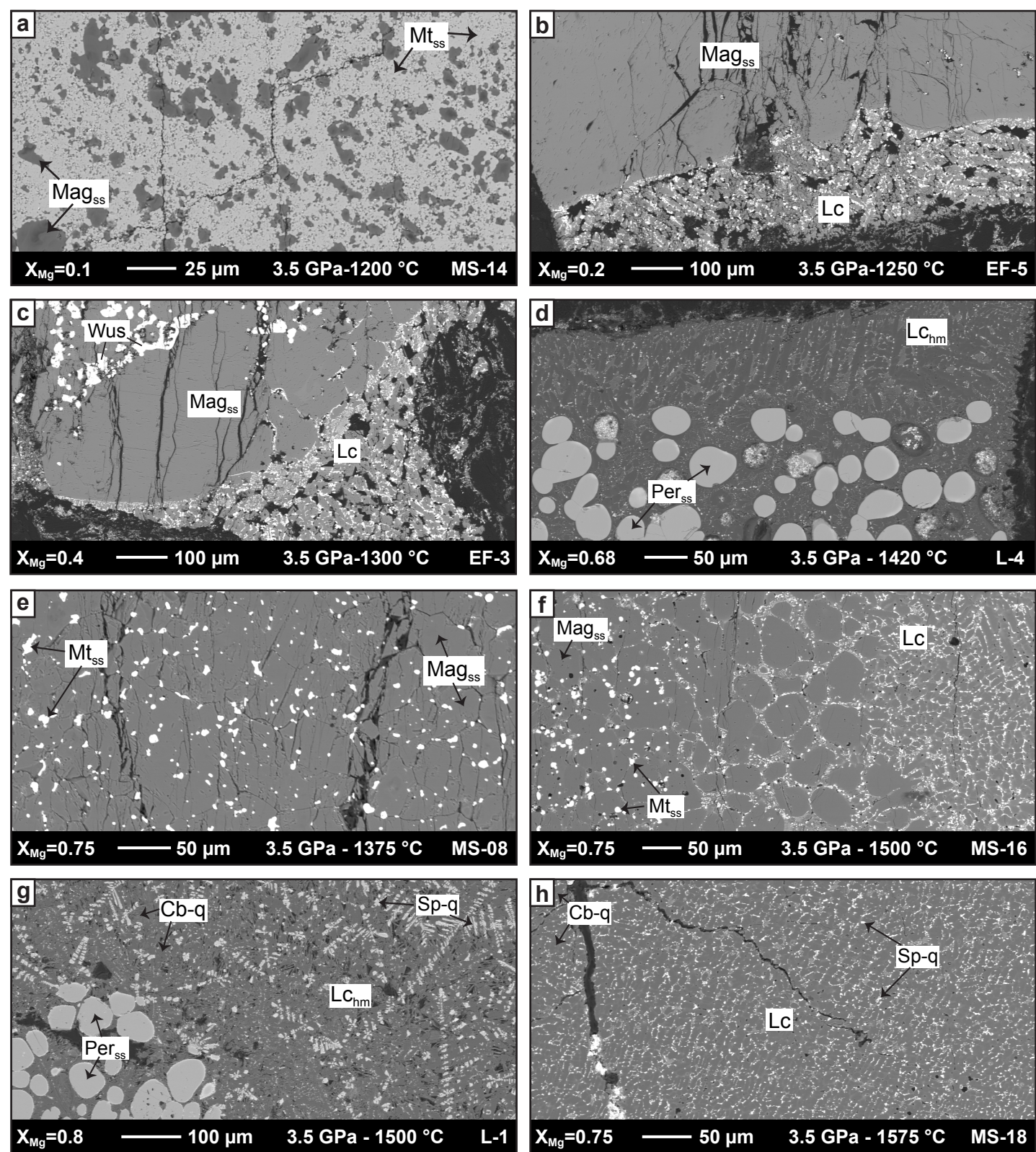801   Science Letters*, 128***,** 313-325.

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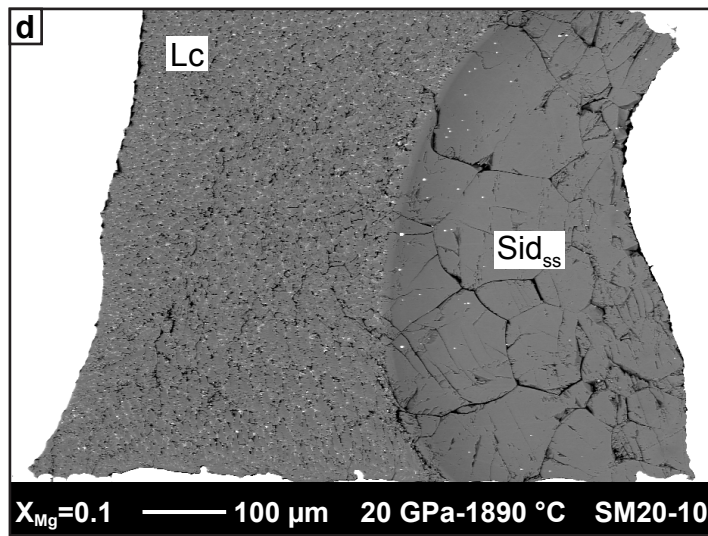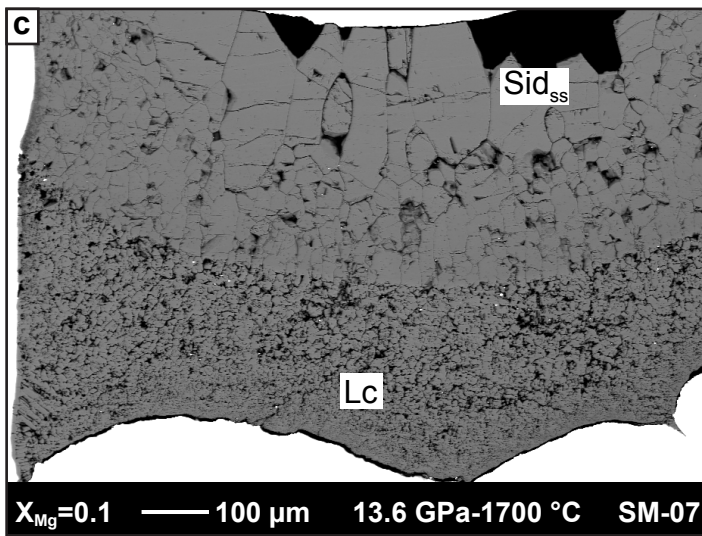**a** — Mt$_{ss}$, Mag$_{ss}$; X$_{Mg}$=0.1; 25 μm; 3.5 GPa-1200 °C; MS-14

b — Mag$_{ss}$, Lc; X$_{Mg}$=0.2; 100 μm; 3.5 GPa-1250 °C; EF-5

c — Wus, Mag$_{ss}$, Lc; X$_{Mg}$=0.4; 100 μm; 3.5 GPa-1300 °C; EF-3

d — Lc$_{hm}$, Per$_{ss}$; X$_{Mg}$=0.68; 50 μm; 3.5 GPa - 1420 °C; L-4

e — Mt$_{ss}$, Mag$_{ss}$; X$_{Mg}$=0.75; 50 μm; 3.5 GPa - 1375 °C; MS-08

f — Mag$_{ss}$, Lc, Mt$_{ss}$; X$_{Mg}$=0.75; 50 μm; 3.5 GPa - 1500 °C; MS-16

g — Cb-q, Sp-q, Lc$_{hm}$, Per$_{ss}$; X$_{Mg}$=0.8; 100 μm; 3.5 GPa - 1500 °C; L-1

h — Cb-q, Sp-q, Lc; X$_{Mg}$=0.75; 50 μm; 3.5 GPa - 1575 °C; MS-18

Fig. 1
1.5 or 2 column

a Sid$_{ss}$ — Au$_{80}$Pd$_{20}$ — X$_{Mg}$=0 — 100 µm — 10 GPa - 1500 °C — pS-02

b Lc — Sid$_{ss}$ — X$_{Mg}$=0.15 — 100 µm — 10 GPa - 1500 °C — SM-02

c Sid$_{ss}$ — Lc — X$_{Mg}$=0.1 — 100 µm — 13.6 GPa-1700 °C — SM-07

d Lc — Sid$_{ss}$ — X$_{Mg}$=0.1 — 100 µm — 20 GPa-1890 °C — SM20-10
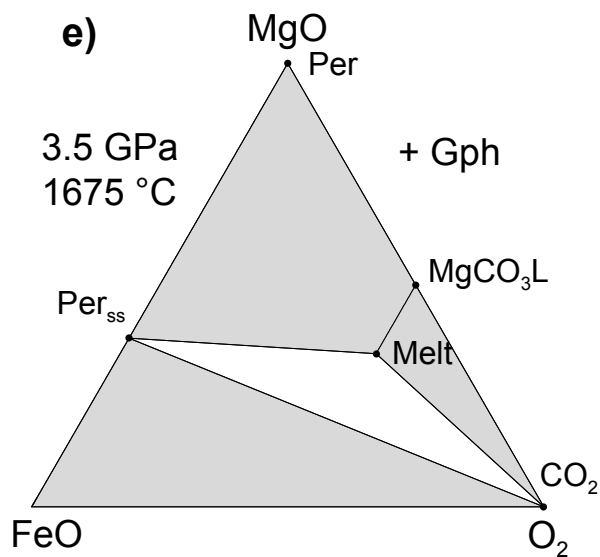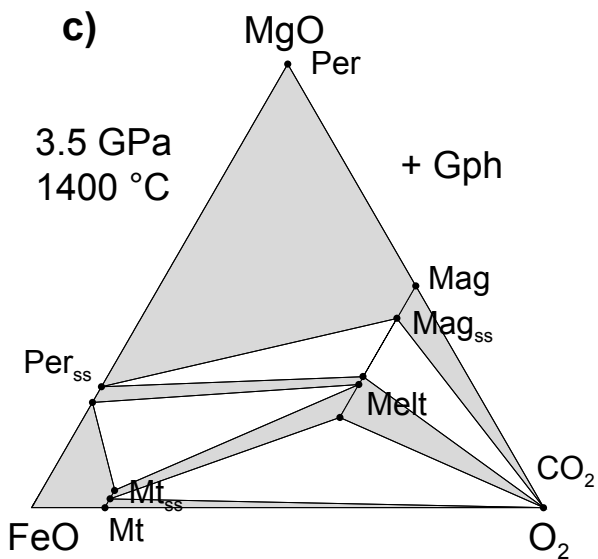
Fig. 2
1.5 or 2 column

Fig. 3
1.5 or 2 column

Fig. 4
1 column

a)
MgO Per
3.5 GPa
1200 °C
+ Gph
Per$_{ss}$
Mag
Mag$_{ss}$
CO$_2$
Mt$_{ss}$
FeO Mt
O$_2$

b)
MgO Per
3.5 GPa
1300 °C
+ Gph
Per$_{ss}$
Mag
Mag$_{ss}$
Melt
CO$_2$
Mt$_{ss}$
FeO Mt
O$_2$

c)
MgO Per
3.5 GPa
1400 °C
+ Gph
Per$_{ss}$
Mag
Mag$_{ss}$
Melt
CO$_2$
Mt$_{ss}$
FeO Mt
O$_2$

d)
MgO Per
3.5 GPa
1550 °C
+ Gph
Per$_{ss}$
Mag
Mag$_{ss}$
Melt
CO$_2$
Mt$_{ss}$
FeO Mt
O$_2$

e)
MgO Per
3.5 GPa
1675 °C
+ Gph
Per$_{ss}$
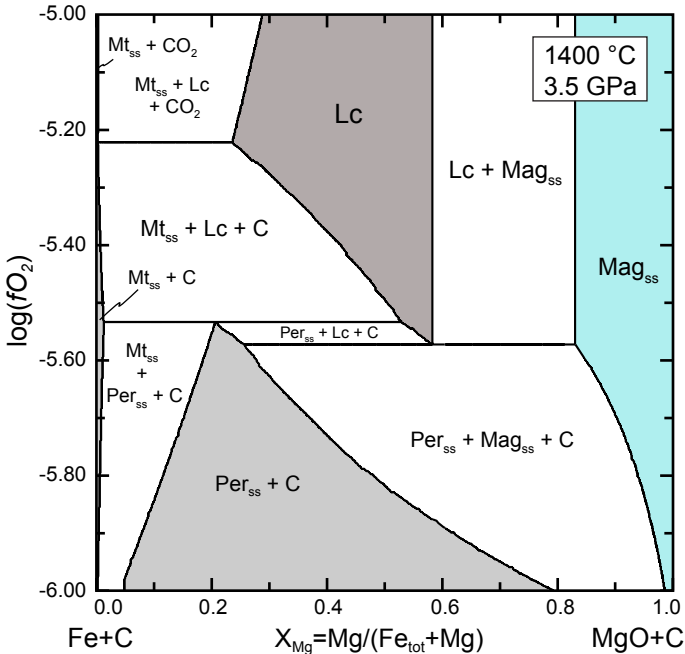MgCO$_3$L
Melt
CO$_2$
FeO
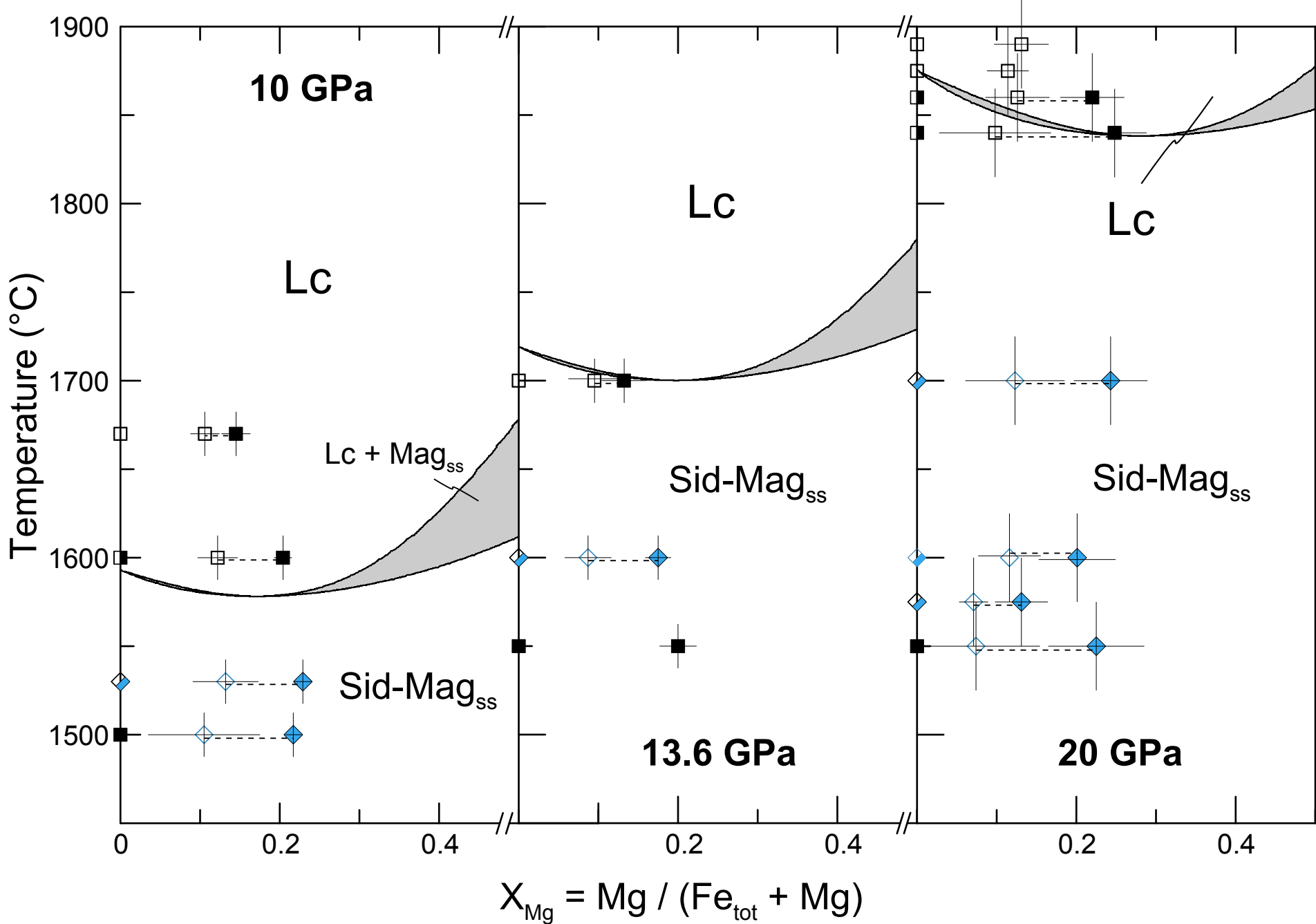O$_2$

Figure caption
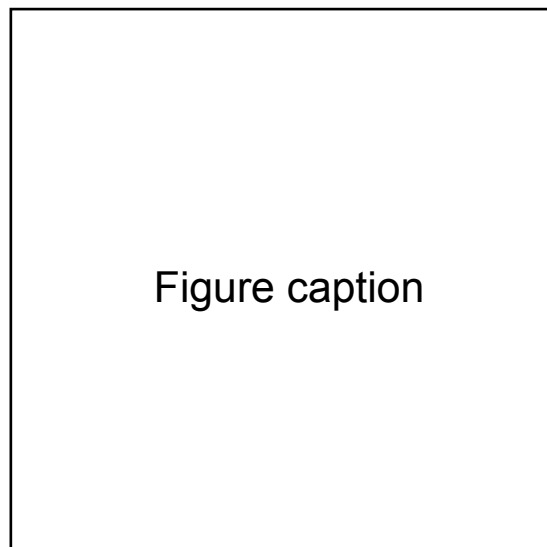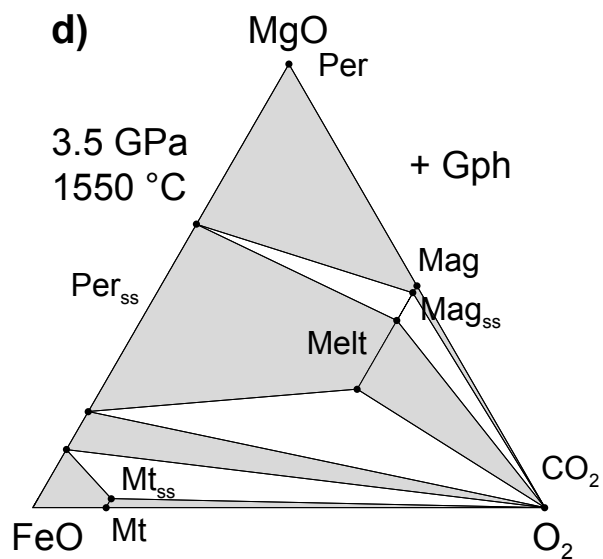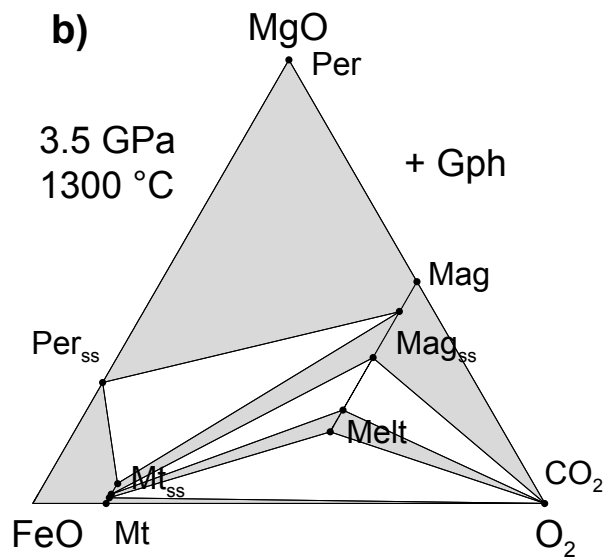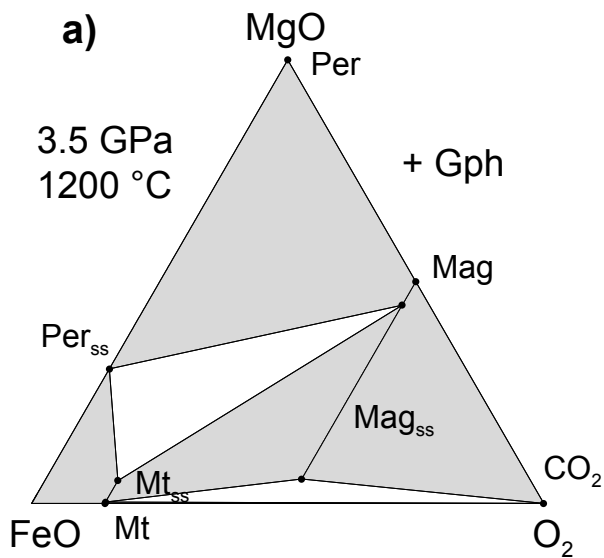
Fig. 5
1.5 or 2 column
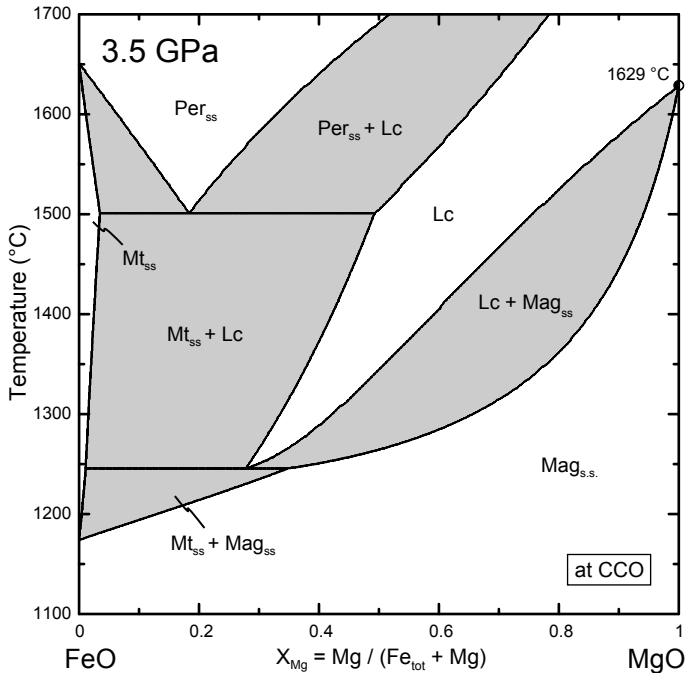
Fig. 6
1 column

Fig. 7
1 column

Fig. 8
1.5 or 2 column