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CO₂ Solubility in Kimberlite melts

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ABSTRACT

Carbon dioxide is the most abundant volatile in kimberlite melts and its solubility exerts a prime influence on the melt structure, buoyancy, transport rate and hence eruption dynamics. The actual primary composition of kimberlite magma is the matter of some debate but the solubility of CO₂ in kimberlitic melts is also poorly constrained due to difficulties in quenching these compositions to a glass that retains the equilibrium CO₂ content. In this study we used a range of synthetic, melt compositions with broadly kimberlitic to carbonatitic characteristics which can, under certain conditions, be quenched fast enough to produce a glass. These materials are used to determine the CO₂ solubility as a function of chemical composition and pressure (0.05-1.5 GPa). Our results suggest that the solubility of CO₂ decreases steadily with increasing amount of network forming cations from ~30 wt% CO₂ at 12 wt% SiO₂ down to ~3 wt% CO₂ at 40 wt% SiO₂. For low silica melts, CO₂ solubility correlates non-linearly with pressure showing a sudden increase from 0.1 to 100 MPa and a smooth increase for pressure >100 MPa. This peculiar pressure-solubility relationship in low silica melts implies that CO₂ degassing must mostly occur within the last 3 km of ascent to

26 the surface having potential links with the highly explosive nature of kimberlite magmas and
27 some of the geo-morphological features of their root zone. We present an empirical CO₂
28 solubility model covering a large range of melt composition from 11 to 55 wt% SiO₂
29 spanning the transition from carbonatitic to kimberlitic at pressures from 1500 to 50 MPa.

30 Keywords: kimberlite; carbonatite; CO₂ solubility; transitional melt

31 **1. INTRODUCTION**

32 Experimental investigation of the solubility of CO₂ in kimberlite melt has been limited due to
33 the difficulty in quenching such melt fast enough to form a pure glass (e.g. Brey and
34 Ryabchikov, 1994). Previous studies have therefore estimated the CO₂ solubility based on: (i)
35 extrapolation from trend defined in silicate melts (Brooker et al., 2001) (ii) solubility of melt
36 in partially to highly crystallised experiments (Brooker et al., 2011) (iii) solubility at 0.1 MPa
37 of simple, four components, synthetic compositions considered as analogue to the natural
38 system (Russell et al., 2012) (iv) molecular dynamics simulation studies (Guillot and Sator,
39 2011). While these studies all suggest that the solubility of CO₂ decreases as the melt
40 becomes enriched in silica, the effect of pressure has remained speculative. Our current
41 knowledge from experimental studies on silicate melt suggests that CO₂ solubility increases
42 with pressure (Blank and Brooker, 1994; Iacono-Marziano et al., 2012; Morizet et al., 2002,
43 2014) while in pure carbonate melts, CO₂ solubility is more related to satisfying
44 stoichiometric requirements and therefore less dependent on pressure as exemplified by
45 Oldoinyo Lengai's alkali carbonatite lava (Kervyn et al., 2008). However, experiments from
46 Wyllie (1989) and Brooker & Kjardgaard (2011) suggest that there is some 'excess' CO₂
47 solubility in pure CaCO₃ melt, apparently causing a decrease in liquidus temperature.
48 The composition of primary kimberlite melts in term of volatile and major element chemistry
49 is poorly constrained. Not only are natural kimberlite laden with xenolith and xenocryst

50 (Mitchell, 2008), but the strong alteration by external fluids they typically endured, in
51 particular serpentinization, strongly affects the volatile and major element composition
52 (Brooker et al., 2011; Sparks et al., 2009). Latest attempt to back-calculate the kimberlite
53 melts chemistry by removal of the serpentinization process points towards an original melt
54 being richer in CO₂ and CaO and poorer in SiO₂, water and MgO than calculated from
55 “uncontaminated” kimberlites (Brooker et al., 2011; Sparks et al., 2009). This findings are
56 corroborated with the fact that the Mg number in kimberlite is too high for equilibrium with a
57 mantle sources (Kopylova et al., 2007; Price et al., 2000) and that liquidus temperature for
58 “uncontaminated” kimberlite composition of 1400°C (Brooker et al., 2011) are higher than
59 predicted from mineral thermometry (Fedortchouk et al., 2002). We therefore chose here to
60 follow from the work of Brooker et al (2011) who argued that kimberlite melts are originally
61 transitional, that is, they have a composition intermediate between a carbonate and a silicate
62 liquid, and investigated several melt compositions with SiO₂ contents between 11 and 32
63 wt%.

64

65 In this contribution, we present results on the first experimental kimberlitic glasses
66 synthesised using an internally heated pressure vessel (IHPV) equipped with an optimised
67 quench configuration. We produced a series of melt compositions across the “transitional”
68 melt field (SiO₂ ~18 to ~32 wt%) to assess the effect of silica activity on CO₂ solubility. The
69 effect of pressure was then investigated by equilibrating melts of similar composition at
70 different pressures (50 to 1500 MPa).

71

72 **2. EXPERIMENTAL METHODOLOGY**

73 **2.1 Starting material**

74 Starting materials were produced by mixing powders from a natural lamproite from Torre
75 Alfina, Italy (table 1, see Peccerillo et al., 1988) with various amounts of synthetic powders
76 of pure oxides and natural dolomite. In order to ensure homogeneity and remove the volatiles
77 present in the Torre Alfina rock, it was fused twice in air at 1400°C and quenched to glass.
78 The composition of all mixtures used as starting materials of all experiments is reported in
79 table 1. The melt compositions we have synthesized here are very Ca-rich when compared to
80 the more Mg-rich typical “contamination free” kimberlite (Mitchell, 1986) but later compare
81 our findings to experiments with more Mg-rich composition. Therefore, an underlying
82 supposition of our work is that Mg and Ca cations behave in a similar way with respect to
83 CO₂ solubility in the melt (see Brey et al., 1991 and Brey and Ryabchikov, 1994 for an
84 investigation of the effect of Mg-Ca substitution on CO₂ solubility in kimberlite melts and see
85 discussion section 5). The Al content of the composition presented here might also be
86 considered slightly high by some authors while the Fe content would be considered low.
87 Notwithstanding these differences, the compositions we explored here provide a close
88 analogue to kimberlite melts (in term of NBO/T for instance) for which the true composition
89 remains unknown and debated (see review by Sparks 2013).

90

91 **2.2 High pressure experiments; internally heated pressure vessels and piston** 92 **cylinder**

93 To investigate the solubility of CO₂ in transitional melts at crustal pressure, we performed a
94 series of solubility experiments in the pressure range 50 to 350 MPa at relatively constant
95 temperature (1225 to 1270°C) in relatively dry and oxidized conditions ($\log f\text{O}_2 = \text{FMQ}+3$).

96 We used internally heated pressure vessels at the ISTO-CNRS laboratory in Orléans, which
97 can reach pressures of up to 400 MPa (± 3 MPa) under controlled temperature up to 1300°C
98 ($\pm 2^\circ\text{C}$). The vessel was pressurised using argon gas as the pressure medium. A two-Mo-
99 winding vertical furnace was used, creating a 5cm isothermal ($\pm 5^\circ\text{C}$) “hot-spot” zone and
100 controlled by two S-type thermocouples located on both side of the sample.

101 Experimental charges consisted of anhydrous sample powder (30 to 150 mg) loaded in gold-
102 palladium (Au₈₀Pd₂₀) or platinum capsules (2 to 4 cm in length, 2.5 mm inner diameter and
103 2.9 mm outer diameter). The capsules were welded shut. Although the initial powder
104 mixtures were stored at 120°C, the strongly hygroscopic character of some oxides (in
105 particular MgO, NaO and K₂O) absorbing atmospheric H₂O within the 15 min necessary to
106 load the capsules, made it impossible to obtain fully water-free experimental charges, hence
107 lowering slightly the XCO₂ in the fluid in equilibrium with the melt at P & T. For each
108 experiment, one to three capsules were hanged by a thin Pt wire. The temperature gradient
109 along the “hot-spot” zone, where the capsules were located, was maintained at about 10°C;
110 the hot zone was always on the top end of the sample. This gradient, although inducing an
111 uncertainty in the run temperature, was part of the quench optimisation strategy as it imposed
112 a thermal profile in the furnace that ensures a strong thermal contrast over a small vertical
113 length located directly below the hanged capsule. Rapid quenching was achieved by passing
114 an electrical current to the holding Pt wire so that the sample dropped into the cold, bottom
115 part of the furnace. The cooling rate was estimated to $>100\text{-}200^\circ\text{C s}^{-1}$ although no precise
116 estimate could be obtained. After each experiment, capsules were weighed (i) before and (ii)
117 after, opening in order to (i) verify that no leakage had occurred, and (ii) determine the
118 amount of gas not incorporated in the glass. Capsules were then opened and a fragment of the
119 charge was embedded in an epoxy resin and polished for SEM and microprobe analyses. We
120 conducted a total of 18 solubility experiments. The strategy was first to produce a complete

121 isobaric section at 350 MPa, for a range of melt chemistry spanning SiO₂ from 11 to 38 wt%
122 (expressed as nominal starting composition, Table 1). We then explored the effect of pressure
123 on several compositions (between 17 and 38 wt% SiO₂; expressed as nominal starting
124 composition) from 50 to 350 MPa at temperatures of 1225 to 1270°C. While most
125 experiments successfully produced a pure glass (Fig. 1 and Fig.S1), experiments performed at
126 50 MPa (run number: TA6_1_6 and TA7_1_3), one experiment at 100 MPa (run number:
127 TA10_1_2) and the experiment with lowest SiO₂ (run number TA15_1_1) could not be
128 quenched fast enough and quench crystals were present throughout the experimental charge
129 (these crystals could not be analysed free of the glass component).

130

131 A single piston cylinder experiment was performed at 1.5 GPa and 1300°C in a ½ inch
132 piston-cylinder apparatus. Experimental charge consisted of natural anhydrous sample
133 powder (30 mg) loaded in gold-palladium (Au₈₀Pd₂₀) capsules (1 cm in length, 2.5 mm inner
134 diameter and 2.9 mm outer diameter). The capsule was introduced in a talc–pyrex–graphite
135 furnace assembly and surrounded by MgO. A B-type thermocouple was located at ~1 mm
136 atop of the capsule and the run temperature should be considered as a minimum value. The
137 quench of the piston cylinder assembly was not fast enough to prevent the pervasive growth
138 of quench crystals (Fig. 1; Fig. S1; experiment TA6_1_5).

139 **3. ANALYTICAL TECHNIQUES**

140 **3.1 EMPA**

141 All experimental products were examined by optical microscope and scanning electronic
142 microscope (SEM) to check for the presence of quench crystals (Fig. S1). Electron
143 microprobe analyses (EMPA) were performed on a Cameca SXFive at the ISTO-CNRS
144 laboratory in Orléans. Glasses were analysed using an accelerating voltage of 15 kV, a beam

145 current of 6 nA and a defocused beam of 10 μm . Na and K were analysed first in order to
146 minimise alkali loss during analysis. The shortfall in the totals for analysed glasses was
147 broadly consistent with the CO₂ content estimated by other techniques, but systematically
148 higher (Fig. S2).

149

150 **3.2 Micro-Raman**

151 We used an Innova 300-5W Argon ion laser (Coherent©) operating at 514 nm as the light
152 source to produce Raman scattering. Spectra were collected by a Jobin-Yvon Labram
153 spectrometer (focal distance = 300 mm) equipped with a 2400 grooves/mm CCD detector.
154 Analyses were performed in confocal mode (hole= 500 μm , slit = 200 μm) and using a x50
155 Olympus objective reducing the analysed volume size to a few μm^3 . Spectra were acquired
156 over the aluminosilicate network and CO₃²⁻ region between 200 and 1350 cm^{-1} . In a few cases
157 spectra were also acquired in the OH region between 2500 and 3900 cm^{-1} . The acquisition
158 time was of 10 x 60 sec and acquisition depth was optimised in order to obtain the highest
159 Raman signal (Mercier et al., 2009). At least three spectra were acquired for each sample.
160 The CO₂ content in the glass was quantify using the calibration method of Morizet et al.
161 (2013), which provided a reproducibility on the CO₂ measurements of ~5% relative,
162 corresponding to an estimated absolute error on the CO₂ measurements less than 1 wt% for
163 the investigated samples.

164

165 **3.3 Elemental Analyser**

166 We used a Thermo Scientific, Flash 2000, CHNS elemental analyser to measure water (as H)
167 and CO₂ (as C) in all experimental products. About 1 mg of sample was loaded together with
168 1 mg of vanadium pentoxide in a tin capsule folded and analysed by combustion at 1800°C.
169 The analyser was calibrated directly prior to analysis and reproducibility on external

170 standards (marble, dolomite and hydrated basalt) was found to be better than 2% for C and
171 10% for H, giving an estimated error on the CO₂ measurement of < 1 wt%.

172

173 **3.4 Gravimetric Weight loss**

174 After experiments the capsules were weighed using a high precision balance before and after
175 puncture, to measure the mass of CO₂ (\pm H₂O) in the excess fluid phase from which, the mass
176 of dissolved CO₂ in the glass can be calculated by mass-balance. The error associated with
177 this technique depends largely on the initial amount of material loaded in the capsule.
178 Considering a maximum error on the weight measurements of 0.5 mg, for a minimum amount
179 of loaded material of 30 mg, the error on the subsequent CO₂ estimate by this method is < 2
180 wt%. There may also be an under-estimation of fluid phase mass if some is retained in
181 enclosed bubbles. However, most vesicles are found at the capsule wall (see Fig 1); as a
182 result, most of the fluid must be released on piercing.

183 **4. RESULTS**

184 All experimental charges were CO₂ saturated. This was attested by the presence of bubbles in
185 all investigated charges (Fig.1) and by weight loss after piercing the capsules. All results
186 from solubility experiments are reported in Table 2 with CO₂ content estimated from
187 elemental analyser, weight loss (after capsule puncture), EMPA and micro-Raman
188 spectroscopy. A comparison of the four different methods used to measure the CO₂ content of
189 the experimental charges is presented in Fig. S2. This figure shows that the agreement
190 between the Raman, elemental analyser and gravimetric weight loss methods is very good.
191 Estimates from EMPA shortfall are consistently overestimating the amount of CO₂ even after
192 correction for H₂O (determined by elemental analyser), suggesting that using EMPA shortfall
193 to estimate the melt CO₂ content might be inaccurate. Unless stated otherwise, all CO₂

194 contents reported in the following figures are from measurements using the elemental
195 analyser. The results of CO₂ solubility experiments at 350 MPa for a range of compositions
196 are reported in Fig. 2 together with a data point from an earlier study using a similar
197 composition (Iacono-Marziano et al., 2012). Fig.2 clearly shows a decrease in CO₂ solubility
198 with increasing amount of network forming cations (Si⁴⁺ and Al³⁺). This decrease appears to
199 be smooth and continuous across the transitional field. The effect of pressure, that is
200 nominally the pressure of CO₂, on solubility is shown in Fig. 3 for starting compositions at 18
201 to 41 wt% SiO₂ (SiO₂ + Al₂O₃ of 21 to 51 wt% respectively, expressed with volatiles at
202 saturation at 350 MPa). Since experiments at 50 MPa could not be quenched fast enough to
203 prevent the growth of quench crystals, CO₂ solubility was estimated from the amount of gas
204 released after capsule puncture and their CO₂ contents are therefore associated with a larger
205 error (estimated at ±2 wt%) than those determined by elemental analyser (estimated at < 1
206 wt%). At 18 wt% SiO₂ (at the edge of the carbonate field) a pressure drop from 1500 to 180
207 MPa seems to have a limited effect on the solubility of CO₂ (25 to 20 wt% CO₂) and most of
208 the solubility drop takes place from 100 to 0.1 MPa (assuming no CO₂ remains in the melt at
209 0.1 MPa). This results in a strongly non-linear dependence of CO₂ solubility with pressure for
210 melt compositions with SiO₂ contents in the range 18-30 wt%. At SiO₂ content higher than 30
211 wt% the solubility dependence on pressure (from 350 to 0.1 MPa) is linear, as expected in
212 silicate melts for the pressure range considered.

213 5. DISCUSSION

214 Evidence for a genetic connection between kimberlite and carbonatite magmas goes beyond
215 their, long noticed, spatial and temporal occurrence (e.g. Janse, 1975; Mitchell, 2005; White
216 et al., 1995). Kimberlite and carbonatite melts can both be produced by very low degree
217 partial melting of a carbonated mantle source as inferred from their high concentration of

218 incompatible trace elements (Nelson et al., 1988) and from high pressure melting experiments
 219 of carbonated peridotite phase assemblages (Dalton and Presnall, 1998; Dasgupta and
 220 Hirschmann, 2006; Ghosh et al., 2009; Gudfinnsson and Presnall, 2005; Rohrbach and
 221 Schmidt, 2011). In addition kimberlite and carbonatite melts have been argued to be related
 222 by fractionation processes (Dalton and Presnall, 1998; Dawson and Hawthorne, 1973; Larsen
 223 and Rex, 1992). This clear link between the two types of magma supports the hypothesis of
 224 Brooker et al. (2011) that kimberlite primary magmas were originally more transitional or
 225 carbonatitic in composition. The set of transitional synthetic super-liquidus melt
 226 compositions that have been produced here should therefore yield a robust approximation of
 227 the solubility law for CO₂ in primary kimberlitic melts.

228

229 **5.1 Empirical model of CO₂ solubility in carbonated melts**

230 Based on the solubility experiments presented here and literature data we developed a purely
 231 empirical model of CO₂ solubility as a function of the amount of network forming cations
 232 (SiO₂ + Al₂O₃) and pressure. We emphasised that it is the first modelling effort addressing
 233 such low silica melt compositions. The simple model is defined as a third order polynomial
 234 linking the amount of CO₂ dissolved in the melt to the SiO₂ + Al₂O₃ content and in which
 235 each coefficient is in turn a function of pressure as follow:

$$236 \text{CO}_{2_{wt\%}} = A \times (\text{SiO}_2 + \text{Al}_2\text{O}_3)^3 + B \times (\text{SiO}_2 + \text{Al}_2\text{O}_3)^2 + C \times (\text{SiO}_2 + \text{Al}_2\text{O}_3) + D \quad (1)$$

237 Where:

$$A = a \times P^b$$

$$B = c \times P^d$$

$$C = e \times P^f$$

238 With D , a , b , c , d , e and f representing adjusted parameters reported in Table 3. The rationale
 239 behind the formulation of equation (1) is to simulate a pressure-dependent process of dilution

240 from a pure carbonate end-member ($D=50$) with the addition of network-forming cations
241 (SiO_2 and Al_2O_3). In order to adjust the parameters in equation (1), we used CO_2 solubility
242 data for basalt (Mattey, 1991; Pawley et al., 1992; Shishkina et al., 2010; Stolper and
243 Holloway, 1988), haplo-phonolite (Morizet et al., 2002), phonotephrite (Behrens et al., 2009),
244 melilitite (Brooker et al., 2001) in addition to selected data from Brey and Ryabchikov,
245 (1994); Brooker, (1995); Brooker et al., (2011); Brooker and Kjarsgaard, (2011); Iacono-
246 Marziano et al., (2012); Morizet et al., (2013); Morizet et al., (2014) and this study (all shown
247 in the subsequent figures). Equation (1) reproduces our experimental data well (standard
248 deviation of 0.9 wt% CO_2 between the modelled and measured values) and allow us to
249 explore a larger P - $X_{(\text{SiO}_2 + \text{Al}_2\text{O}_3)}$ space. Fig. 4 shows the modelled solubility of CO_2 as a
250 function of pressure for compositions ranging from $\text{SiO}_2 + \text{Al}_2\text{O}_3$ of 0 to 51 wt% and pressure
251 from 1500 to 10 MPa. Fig.4 shows the gradual change in the CO_2 solubility behaviour from
252 carbonate to silicate end-member melts as a function of pressure. We note that from Fig.4, a
253 typical transitional melt enters the kimberlite “root zone” (see the classical model from
254 Hawthorne, 1975) with a CO_2 content of 10 to 18 wt%, consistent with the “target value” of
255 15 wt% determined by Brooker et al. (2011) for kimberlites.

256

257 The range of experiments presented here is not extensive enough to incorporate the effect of
258 temperature and alkali content in equation (1). For this, we considered the available from the
259 literature. Fig. 5 compares data from a range of studies and shows the evolution of CO_2
260 solubility as a function of network forming cations ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) for a large range of
261 composition and pressure from 2000 to 50 MPa. The predicted evolution from equation (1) is
262 also shown for pressure between 2000 and 20 MPa. The melt composition of all data shown
263 in Fig 5 is reported in Table S2, where one can notice the wide range of compositions
264 explored by these various studies. The variety of methods used to estimate the CO_2 content in

265 these studies (EMP shortfall, Raman, FTIR, elemental analyser and gas chromatography),
266 makes the comparison of dataset not ideal. In addition, while the present study, that of
267 Iacono-Marziano et al., (2012), Morizet et al., (2014), Brooker et al., (2001) and Brey and
268 Ryabchikov, (1994) are from super-liquidus experiments, data from Brooker *et al.*, (2011) are
269 from patches of glass in mostly crystallised charges while data from Brooker and Kjarsgaard
270 (2011) and Brooker (1995) are from silicate melts coexisting with an immiscible carbonate
271 melt. Perhaps most importantly, the CO₂/H₂O ratio varies widely over the reported dataset
272 with volatile component in experiments from Iacono-Marziano et al., (2012) and Morizet et
273 al., (2014) being dominated by H₂O. Keeping in mind these limitations in the comparison, we
274 can see that the set of data from Morizet et al. (2014) at 350 and 100 MPa and Morizet et al.
275 (2013) at 1000 MPa are well reproduced by our model. A similar agreement is noted with the
276 data at 2000 MPa from Brooker et al., (2001), at 200 MPa from Brooker et al (2011) and (to a
277 lesser extent) at 1500 MPa from Brooker (1995). We also note that data at 1000 MPa from
278 Brey and Ryabchikov (1994) (we only report experimental data at 1000 MPa where they
279 reported clear glass) are also well reproduced despite the significant difference in terms of
280 chemical composition (MgO up to 27wt%). Fig 6, shows a plot of experimentally determined
281 vs. calculated CO₂ solubility from which it appears that the highest deviation from the model
282 are for data by Brooker et al (2011) and Brooker and Kjarsgaard (2010). We made several
283 attempt to link the deviation from the modelled value to the melt composition (Na₂O, K₂O,
284 Na₂O+K₂O, SiO₂/Al₂O₃) but could not find any robust correlations. There is however a hint
285 that melt compositions rich in alkali can incorporate more CO₂ than comparatively Ca and
286 Mg-rich compositions (see in Fig. 5 the isolated experiment from Brooker (1995) at 1500
287 MPa with 15.6 wt% CO₂ and a composition of 0 wt% CaO and 37 wt% Na₂O). As additional
288 experimental data become available, future models should be able to explore the full effect of
289 composition (in term of Mg, Ca, Na, K, Fe cations) on CO₂ solubility.

290 A strong correlation was found between the method used to determine CO₂ content and
291 deviation from our model value. Indeed, 70% of the data located further than two standard
292 deviations away from their calculated value had CO₂ content determined by shortfall of
293 EMPA analyses. Comparing our own EMPA shortfall measurements to CO₂ determined by
294 bulk analyser (Fig. S2), we observe that determining the CO₂ content by EMPA shortfall can
295 lead to an overestimation of 2 to 6 wt% CO₂. We therefore conclude (i) that most of the
296 literature data yielding CO₂ solubility values that deviates from our model can be attributed to
297 the large error associated with estimating CO₂ content from EMPA shortfall and (ii) that from
298 the current, limited, dataset there is no identifiable systematic deviations related to the melt
299 composition. Equation (1) therefore provides a good first order approximation of the CO₂
300 content of carbonated melt over a large range of composition (SiO₂ < 55 wt%; Na₂O+K₂O <
301 22 wt%). The entrapment pressure of recently reported CO₂-rich melt inclusions from
302 Oldoinyo Lengai (de Moor et al., 2013) for instance, can be estimated using equation (1)
303 (yielding an entrapment depth of 265 to 2085 MPa for inclusions containing 3 to 8 wt%
304 CO₂).

305

306 **5.2 Implications for Kimberlite ascent and volcanism**

307 As hypothesised by Brooker et al (2011) our results indicate that CO₂ solubility decreases
308 with increasing amount of network forming cations over the carbonate-silicate transitional
309 field. This finding supports the conclusions of Russell et al., (2012) that an ascending
310 carbonate melt, assimilating mantle orthopyroxene (OPX) and becoming progressively
311 enriched in silica, will release an increasing amount of CO₂ into the gas phase and promote
312 magma ascent by keeping it buoyant in spite of increasing xenocryst loading. The effect of
313 pressure (shown in Fig. 3 and 4) on transitional melts appears to be a function of their
314 composition; melts with a composition closer to the carbonate end-member retain a large

315 quantity of CO₂ until very shallow (3 km) depth while slightly more silicate-rich melts show
316 a continuous and progressive degassing profile with CO₂ being equally released from mantle
317 depth to the surface. The solubility-pressure relationships shown by the transitional melt
318 compositions in Fig. 3 and 4 are intermediate between the behaviour of a carbonate melt
319 which will show little pressure dependence on solubility, and that of a typical silicate melt
320 which will show a mostly linear relationship in the pressure range considered (Fig. 3, 4, e.g.
321 Papale et al., 2006; Iacono-Marziano et al 2012).

322

323 The behaviour of transitional melts, retaining more than 18 wt% CO₂ up until very shallow
324 depth should lead to a rapid increase in ascent velocity while reaching the last 3 km depth
325 where important quantities of CO₂ will be released (Fig. 4). This acceleration will be
326 exacerbated by the fact that the volume fraction of gas will reach values higher than 77%,
327 corresponding to the point at which the bubble foam will collapse (Woods, 1995) changing
328 the continuous phase from a bubbly liquid magma to an ash-laden gas and therefore
329 considerably increasing the flow speed as the frictional force become much smaller and the
330 viscosity becomes closer to that of the gas phase. This ascent scenario can readily explain
331 some of the typical morphological features of kimberlite pipes. (i) The widening upward
332 geometry of the pipe, typical of eruptions happening at depth, can be explained by the high
333 amount of CO₂ released over a, most probably, very small time increment leading to
334 overpressure and explosion below the surface. (ii) The appearance of breccias and irregularly
335 shaped blocks at depth of ~3 km, in the “root zone” (see the classical model from Hawthorne,
336 1975) is consistent with large amount of CO₂ starting to be released at this depth and the
337 associated rapid volumetric expansion (Fig. 4). The occurrence of hypabyssal intrusions of
338 kimberlites however suggests that some kimberlite stall during their ascent through the crust.
339 Although we cannot confidently assign a reason for this, possibilities include the loss of

340 volatiles, segregating from the magma during ascent or the progressive cooling of the magma
341 (Kavanagh and Sparks, 2009), both process inducing crystallisation and greatly increasing
342 magma viscosity. Experiments on these compositions suggest that crystallisation is extremely
343 rapid, as illustrated by the speed at which quench crystals formed in some of our experiments.

344

345 While CO₂ is the most abundant volatile in kimberlite magmas, an unknown but probably
346 significant amount of water is also dissolved in these melts (up to 10 wt%; Kopylova et al.,
347 2007; also see discussion in Sparks et al., 2009 and experimental investigation by Keppler,
348 2003). Water degassing is therefore likely to exert a large influence on the ascent dynamics of
349 Kimberlite melts. It remains unclear however whether this process would enhance, limit or
350 displace the depth at which the CO₂-exsolution-triggered acceleration of kimberlite melts that
351 we predict takes place.

352

353 **6. CONCLUSIONS**

354 We have determined CO₂ solubility laws for kimberlite melt and have also provided a general
355 solubility model for carbonated melt composition (SiO₂ < 55 wt%) at pressure between 50
356 and 1500 MPa. We found that (i) CO₂ solubility decreases steadily with increasing amount of
357 network forming cations (ii) The effect of pressure on CO₂ solubility is a strong function of
358 composition with low SiO₂ melts retaining large amount (~15 wt%) of CO₂ up to very
359 shallow pressure (~100 MPa) while more silicated melts have a near linear CO₂ solubility
360 dependence on pressure. We propose that this peculiar pressure-solubility dependency should
361 result in a strong acceleration of an ascending kimberlite magma in the last 3 km of crust
362 where CO₂ starts to exsolve in large quantities. This behaviour can explain morphological
363 features of kimberlite pipes, notably the depth extent of the root zone and the widening-

364 upward shape of the conduit and can account for the highly explosive character of Kimberlite
365 eruptions.

366

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501

502 TABLES

503 **Table 1:** Starting oxide and natural rock powder mix compositions. The composition of a
504 natural lamproite from Torre Alfina, Italy, (Peccerillo et al., 1998), fused twice at 1400°C and
505 used to prepare the oxide-mix compositions is reported at the top of the table.

506

507 **Table 2:** Run conditions, EMPA analyses (averaged from 20), H₂O determined by elemental
508 analyser (Flash) and CO₂ determined from: (i) EMPA (by subtracting H₂O content to EMPA
509 shortfall), (ii) Elemental analyser (Flash), (iii) Micro-Raman spectroscopy (following the
510 method of Morizet et al., (2013) and (iv) Weight loss measured by puncturing the capsule
511 (allowing the CO₂ to escape) after each run. Run duration was of 2 hours in all experiments.

512

513 **Table 3:** Adjusted parameters (and corresponding standard error on multiple non-linear
514 regression fit) to calculate CO₂ solubility from Eq. (1)

515

516 FIGURES

517 **Figure 1:** Optical microphotograph showing the results from various supra-liquidus
518 experimental run producing a pure glass in all cases excepted for sample TA6_1_5 (lower
519 right) in which quench crystals give a “milky” aspect to the otherwise glassy product. All
520 samples shown are synthesised in IHPV apparatus excepted sample TA6_1_5 which was
521 synthesised with piston cylinder. Corresponding SEM images are shown in Fig S1.

522

523 **Figure 2:** CO₂ solubility measurements for a series of compositions across the silicate to
524 carbonate melt transitions equilibrated at 350 MPa. The SiO₂+Al₂O₃ content is reported
525 including volatiles. For most experiments, CO₂ content is estimated from elemental analyser
526 and associated error is estimated at ± 1 wt%. CO₂ content from Iacono-Marziano et al.,
527 (2012) is estimated from FTIR analyses.

528

529 **Figure 3:** CO₂ solubility as a function of pressure for three Kimberlite/Transitional and two
530 silicate melt compositions spanning SiO₂ content of 18 to 41 wt% and SiO₂ + Al₂O₃ content
531 of 21 to 51 wt% respectively (calculated including volatiles and corresponding to SiO₂ +
532 Al₂O₃ contents of 27 to 54 wt% on a volatile-free basis). The light-brown to green colour part
533 of the plot represents the upper 3 km of crust, corresponding to the typical “root zone” of
534 Kimberlites. Dashed lines are fitted by eye through the data points.

535

536 **Figure 4:** Modelled evolution of CO₂ solubility as a function of pressure using equation (1)
537 for melt compositions ranging from 0 to 41 wt% SiO₂ and 0 to 51 wt% SiO₂ + Al₂O₃.
538 Experiments of corresponding chemistry are shown as squares of matching colour.

539

540 **Figure 5:** CO₂ solubility measurements from this study and the literature for compositions
541 across the silicate to carbonate melt transition, equilibrated at 2000, 1500, 350, 200, 100 and
542 50 MPa. Literature data are from Brooker and Kjarsgaard, 2011; Brooker et al., 2011; Iacono-
543 Marziano et al., 2012; Brooker et al., 2001; Brooker 1995; Morizet et al., 2013 Morizet et al.,
544 2014 and Brey and Ryabchikov, 1994. Note that literature data are reported using the
545 experiment total pressure and not the P_{CO₂}. Model prediction values from equation (1) are
546 shown for a range of pressure (2000 to 20 MPa) as dotted black curves.

547

548 **Figure 6:** Experimentally determined vs. calculated CO₂ solubility using equation (1). Doted
549 red line represent the 1:1 line while continuous red lines on either sides represent the $\pm 2\sigma$
550 deviation.

551

552 SUPPLEMENTARY INFORMATION

553 **TableS1:** Standard deviation for EMP analyses reported in Table 2 (n=20).

554

555 **Table S2:** Run conditions, EMPA analyses and CO₂ determined from Raman or by bulk CO₂
556 LECO analyser for experiments from Brooker et al., (2011); Brooker and Kjarsgaard, (2011);
557 Iacono-Marziano et al., (2012); Brooker (1995) and Morizet et al., (2014).

558

559 **Figure S1:** Scanning electron microscopy (SEM) images of experimental charges shown in
560 Fig. 1. All run produced a pure glass, excepted sample TA6_1_5 (lower right) in which
561 quench crystals are pervasive.

562

563 **Figure S2:** Comparison between CO₂ content in experimental charges determined by (i)
564 EMPA (by subtracting H₂O content to EMPA shortfall), (ii) Elemental analyser (Flash), (iii)
565 Micro-Raman spectroscopy (following the method of Morizet et al., 2013), (iv) Weight loss
566 measured by puncturing the capsule (allowing the CO₂ to escape) after each run and (v)
567 EMPA shortfall without correction.

568

Name	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	Total
TA	55.74	1.34	13.05	5.83	9.43	5.45	0.96	7.68	0.51	0.00	100
TA15	11.01	0.09	2.34	0.41	8.45	36.36	0.27	2.14	0.04	38.90	100
TA6	16.60	0.20	3.85	0.86	6.93	35.48	0.28	2.27	0.07	33.47	100
TA7	20.08	0.25	4.66	1.08	8.16	32.50	0.34	2.74	0.10	30.09	100
TA8	21.66	0.30	5.03	1.30	8.21	31.30	0.37	2.96	0.11	28.75	100
TA9	23.11	0.34	5.37	1.49	8.26	30.20	0.40	3.16	0.13	27.53	100
TA10	23.79	0.36	5.53	1.58	8.29	29.68	0.41	3.26	0.14	26.95	100
TA11	30.18	0.56	7.04	2.43	8.52	24.84	0.52	4.14	0.21	21.56	100
TA12	37.70	0.79	8.81	3.43	8.78	19.14	0.65	5.18	0.30	15.22	100

Table 1: Starting oxide and natural rock powder mix compositions. The composition of a natural lamproite from Torre Alfina, Italy, (Peccerillo et al., 1998), fused twice at 1400°C and used to prepare the oxide-mix compositions is reported at the top of the table.

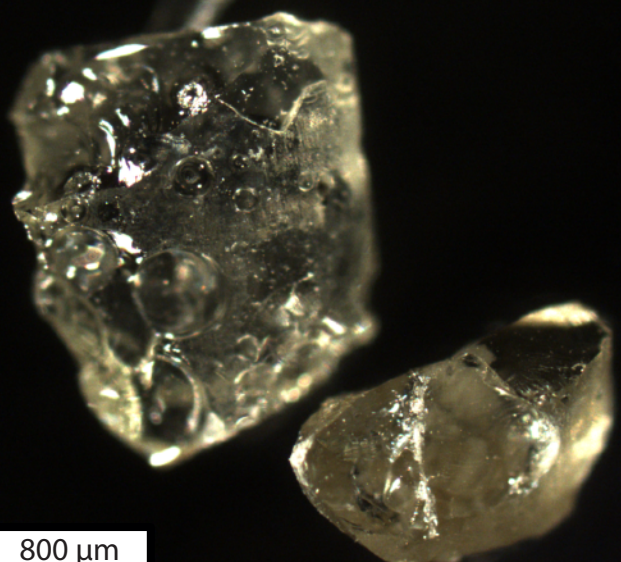
Experiment	Pressure (MPa)	Temperature (°C)	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	Shortfall	H ₂ O (Flash)	CO ₂ (EMPA)	CO ₂ (Flash)	CO ₂ (Raman)	CO ₂ (weight loss)
TA6_1_1	357.2	1225	18.44	0.2	2.05	0.74	0.03	6.87	45.25	0.3	2.3	0.04	76.22	23.8	1.54	22.24	21.84	21.4	24.4
TA6_1_4	178	1220-1260	17.97	0.19	2.63	0.81	0.04	6.75	44.8	0.41	2.19	0.04	75.83	24.2	1.19	22.98	20.07	23.4	18.9
TA7_1_1	340.2	1190	23.58	0.29	4.27	1.12	0.03	9.91	37.22	0.3	3.26	0.07	80.07	19.9	1.09	18.84	16.28	18.2	nd
TA9_1_1	336.4	1225	26.07	0.35	5.7	1.49	0.04	8.18	36.87	0.45	3.28	0.09	82.52	17.5	1.57	15.91	14.95	14.7	13.4
TA10_1_1	336.4	1225	26.77	0.35	5.8	1.64	0.05	8.52	36.24	0.4	3.39	0.09	83.25	16.8	1.73	15.02	13.80	14.4	12.0
TA11_1_1	347.8	1225	34.48	0.6	7.81	2.85	0.06	10	29.05	0.66	4.42	0.12	90.04	10.0	0.99	8.97	7.50	4.7	7.8
TA12_1_1	347.8	1225	40.97	0.82	9.74	3.68	0.06	9.38	22.96	0.82	5.58	0.19	94.19	5.8	0.59	5.22	2.79	3.5	3.7
TA6_1_5	1500	1300	<i>Crystallised</i>												1.36		24.85		nd
TA6_1_6	59.3	1225	<i>Crystallised</i>												0.84		15.87		12.7
TA7_1_2	179.2	1225	21.50	0.30	4.00	1.20	0.10	8.00	39.70	0.40	4.30	0.10	79.60	20.40	0.77	19.63	16.36	13.3	15.3
TA7_1_3	48.9	1215-1290	<i>Crystallised</i>												0.54		12.86		9.1
TA6_2_1	105.4	1270	17.80	0.20	2.40	0.70	0.10	8.10	45.20	0.20	2.50	0.10	77.20	22.80	0.79	22.01	16.47	16.3	18.3
TA7_1_4	100.7	1225	20.40	0.40	3.00	1.20	0.00	7.10	43.30	0.50	3.80	0.10	79.80	20.20	0.76	19.44	15.09	17.1	13.0
TA9_1_2	100.7	1225	24.50	0.50	4.40	1.90	0.00	8.10	39.80	0.50	4.20	0.10	84.20	15.80	0.59	15.22	10.12	10.8	11.0
TA15_1_1	351	1225	<i>Crystallised</i>												1.60		28.63		31.4
TA10_1_2	101	1225	<i>Crystallised</i>												0.71		9.00	10.18	8.59
TA11_1_2	101	1225	34.68	0.96	9.87	3.95	0.05	8.20	26.50	0.67	6.31	0.22	91.42	8.58	0.50	8.08	2.58	2.37	2.09
TA12_1_3	101	1225	43.16	0.85	9.82	3.80	0.06	9.85	22.09	0.96	5.74	0.23	96.57	3.43	0.56	2.87	1.02	1.35	1.55

Table 2: Run conditions, EMP analyses (averaged from 20), H₂O determined by elemental analyser (Flash) and CO₂ determined from: (i) EMPA (by subtracting H₂O content to EMPA shortfall), (ii) Elemental analyser (Flash), (iii) Micro-Raman spectroscopy (following the method of Morizet *et al.*, 2013) and (iv) Weight loss measured by puncturing the capsule (allowing the CO₂ to escape) after each run . Run duration was of 2 hours in all experiments.

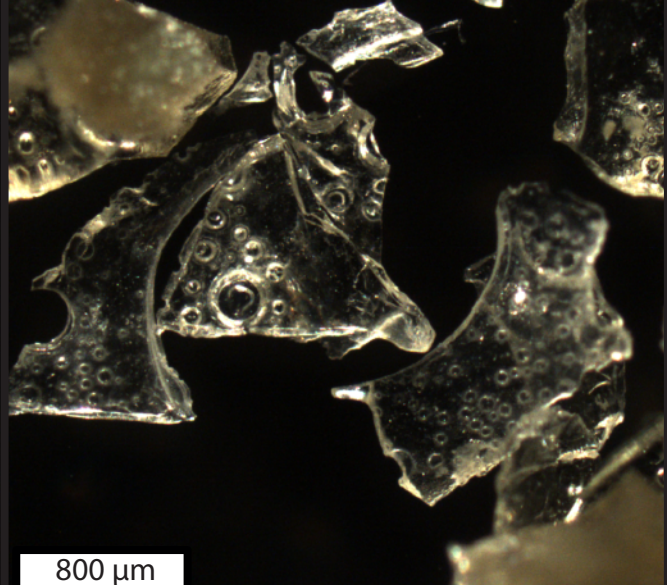
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Value	-0.001271	-0.476116	0.132494	-0.322187	-4.501117	-0.163249	50
Std. Err.	0.000244	0.040612	0.016065	0.020635	0.281876	0.008332	1.4

Table 3: Adjusted parameters (and corresponding standard error on multiple non-linear regression fit) to calculate CO₂ solubility from Eq. (1). Regression was calculated from over 160 data points (detail in text).

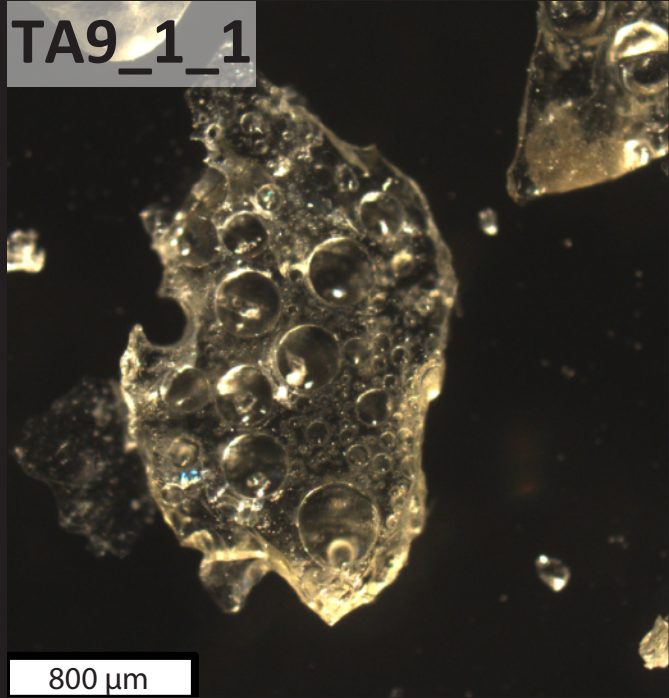
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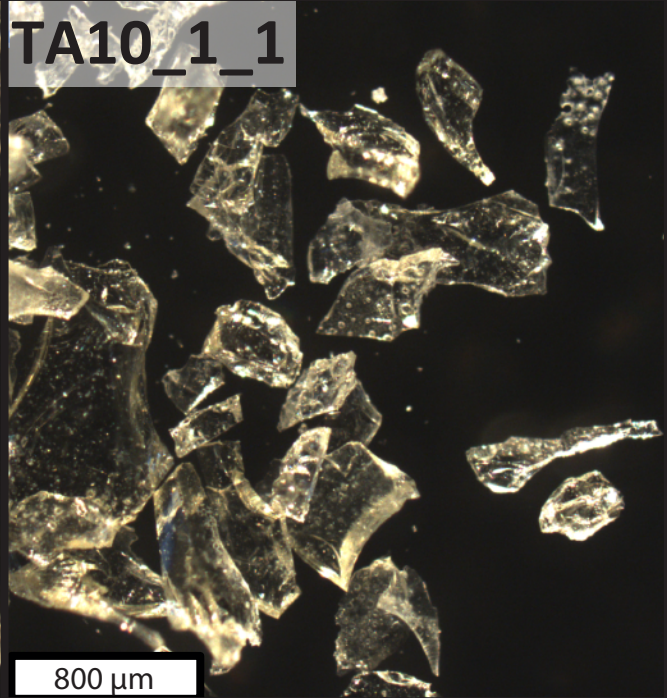
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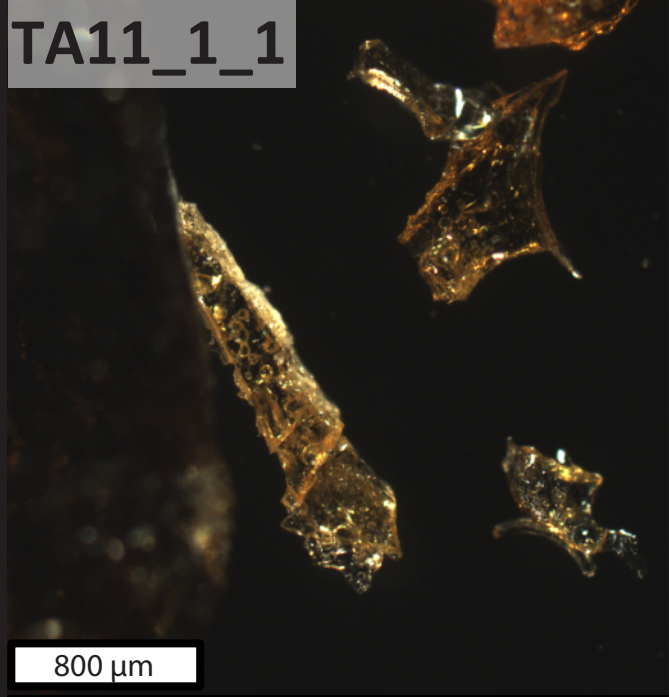
TA9_1_1



TA10_1_1



TA11_1_1



TA6_1_5

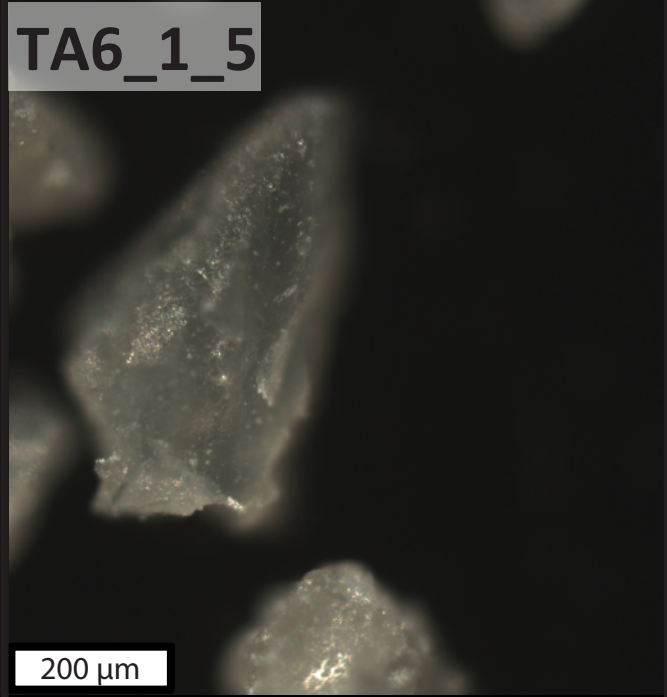


Figure 1. Moussallam et al.

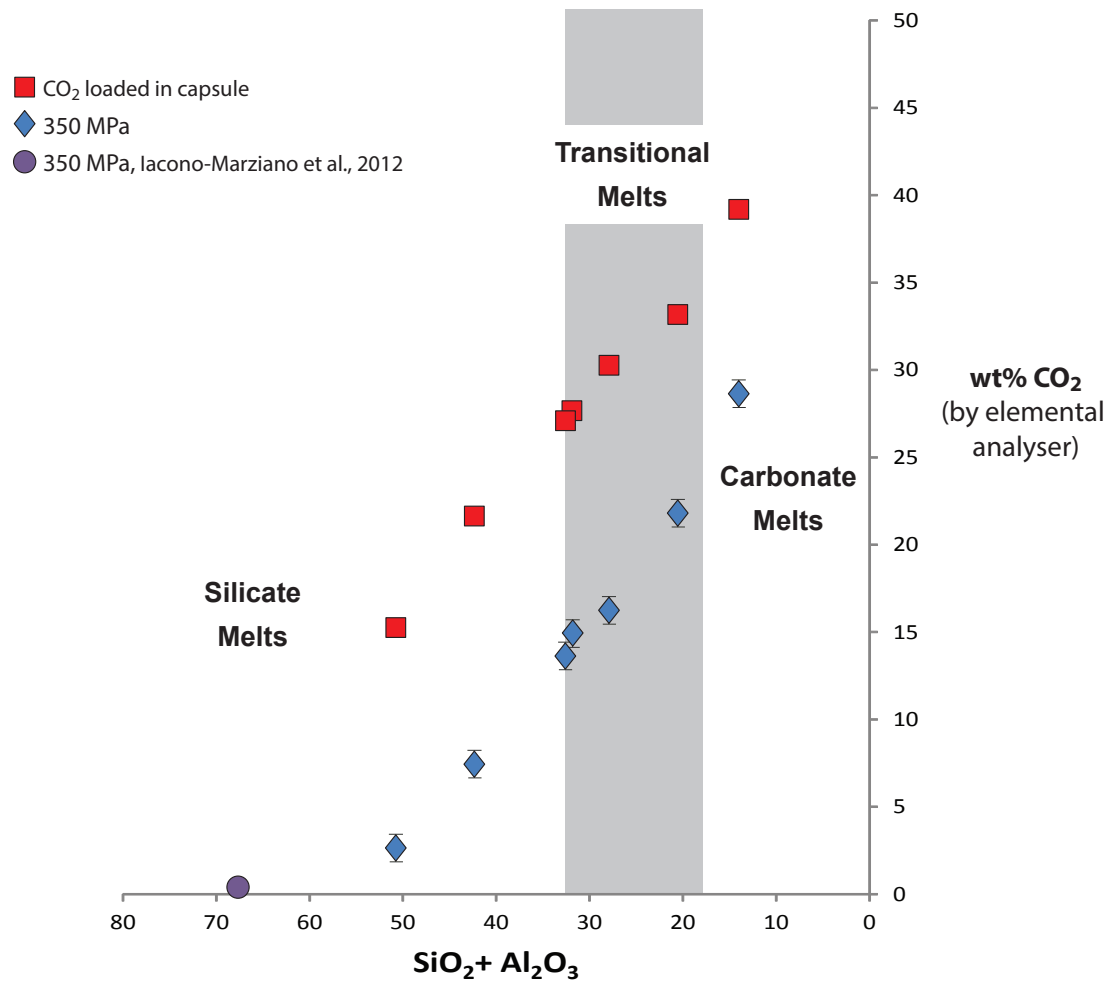


Figure 2, Moussallam et al.

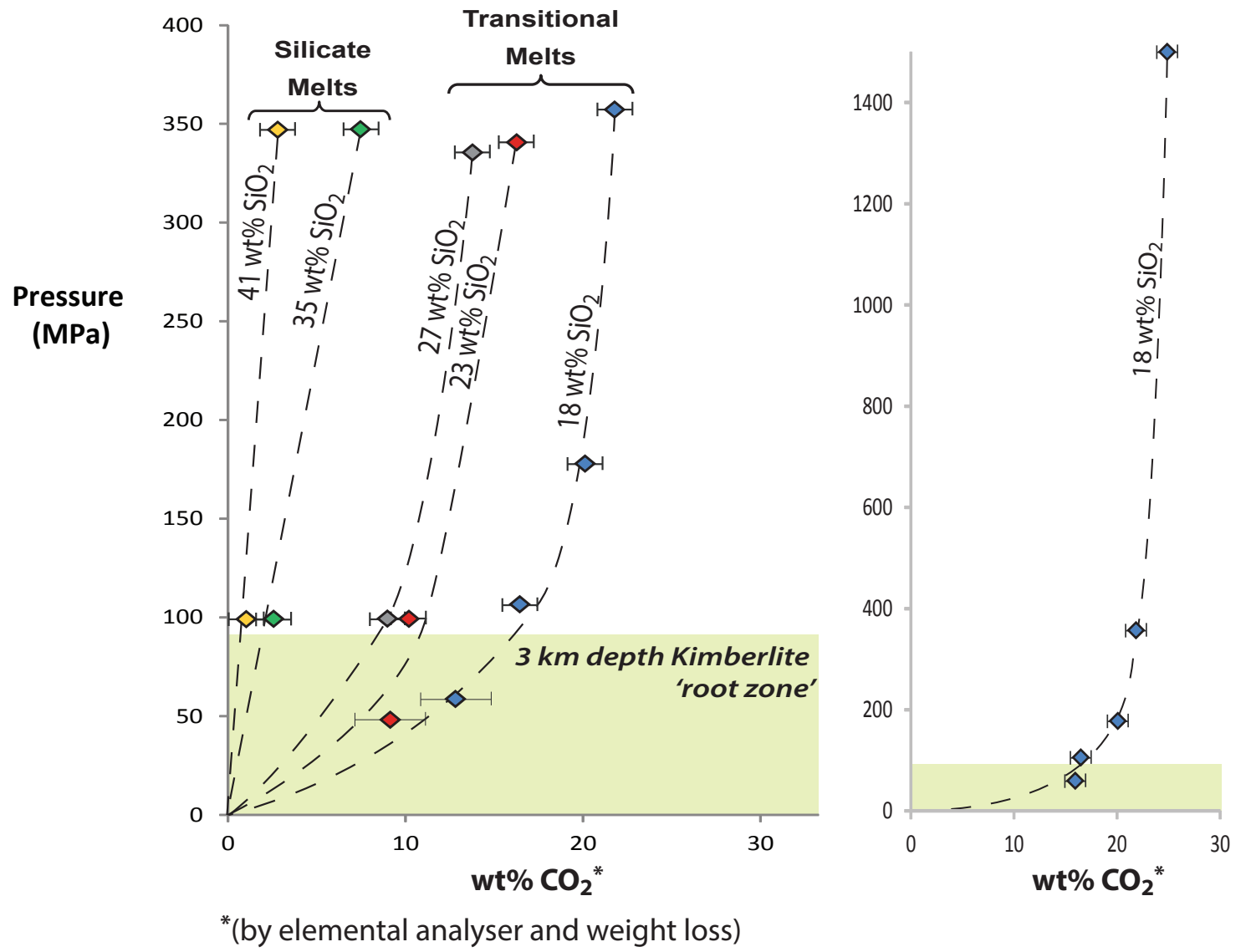


Figure 3, Moussallam et al.

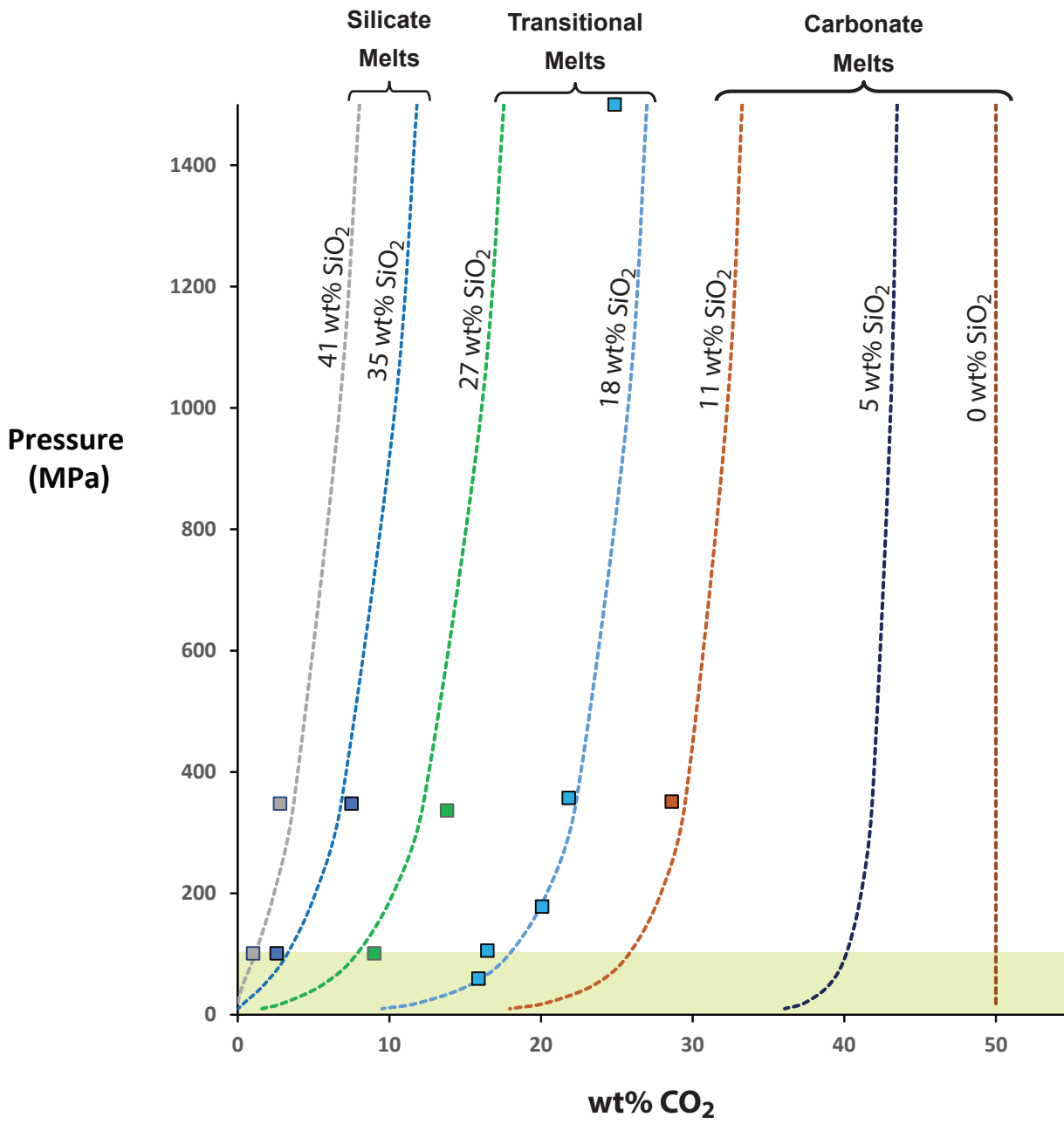


Figure 4, Moussallam et al.

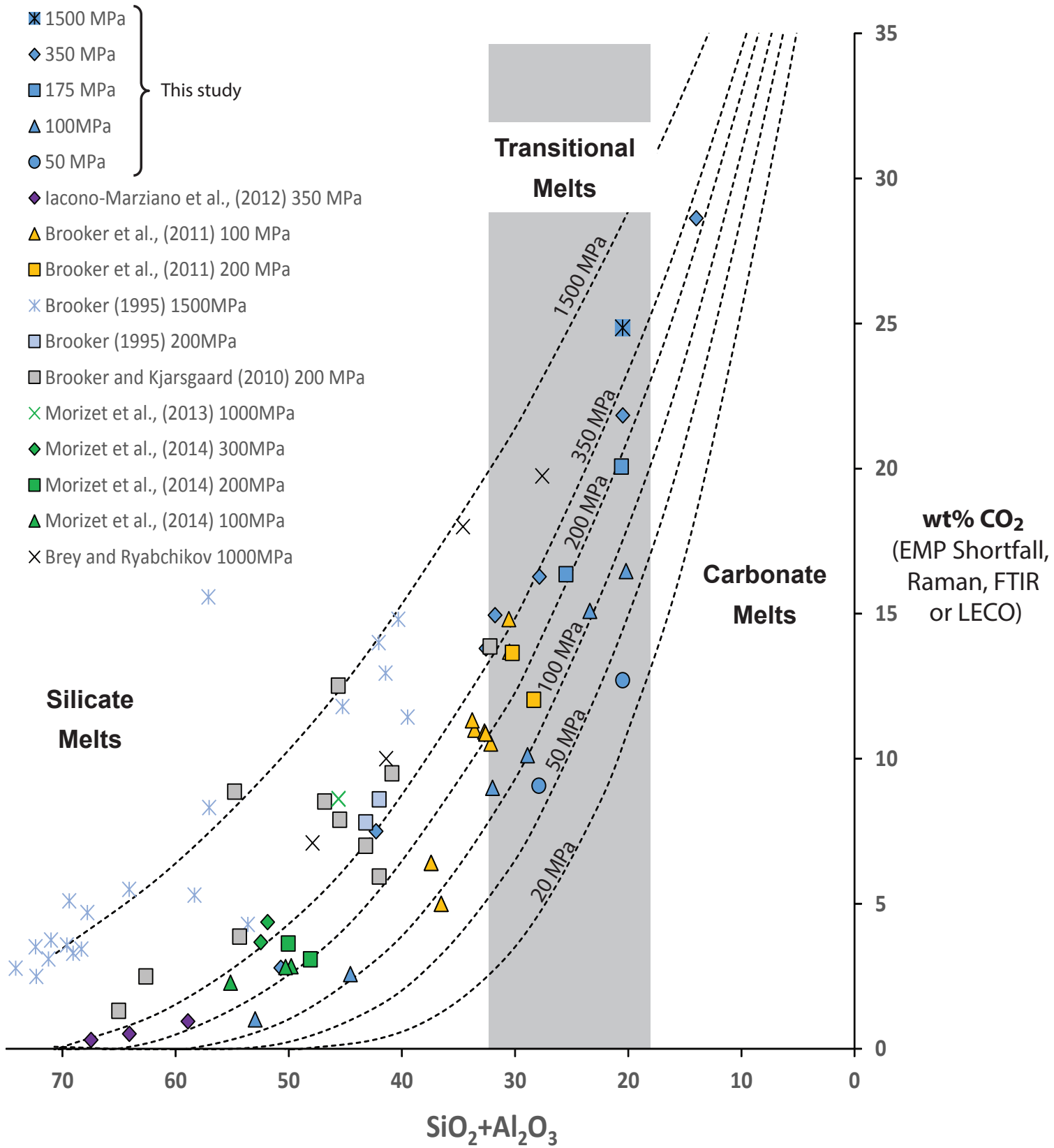


Figure 5, Moussallam et al.

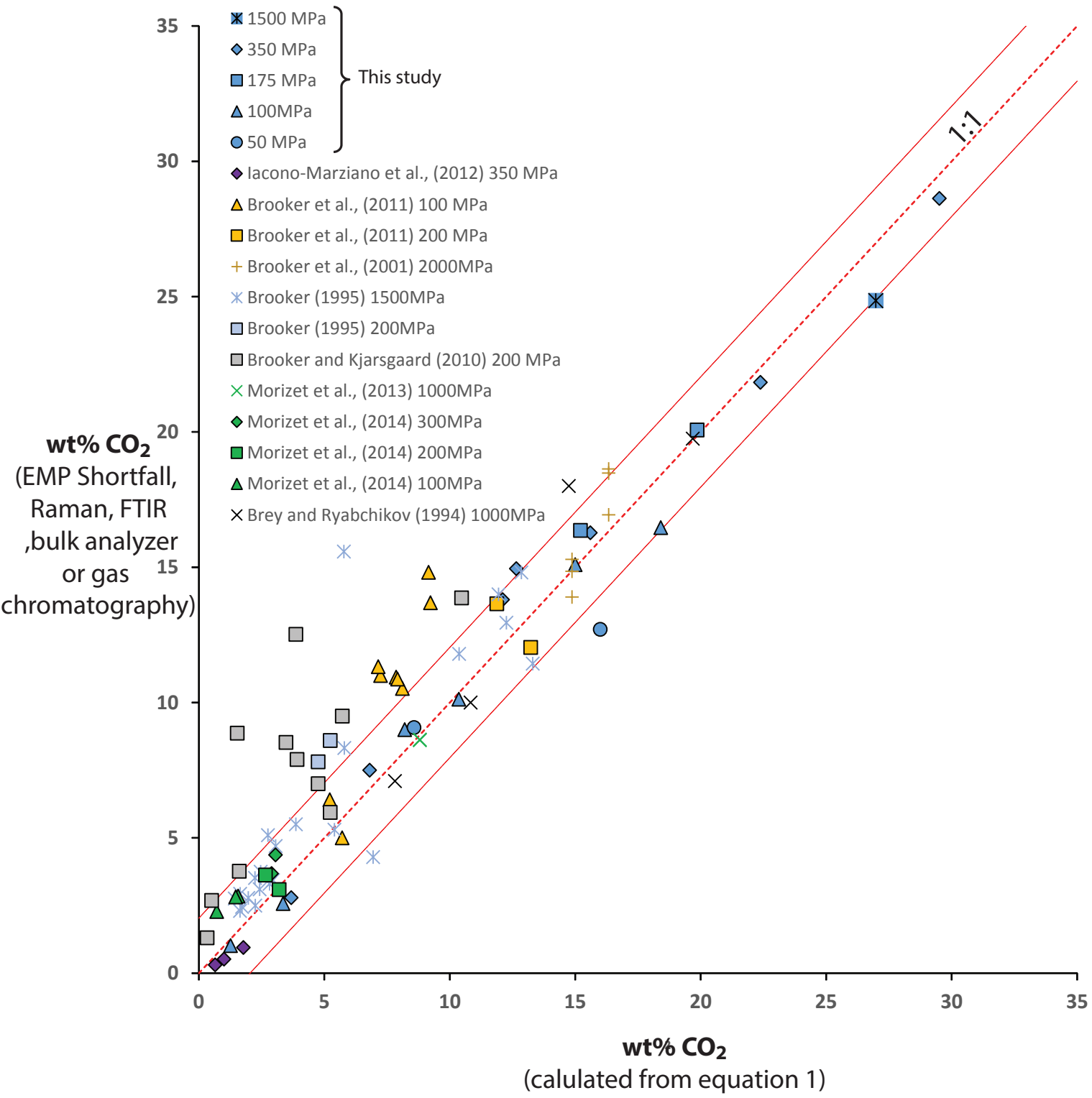


Figure 6, Moussallam et al.

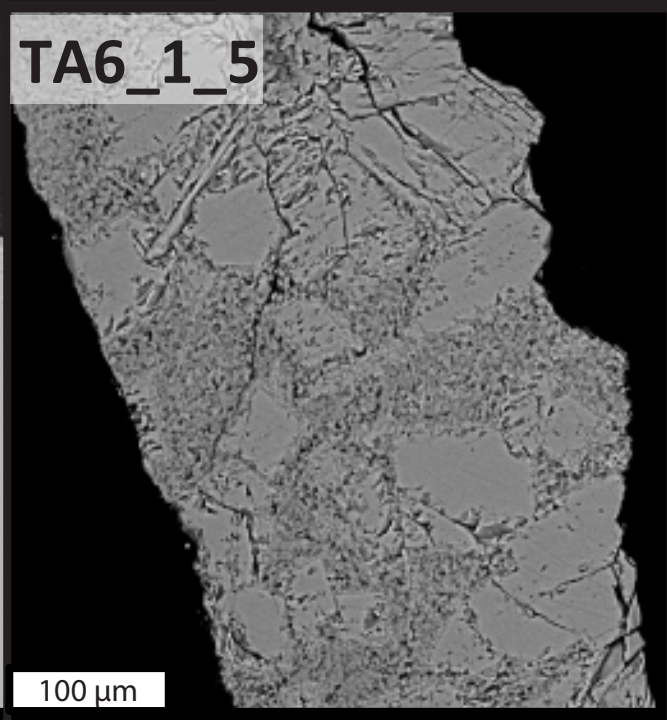
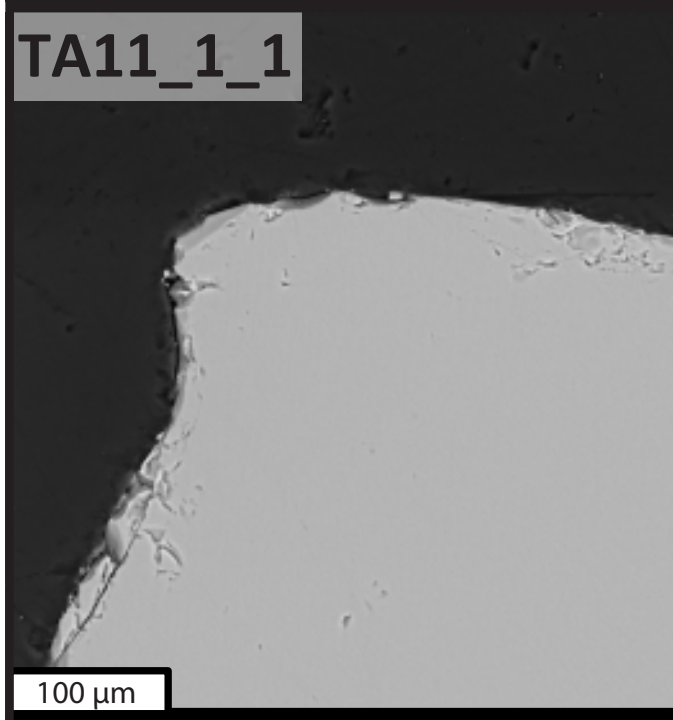
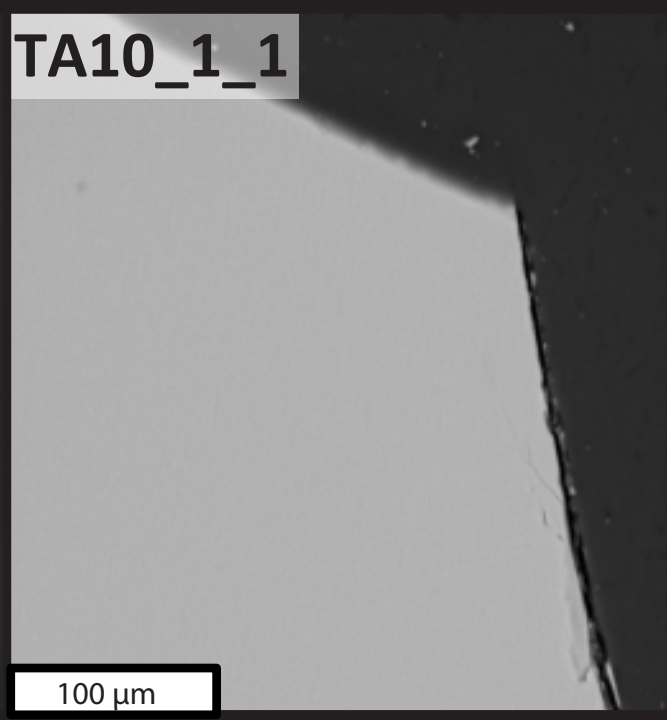
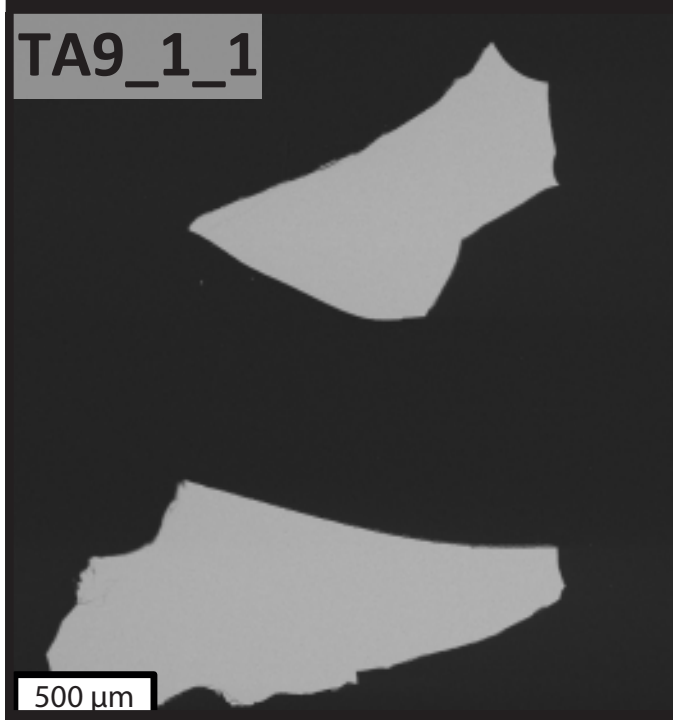
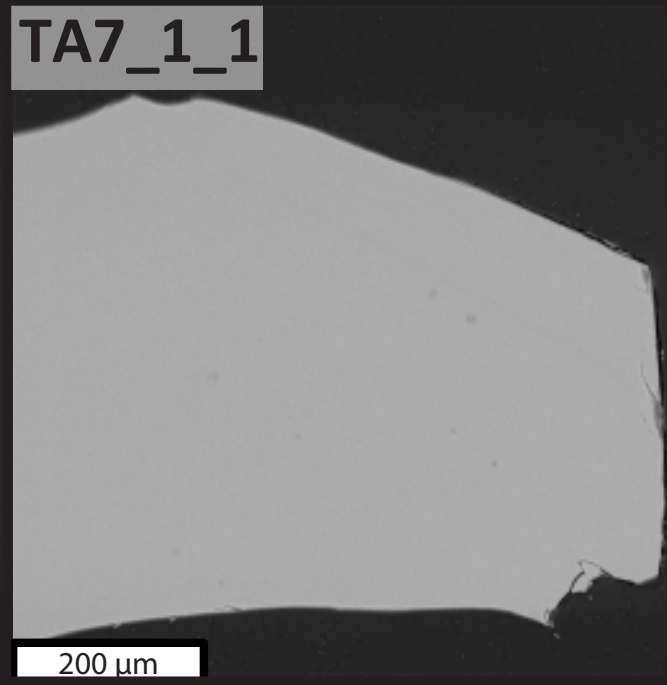
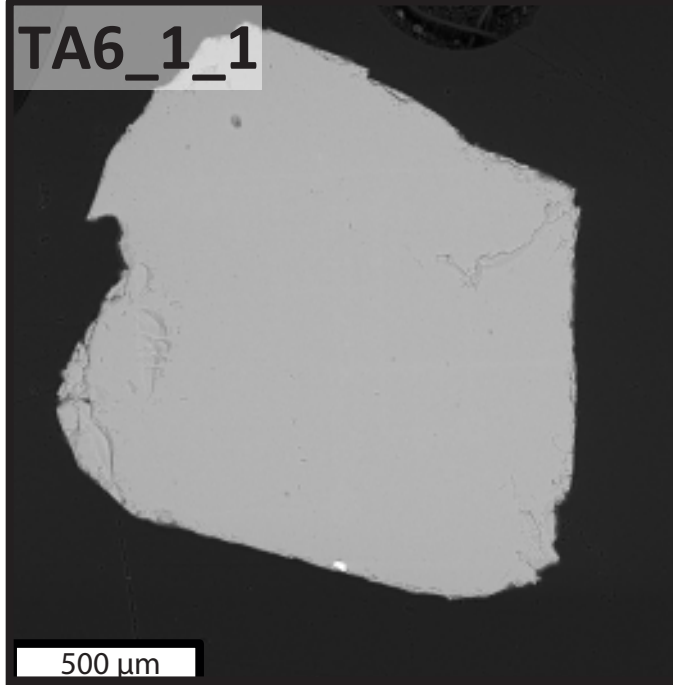


Figure S1. Moussallam et al.

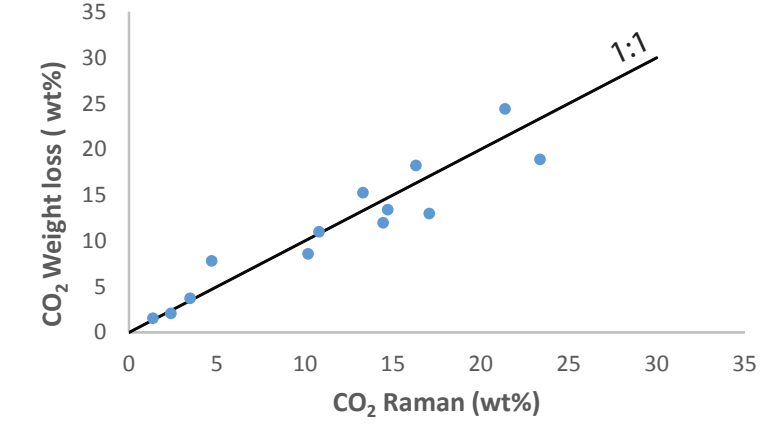
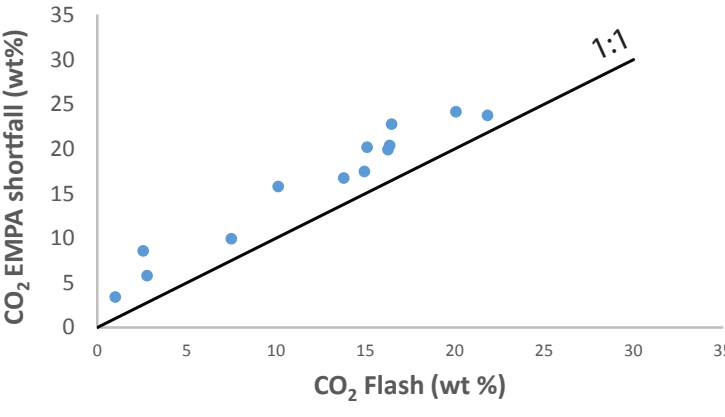
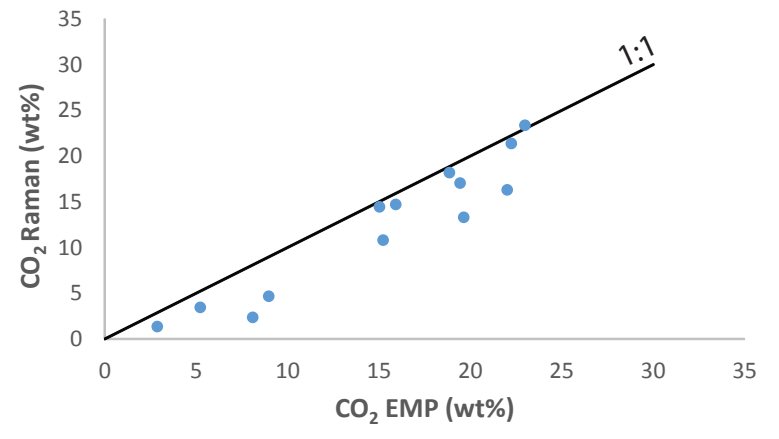
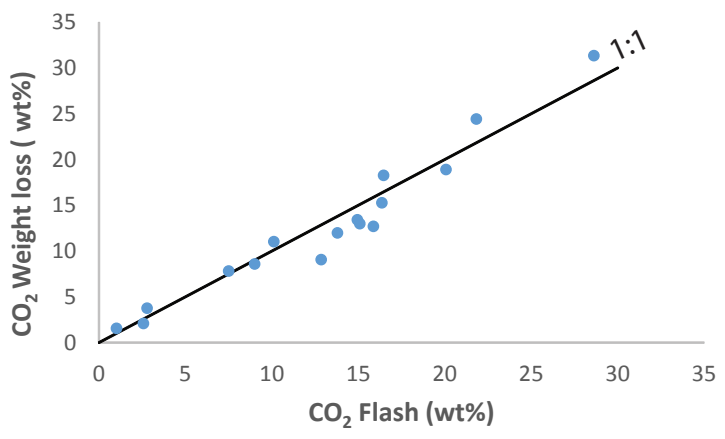
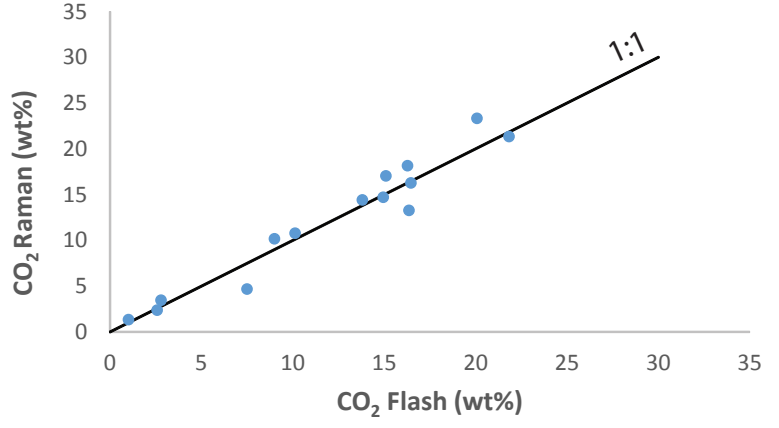
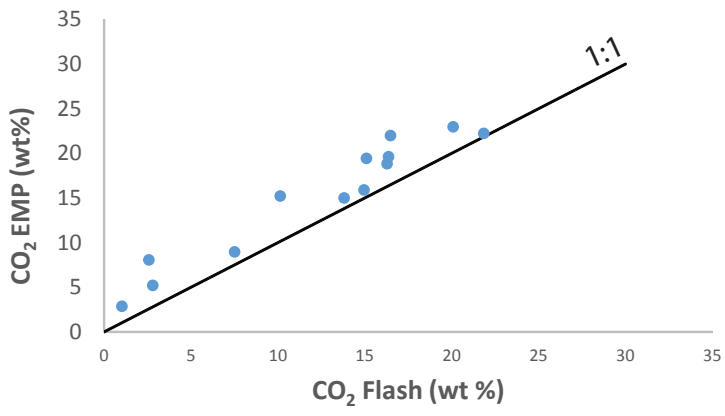


Figure S2, Moussallam et al.