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► **To cite this version:**

Yves Moussallam, Yann Morizet, Malcolm Massuyeau, Mickaël Laumonier, Fabrice Gaillard. CO<sub>2</sub> Solubility in Kimberlite melts CO<sub>2</sub> Solubility in Kimberlite melts. *Chemical Geology*, 2015, 418, pp.198-205. <10.1016/j.chemgeo.2014.11.017>. <insu-01092334>

**HAL Id: insu-01092334**

**<https://insu.hal.science/insu-01092334v1>**

Submitted on 9 Dec 2014

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# CO<sub>2</sub> 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 CO<sub>2</sub> in kimberlitic melts is also poorly constrained due to difficulties in quenching these compositions to a glass that retains the equilibrium CO<sub>2</sub> 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 CO<sub>2</sub> solubility as a function of chemical composition and pressure (0.05-1.5 GPa). Our results suggest that the solubility of CO<sub>2</sub> decreases steadily with increasing amount of network forming cations from ~30 wt% CO<sub>2</sub> at 12 wt% SiO<sub>2</sub> down to ~3 wt% CO<sub>2</sub> at 40 wt% SiO<sub>2</sub>. For low silica melts, CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>  
28 solubility model covering a large range of melt composition from 11 to 55 wt% SiO<sub>2</sub>  
29 spanning the transition from carbonatitic to kimberlitic at pressures from 1500 to 50 MPa.

30 Keywords: kimberlite; carbonatite; CO<sub>2</sub> solubility; transitional melt

## 31 **1. INTRODUCTION**

32 Experimental investigation of the solubility of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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, CO<sub>2</sub> 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' CO<sub>2</sub>  
47 solubility in pure CaCO<sub>3</sub> 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 CO<sub>2</sub> and CaO and poorer in SiO<sub>2</sub>, 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 SiO<sub>2</sub> 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 (SiO<sub>2</sub> ~18 to ~32 wt%) to assess the effect of silica activity on CO<sub>2</sub> solubility. The  
69 effect of pressure was then investigated by equilibrating melts of similar composition at  
70 different pressures (50 to 1500 MPa).

71

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## 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      CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 ( $\pm 3$  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 (Au<sub>80</sub>Pd<sub>20</sub>) 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 K<sub>2</sub>O) absorbing atmospheric H<sub>2</sub>O 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 XCO<sub>2</sub> 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 SiO<sub>2</sub> 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% SiO<sub>2</sub>; 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 SiO<sub>2</sub> (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 (Au<sub>80</sub>Pd<sub>20</sub>) 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  $\mu\text{m}$ . 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 CO<sub>2</sub> 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  $\mu\text{m}$ , slit = 200 $\mu\text{m}$ ) and using a x50  
155 Olympus objective reducing the analysed volume size to a few  $\mu\text{m}^3$ . Spectra were acquired  
156 over the aluminosilicate network and CO<sub>3</sub><sup>2-</sup> region between 200 and 1350  $\text{cm}^{-1}$ . In a few cases  
157 spectra were also acquired in the OH region between 2500 and 3900  $\text{cm}^{-1}$ . 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 CO<sub>2</sub> content in the glass was quantify using the calibration method of Morizet et al.  
161 (2013), which provided a reproducibility on the CO<sub>2</sub> measurements of ~5% relative,  
162 corresponding to an estimated absolute error on the CO<sub>2</sub> 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 CO<sub>2</sub> (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

standards (marble, dolomite and hydrated basalt) was found to be better than 2% for C and 10% for H, giving an estimated error on the CO<sub>2</sub> 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 CO<sub>2</sub> ( $\pm$  H<sub>2</sub>O) in the excess fluid phase from which, the mass  
176 of dissolved CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> even after  
192 correction for H<sub>2</sub>O (determined by elemental analyser), suggesting that using EMPA shortfall  
193 to estimate the melt CO<sub>2</sub> content might be inaccurate. Unless stated otherwise, all CO<sub>2</sub>

194 contents reported in the following figures are from measurements using the elemental  
195 analyser. The results of CO<sub>2</sub> 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 CO<sub>2</sub> solubility  
198 with increasing amount of network forming cations (Si<sup>4+</sup> and Al<sup>3+</sup>). This decrease appears to  
199 be smooth and continuous across the transitional field. The effect of pressure, that is  
200 nominally the pressure of CO<sub>2</sub>, on solubility is shown in Fig. 3 for starting compositions at 18  
201 to 41 wt% SiO<sub>2</sub> (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> 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, CO<sub>2</sub> solubility was estimated from the amount of gas  
204 released after capsule puncture and their CO<sub>2</sub> 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% SiO<sub>2</sub> (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 CO<sub>2</sub> (25 to 20 wt% CO<sub>2</sub>) and most of  
208 the solubility drop takes place from 100 to 0.1 MPa (assuming no CO<sub>2</sub> remains in the melt at  
209 0.1 MPa). This results in a strongly non-linear dependence of CO<sub>2</sub> solubility with pressure for  
210 melt compositions with SiO<sub>2</sub> contents in the range 18-30 wt%. At SiO<sub>2</sub> 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 CO<sub>2</sub> in primary kimberlitic melts.

228

### 229 **5.1 Empirical model of CO<sub>2</sub> solubility in carbonated melts**

230 Based on the solubility experiments presented here and literature data we developed a purely  
 231 empirical model of CO<sub>2</sub> solubility as a function of the amount of network forming cations  
 232 (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>) 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 CO<sub>2</sub> dissolved in the melt to the SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>). In order to adjust the parameters in equation (1), we used CO<sub>2</sub> 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<sub>2</sub> between the modelled and measured values) and allow us to  
249 explore a larger P-X<sub>(SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>)</sub> space. Fig. 4 shows the modelled solubility of CO<sub>2</sub> as a  
250 function of pressure for compositions ranging from SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> of 0 to 51 wt% and pressure  
251 from 1500 to 10 MPa. Fig.4 shows the gradual change in the CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>  
260 solubility as a function of network forming cations (SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>) 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<sub>2</sub> 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 CO<sub>2</sub>/H<sub>2</sub>O 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 H<sub>2</sub>O. 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 CO<sub>2</sub> 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 (Na<sub>2</sub>O, K<sub>2</sub>O,  
284 Na<sub>2</sub>O+K<sub>2</sub>O, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) but could not find any robust correlations. There is however a hint  
285 that melt compositions rich in alkali can incorporate more CO<sub>2</sub> 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% CO<sub>2</sub> and a composition of 0 wt% CaO and 37 wt% Na<sub>2</sub>O). 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 CO<sub>2</sub> solubility.

290 A strong correlation was found between the method used to determine CO<sub>2</sub> 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 CO<sub>2</sub> content determined by shortfall of  
293 EMPA analyses. Comparing our own EMPA shortfall measurements to CO<sub>2</sub> determined by  
294 bulk analyser (Fig. S2), we observe that determining the CO<sub>2</sub> content by EMPA shortfall can  
295 lead to an overestimation of 2 to 6 wt% CO<sub>2</sub>. We therefore conclude (i) that most of the  
296 literature data yielding CO<sub>2</sub> solubility values that deviates from our model can be attributed to  
297 the large error associated with estimating CO<sub>2</sub> 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 CO<sub>2</sub>  
300 content of carbonated melt over a large range of composition (SiO<sub>2</sub> < 55 wt%; Na<sub>2</sub>O+K<sub>2</sub>O <  
301 22 wt%). The entrapment pressure of recently reported CO<sub>2</sub>-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 CO<sub>2</sub>).

305

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

307 As hypothesised by Brooker et al (2011) our results indicate that CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> until very shallow (3 km) depth while slightly more silicate-rich melts show  
316 a continuous and progressive degassing profile with CO<sub>2</sub> 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% CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>-exsolution-triggered acceleration of kimberlite melts that  
351 we predict takes place.

352

## 353 **6. CONCLUSIONS**

354 We have determined CO<sub>2</sub> solubility laws for kimberlite melt and have also provided a general  
355 solubility model for carbonated melt composition (SiO<sub>2</sub> < 55 wt%) at pressure between 50  
356 and 1500 MPa. We found that (i) CO<sub>2</sub> solubility decreases steadily with increasing amount of  
357 network forming cations (ii) The effect of pressure on CO<sub>2</sub> solubility is a strong function of  
358 composition with low SiO<sub>2</sub> melts retaining large amount (~15 wt%) of CO<sub>2</sub> up to very  
359 shallow pressure (~100 MPa) while more silicated melts have a near linear CO<sub>2</sub> 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 CO<sub>2</sub> 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

## 367 **ACKNOWLEDGEMENTS**

368 We are very grateful to Rémi Champallier and Leïla Hashim for their help with various  
369 instruments. Special thanks also go to Ida Di Carlo for help with the electron probe analyses  
370 and to Marielle Hatton for help with the elemental analyser. Funding for this work was  
371 provided by the European Research Council (ERC grant number 279790) and the Agence  
372 Nationale de la Recherche (ANR-10-BLAN-62101). Valuable reviews by K. Russell and R.  
373 Brooker improved the quality of the manuscript. We also thanks the guest Editors of this  
374 special issue.

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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), H<sub>2</sub>O determined by elemental  
508 analyser (Flash) and CO<sub>2</sub> determined from: (i) EMPA (by subtracting H<sub>2</sub>O 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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:** CO<sub>2</sub> solubility measurements for a series of compositions across the silicate to  
524 carbonate melt transitions equilibrated at 350 MPa. The SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> content is reported  
525 including volatiles. For most experiments, CO<sub>2</sub> content is estimated from elemental analyser  
526 and associated error is estimated at  $\pm 1$  wt%. CO<sub>2</sub> content from Iacono-Marziano et al.,  
527 (2012) is estimated from FTIR analyses.

528

529 **Figure 3:** CO<sub>2</sub> solubility as a function of pressure for three Kimberlite/Transitional and two  
530 silicate melt compositions spanning SiO<sub>2</sub> content of 18 to 41 wt% and SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> content  
531 of 21 to 51 wt% respectively (calculated including volatiles and corresponding to SiO<sub>2</sub> +  
532 Al<sub>2</sub>O<sub>3</sub> 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 CO<sub>2</sub> solubility as a function of pressure using equation (1)  
537 for melt compositions ranging from 0 to 41 wt% SiO<sub>2</sub> and 0 to 51 wt% SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>.  
538 Experiments of corresponding chemistry are shown as squares of matching colour.

539

540 **Figure 5:** CO<sub>2</sub> 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<sub>CO<sub>2</sub></sub>. 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 CO<sub>2</sub> 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 CO<sub>2</sub> determined from Raman or by bulk CO<sub>2</sub>  
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 CO<sub>2</sub> content in experimental charges determined by (i)  
564 EMPA (by subtracting H<sub>2</sub>O 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 CO<sub>2</sub> to escape) after each run and (v)  
567 EMPA shortfall without correction.

568

Name	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	CO <sub>2</sub>	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.

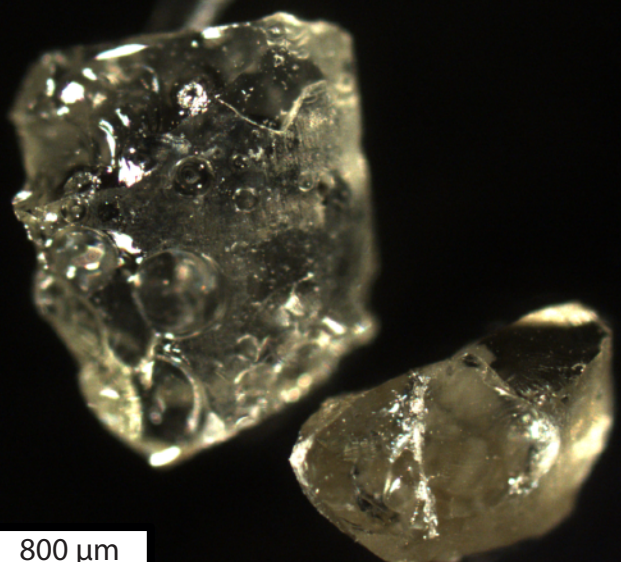
Experiment	Pressure (MPa)	Temperature (°C)	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Total	Shortfall	H <sub>2</sub> O (Flash)	CO <sub>2</sub> (EMPA)	CO <sub>2</sub> (Flash)	CO <sub>2</sub> (Raman)	CO <sub>2</sub> (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), H<sub>2</sub>O determined by elemental analyser (Flash) and CO<sub>2</sub> determined from: (i) EMPA (by subtracting H<sub>2</sub>O 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 CO<sub>2</sub> to escape) after each run . Run duration was of 2 hours in all experiments.

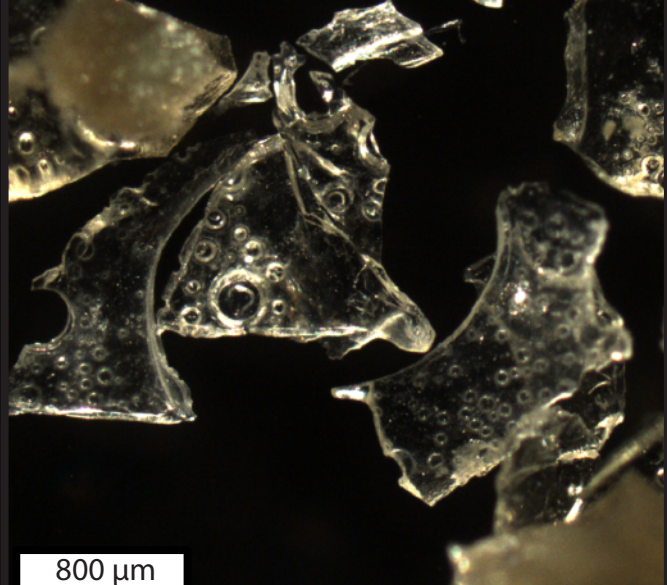
	a	b	c	d	e	f	D
Value	-0.001271	-0.476116	0.132494	-0.322187	-4.501117	-0.163249	50
Std. Err.	0.000244	0.040612	0.016065	0.020635	0.281876	0.008332	1.4

**Table 3:** Adjusted parameters (and corresponding standard error on multiple non-linear regression fit) to calculate CO<sub>2</sub> solubility from Eq. (1). Regression was calculated from over 160 data points (detail in text).

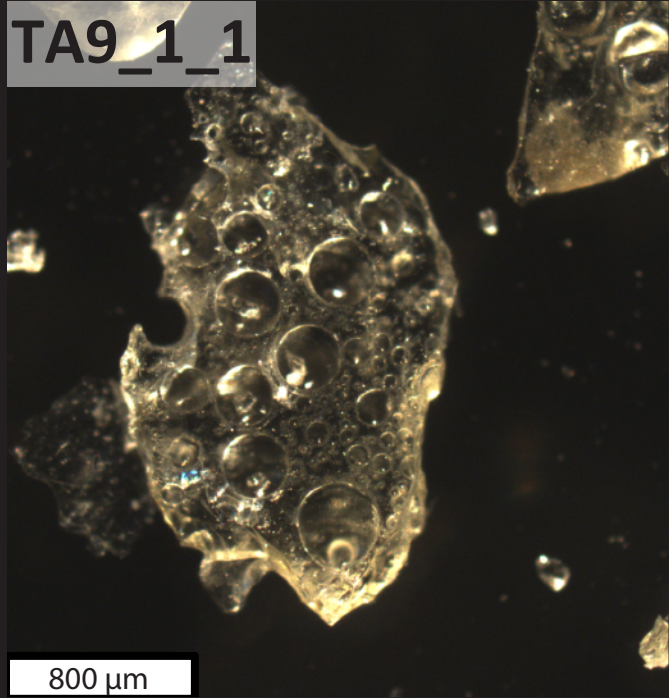
TA6\_1\_1



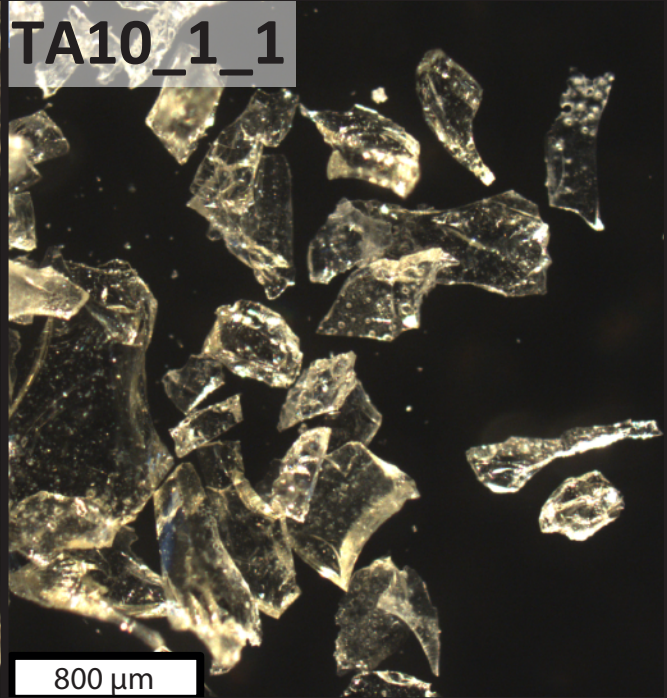
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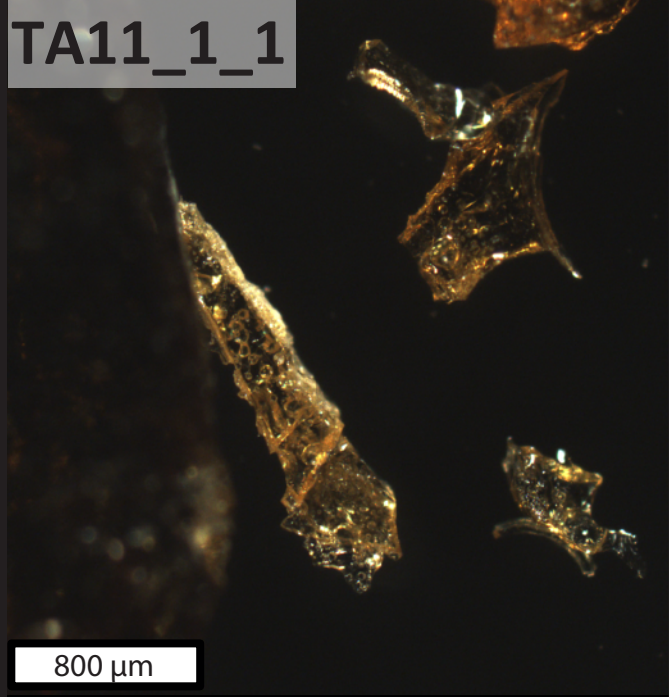
TA9\_1\_1



TA10\_1\_1



TA11\_1\_1



TA6\_1\_5

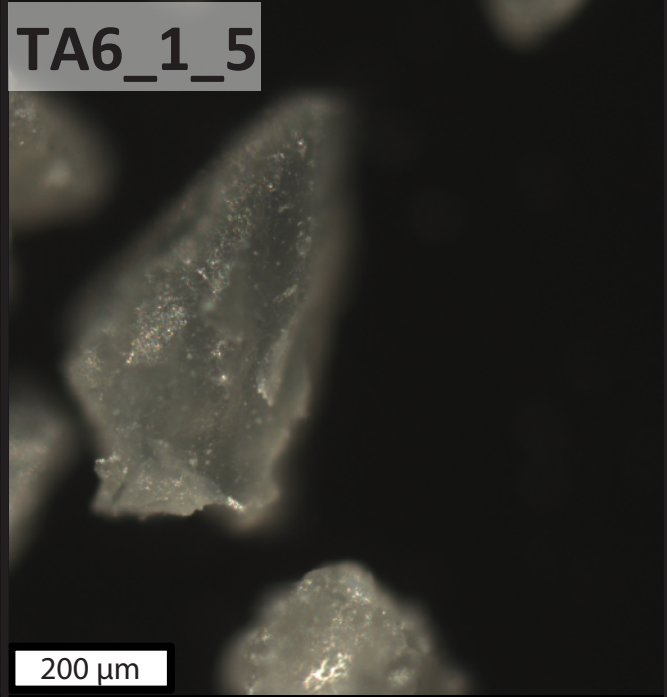
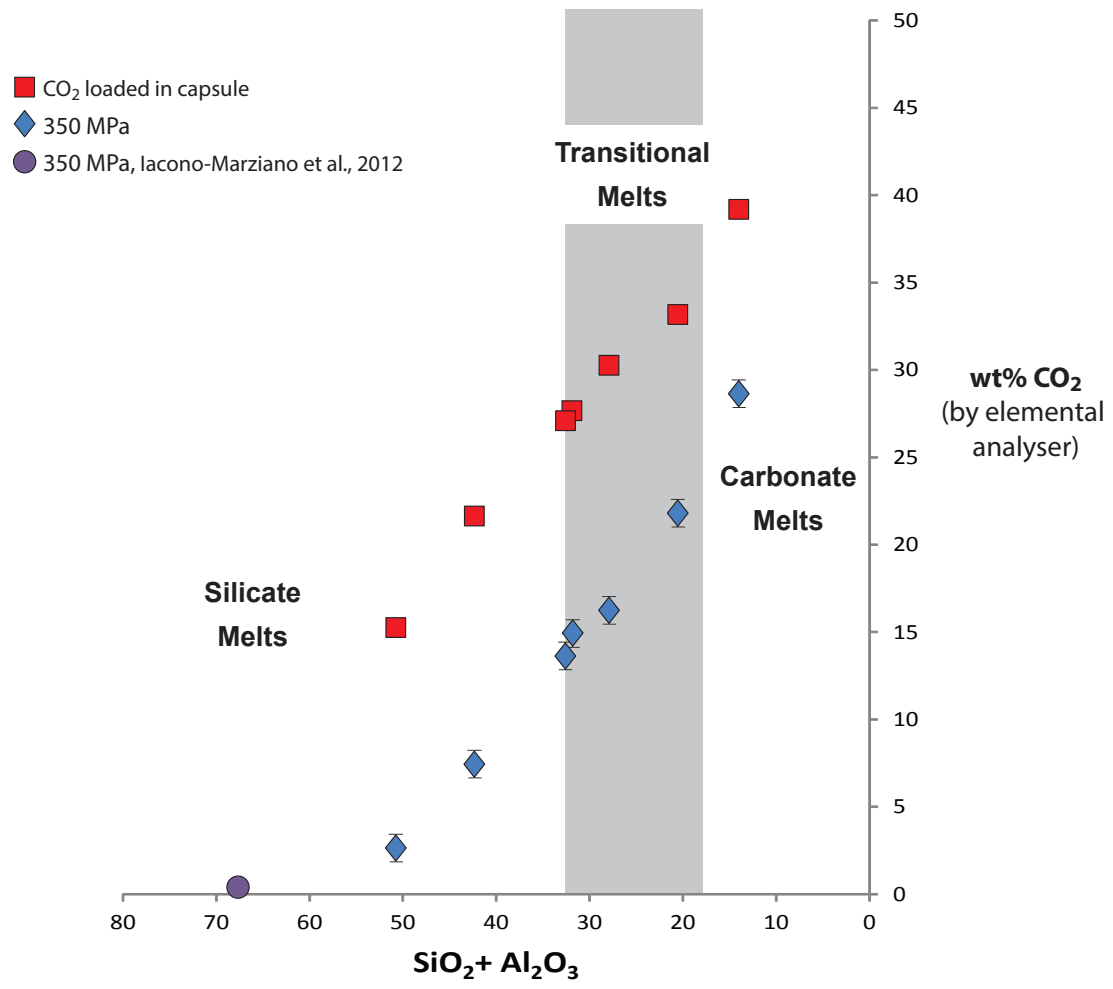


Figure 1. Moussallam et al.



**Figure 2, Moussallam et al.**



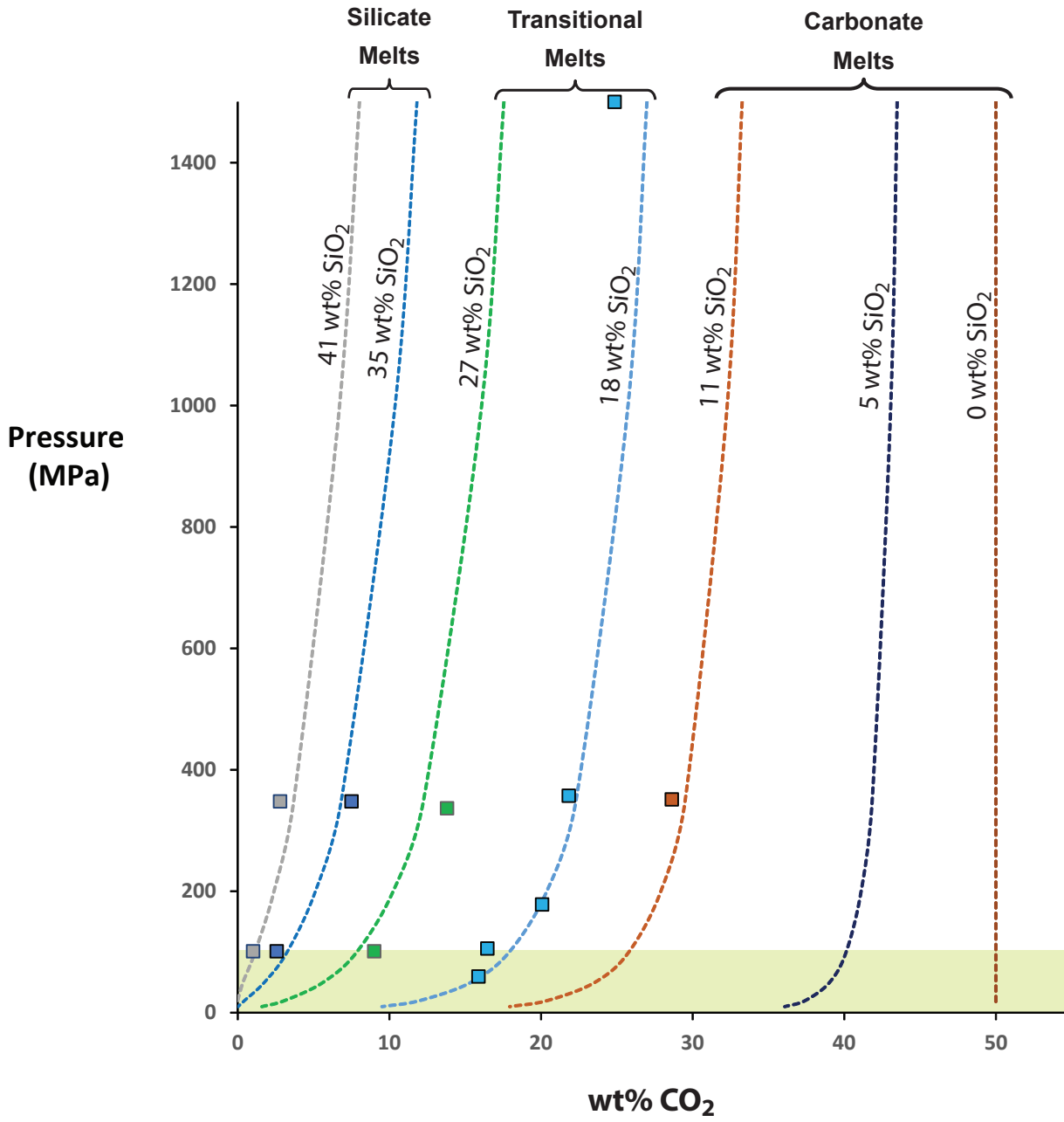
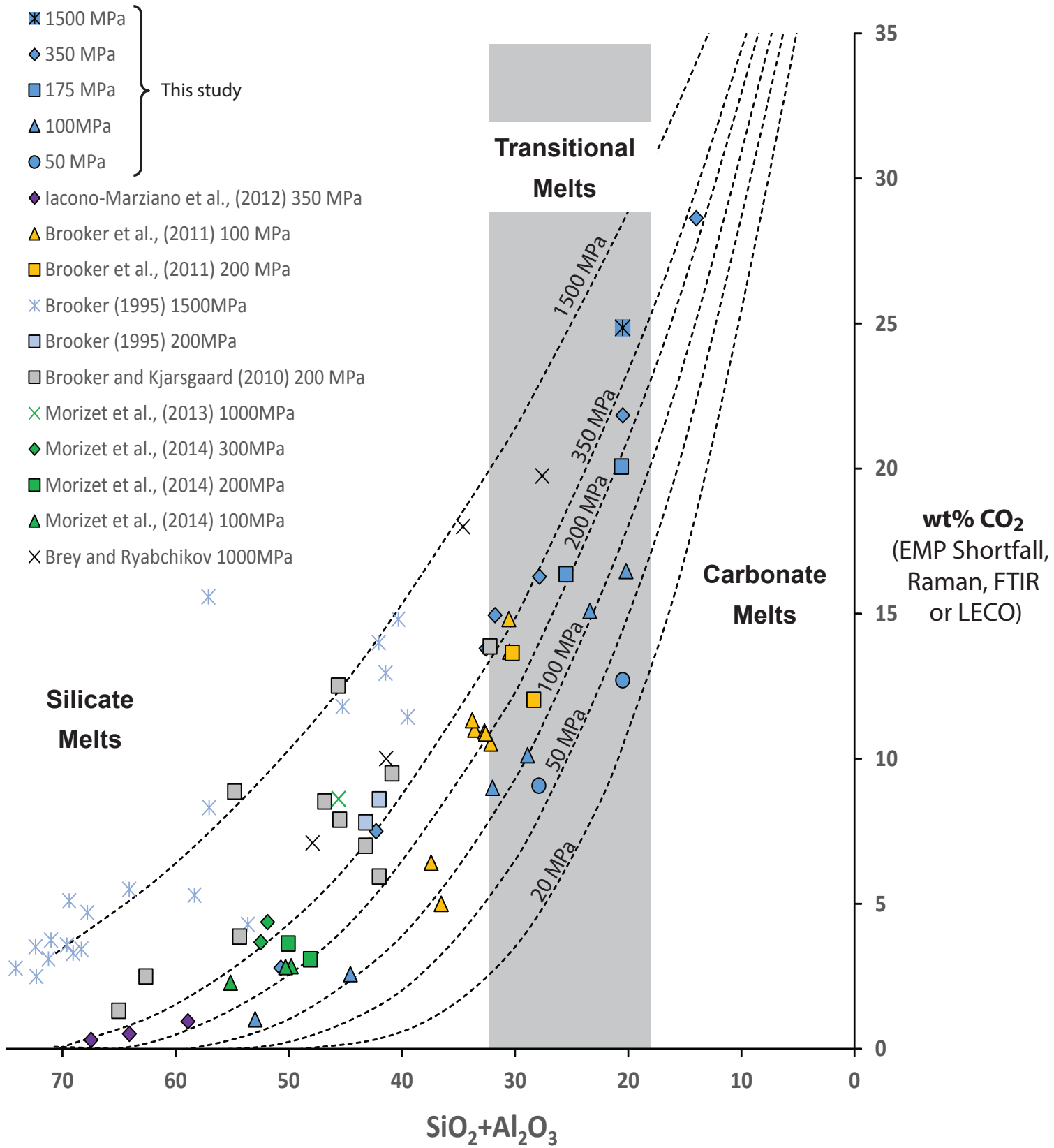
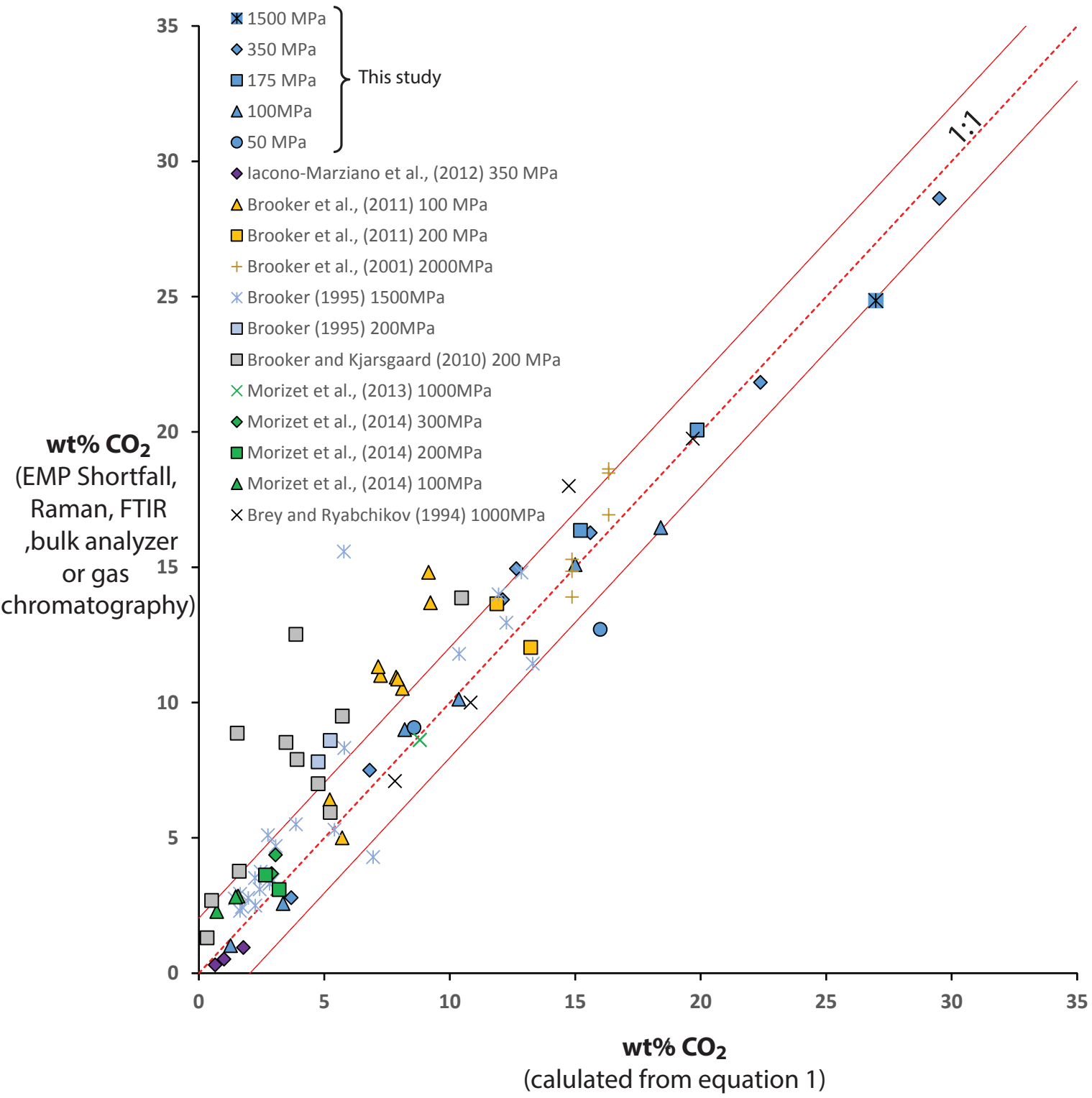


Figure 4, Moussallam et al.



**Figure 5, Moussallam et al.**



**Figure 6, Moussallam et al.**

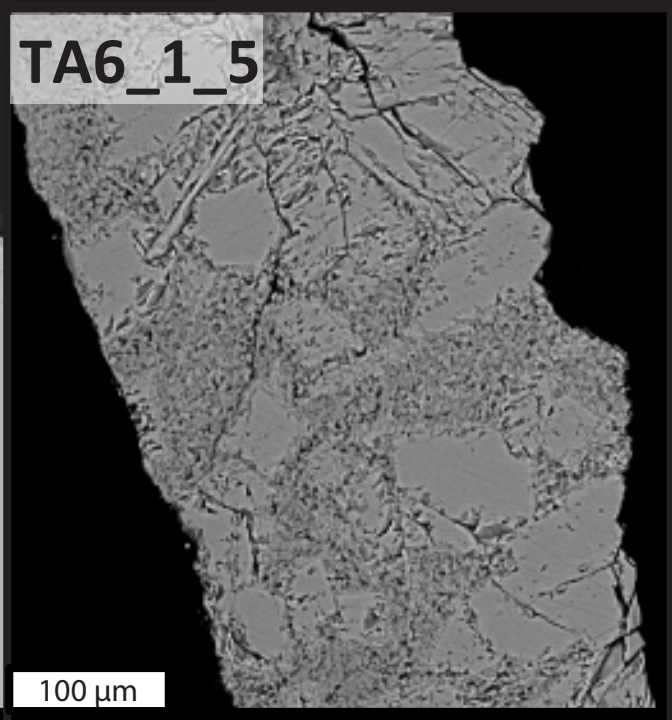
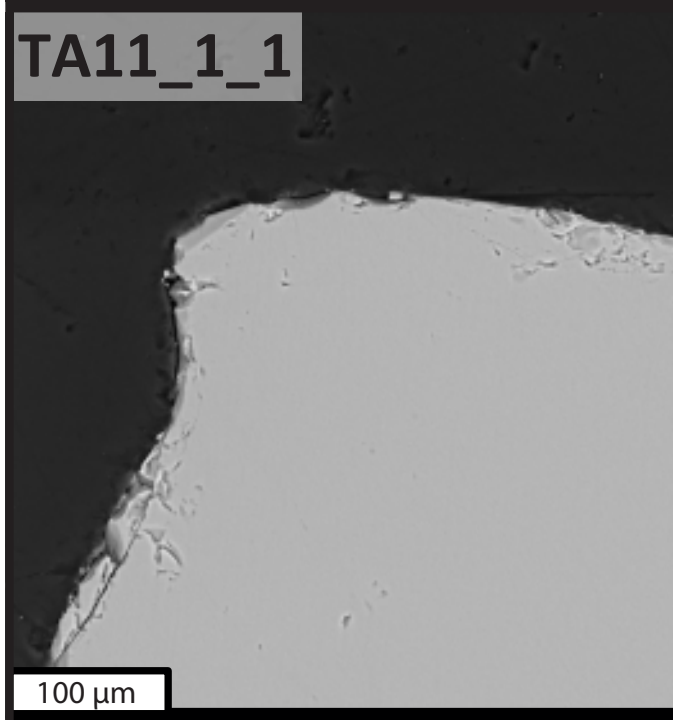
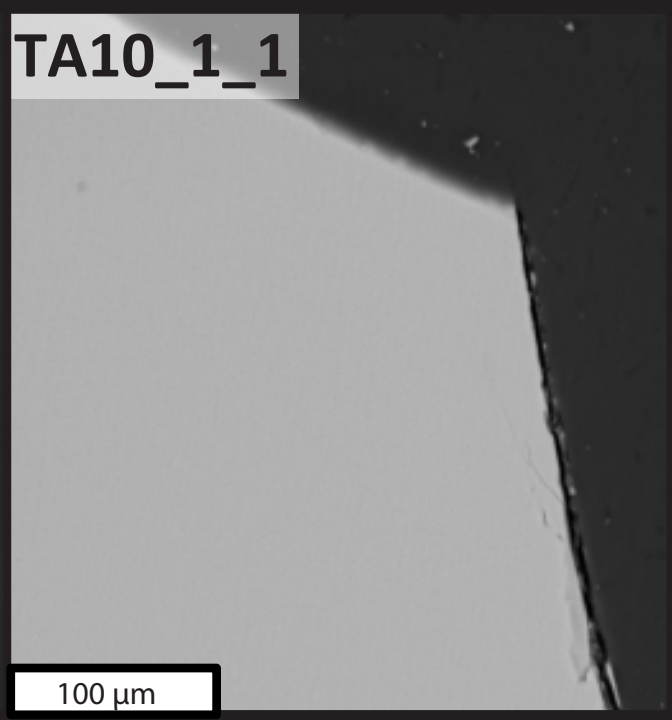
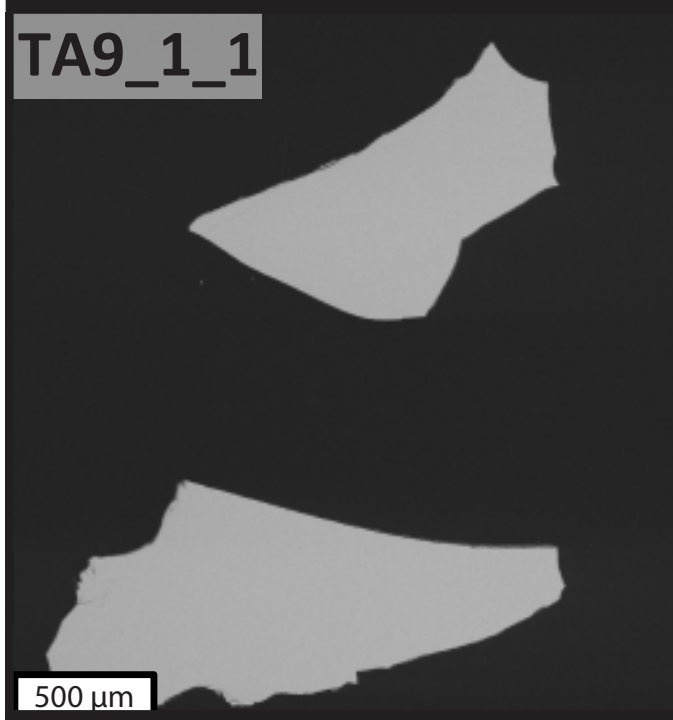
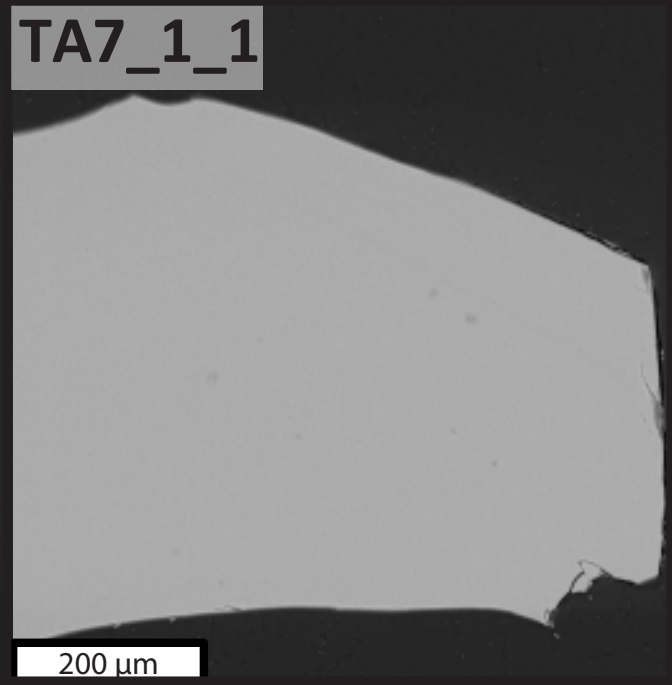
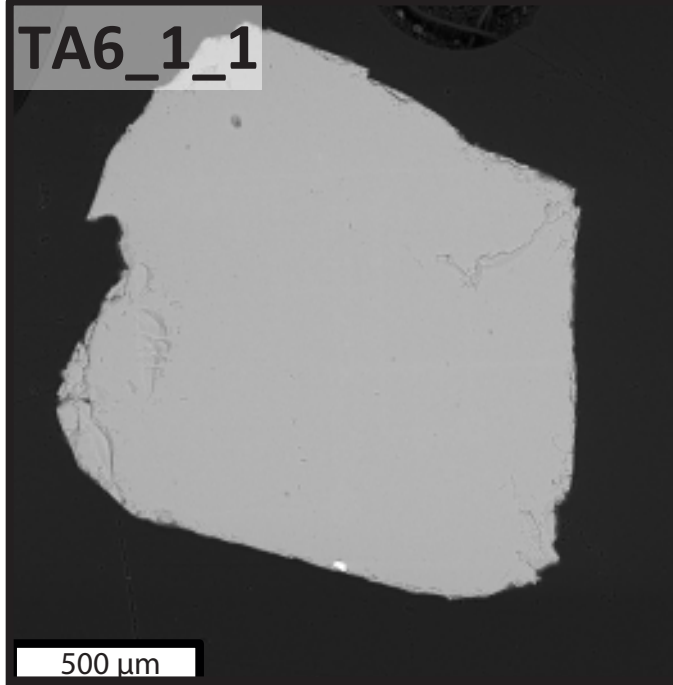
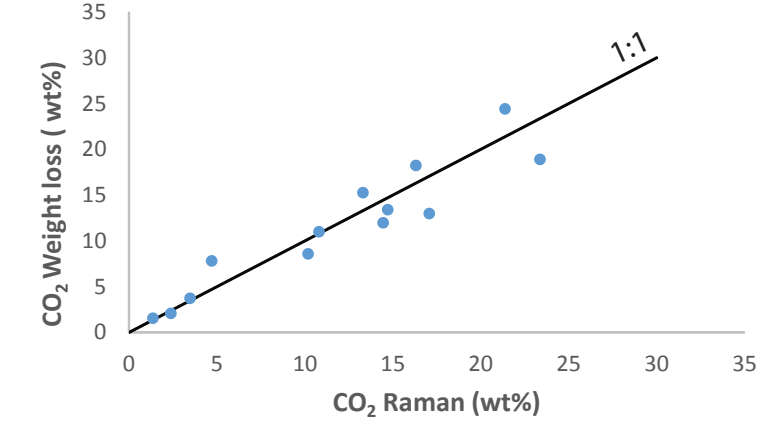
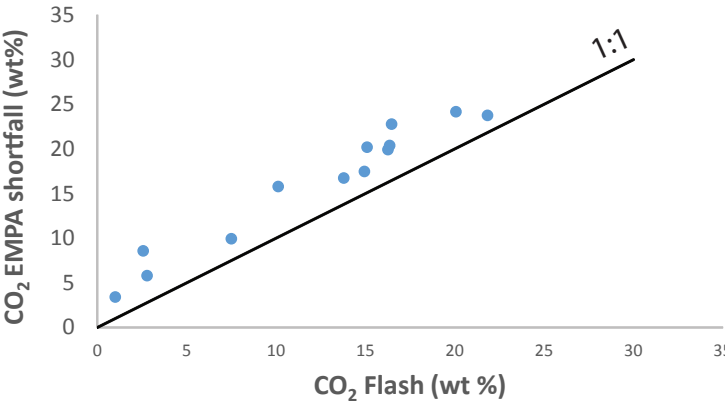
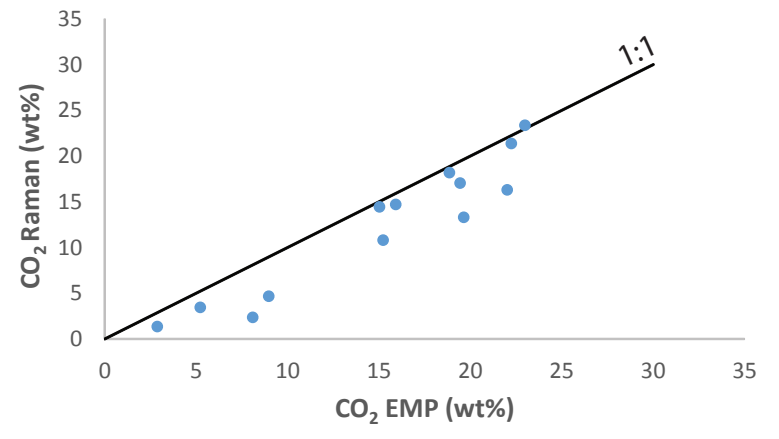
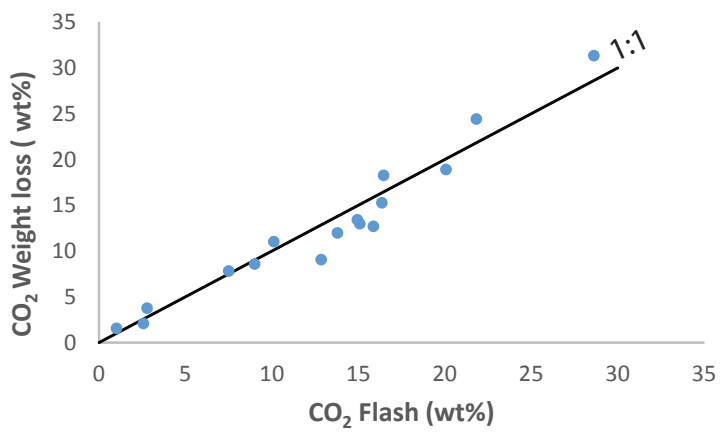
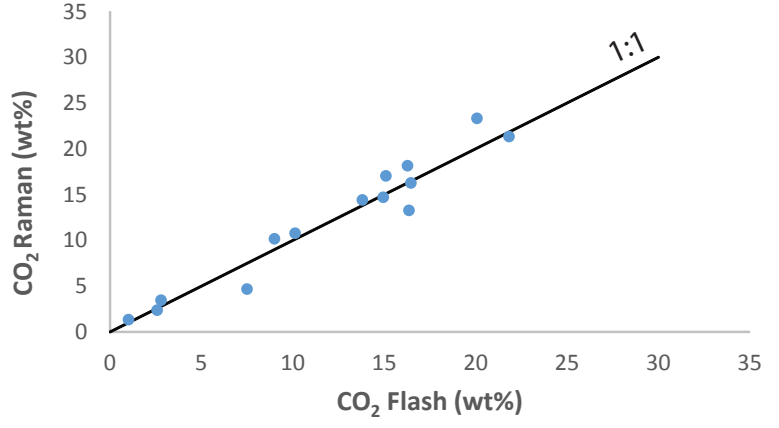
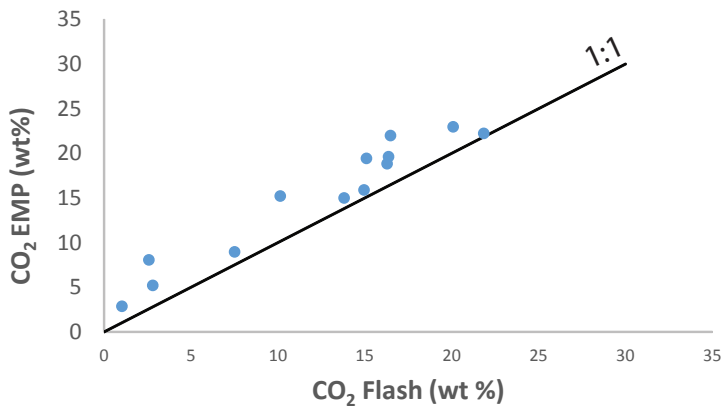


Figure S1. Moussallam et al.



**Figure S2, Moussallam et al.**