1	Revision 1
2	A systematic assessment of the diamond trap method for measuring fluid
3	compositions in high-pressure experiments
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8	ABSTRACT

9 A variety of experimental techniques have been proposed to measure the composition of aqueous fluids in 10 high-pressure experiments. In particular, the "diamond trap method", where the fluid is sampled in the pore space of diamond powder and analyzed by laser-ablation ICP-MS after the experiment, has become a 11 12 popular tool. Here, we carried out several tests in order to assess the reliability of this method. (i) We 13 prepared several capsules loaded with fluid of known composition and analyzed the fluid by laser-14 ablation ICP-MS, either (a) after drying the diamond trap at ambient condition, (b) after freezing and 15 subsequent freeze-drying, and (c) after freezing and by analyzing a frozen state. Of these methods, the 16 analysis in the frozen state (c) was most accurate, while the results from the other two methods were poorly reproducible and the averages sometimes deviated from the expected composition by more than a 17 factor of 2. (ii) We tested the reliability of the diamond trap method by using it to measure mineral 18 19 solubilities in some well-studied systems at high pressure and high temperature in piston cylinder runs. In 20 the systems quartz-H₂O, forsterite-enstatite-H₂O, and albite-H₂O, the results from analyzing the diamond 21 trap in frozen state by laser-ablation ICP-MS generally agreed well with the expected compositions 22 according to literature data. However, in the systems corundum-H₂O and rutile-H₂O, the data from the

23 analysis of the diamond trap were poorly reproducible and appeared to indicate much higher solubilities 24 than expected. We attribute this not to some unreliability of the analytical method, but rather to the fact that in these systems, minor temperature gradients along the capsule may induce the dissolution and re-25 precipitation of material during the run, which causes a contamination of the diamond trap by solid 26 27 phases. (iii) We carried out several tests on the reliability of the diamond trap to measure fluid 28 compositions and trace element partition coefficients in the eclogite-fluid system at 4 GPa and 800 °C 29 using piston cylinder experiments. The good agreement between "forward" and "reversed" experiments -30 with trace elements initially either doped in the solid starting material or the fluid – as well as the 31 independence of partition coefficients on bulk concentrations suggests that the data obtained are reliable 32 in most cases. We also show that the rate of quenching/cooling has little effect on the analytical results, that temperature oscillations during the run can be used to enhance grain growth, and that well 33 34 equilibrated samples can be obtained in conventional piston cylinder runs. Overall, our results suggest 35 that the diamond trap method combined with laser-ablation ICP-MS in frozen state yields reliable results 36 accurate within a factor of two in most cases; however, the precipitation of accessory minerals in the 37 diamond trap during the run may severely affect the data in some systems and may lead to a gross overestimation of fluid concentrations. 38

Keywords: Fluids, diamond trap, high-pressure experiments, laser-ablation ICP-MS, solubility,
fluid/mineral partitioning

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INTRODUCTION

Aqueous fluids are important agents of metasomatism in Earth's mantle, particularly above subduction
zones (e.g. Tatsumi 1989, Manning 2004, Kelley and Cottrell 2009, Keppler 2017). Traces of such fluids
are sometimes sampled as fluid inclusions in mantle xenoliths and in diamonds (e.g. Kawamoto et al.
2013, Weiss et al. 2015). However, in particular the fluids sampled by diamonds may be the result of

47 extensive fractionation processes, which are not easy to unravel. Constraining the primary composition of 48 mantle fluids therefore requires experimental studies. Unfortunately, methods for the direct withdrawal and analysis of fluids are limited to very low pressures (Potter et al. 1987) and cannot be used under 49 typical mantle P, T conditions. Simply quenching fluids equilibrated with minerals at high P and T and 50 51 analyzing the quenched fluid at ambient conditions is not likely to yield meaningful results, because in 52 most cases, solutes will precipitate as solid phases even during rapid quenching (e.g. Ryabchikov and 53 Boettcher 1980). Various methods have been proposed to solve this problem. In simple systems, where 54 minerals dissolve congruently, the weight loss of single crystals may allow very accurate solubility 55 measurements, since during quenching, solute will precipitate throughout the fluid, and only a very minor 56 fraction could produce an overgrowth on the original single crystal (e.g. Manning 1994, Tropper and 57 Manning 2007). Separating the charge into different, but connected compartments for solid phases and fluid - by using a double capsule technique (Anderson and Burnham 1965) or folded capsules 58 59 (Ryabchikov and Boettcher 1980) – may also help to distinguish material precipitated from the fluid from 60 solids that were stable during run conditions.

61 Synthetic fluid inclusions offer an attractive possibility to trap fluids in high-pressure experiments. The 62 fluid inclusions may be analyzed at ambient conditions by laser-ablation ICP-MS or other methods, such 63 as synchrotron X-ray fluorescence. This technique has been used successfully to study fluid compositions 64 in various systems (Bali et al. 2011, 2012, Tsay et al. 2014). One limitation of the method is that elements 65 contained in the host crystal (typically quartz or olivine) obviously cannot be quantified. Moreover, it is 66 not always possible to accurately control the time at which the inclusions seal off and lose contact to the main fluid reservoir. In systems where chemical equilibrium is attained slowly, this may have the effect 67 that the fluid trapped in the inclusions has not yet fully equilibrated with the other phases present. 68

69 Direct observation of mineral dissolution in the externally-heated diamond anvil cell can provide accurate 70 solubility data for minerals that dissolve congruently in the fluid (e.g. Audétat and Keppler 2005, Bernini 71 et al. 2013), but the approach does not allow to determine the solubility of minerals that dissolve

72 incongruently. Solubility studies may also be carried out by directly measuring fluid compositions in-situ 73 by X-ray fluorescence or X-ray absorption spectroscopy (e.g. Wilke et al. 2012). Other spectroscopic methods, in particular Raman spectroscopy, may also be used to infer solute concentrations. However, 74 75 Raman spectroscopic measurements in the diamond cell require an extremely careful calibration (see 76 Zarei et al. 2018 for discussion). A general limitation of solubility studies in the externally-heated 77 diamond cell is that run durations are usually relatively short, such that systems that require long 78 timescales (more than a few hours) for equilibration cannot be studied. Moreover, controlling oxygen 79 fugacity in the diamond cell is nearly impossible.

80 The "diamond trap method" for measuring fluid (and melt) compositions was first introduced by 81 Ryabchikov et al. (1989). It may be used in conventional piston cylinder or multi anvil experiments. A 82 layer of diamond powder is placed together with the other starting materials inside a noble metal capsule. 83 During the experiment, the fluid infiltrates the pore space between the diamond grains. Upon quenching, 84 any material precipitating from the fluid will remain trapped between the diamond grains. Therefore, ideally, it should be possible to determine the original bulk composition of the fluid by analyzing the 85 86 entire diamond trap containing the precipitated material together with the residual fluid. Since its first 87 description, the diamond trap method has been used extensively to infer fluid or melt compositions. For 88 analyzing aqueous fluids, in earlier studies (e.g. Stalder et al. 1998, Johnson and Plank 1999) the water 89 was simply allowed to evaporate after opening the capsule and the remaining solid residue was analyzed. 90 Kessel et al. (2004) introduced a more advanced method, where the capsule is first frozen and then cut 91 open and analyzed in frozen state.

Even though the diamond trap method – in various variants (e.g. Stalder et al. 1998, Johnson and Plank 1999, Kessel et al. 2005a, Rustioni et al. 2019) – has become rather popular for determining fluid compositions, the accuracy and precision of this method have been evaluated only for a single measurement of quartz solubility in water (Aerts et al. 2010). In this study, we therefore carried out additional tests to verify the reliability of the diamond trap technique: (i) We loaded capsules containing

97 diamond traps with fluids of known composition and analyzed them by laser-ablation ICP-MS, either 98 after simple evaporation of H₂O, after freeze-drying, or in frozen state; (ii) we used the diamond trap technique to measure mineral solubilities at high pressure and temperature in several simple systems, 99 100 where independent, high-quality solubility data exist; and (iii) we used the method to determine fluid 101 compositions and fluid/mineral partition coefficients of trace elements in the eclogite-H₂O±NaCl system. 102 In the latter experiments, we tested the attainment of equilibrium by forward and reverse experiments and 103 we investigated the effect of various experimental parameters, such as cooling or quench rates on the 104 analytical results.

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EXPERIMENTAL METHODS

107 Starting materials

108 Several solid starting materials and solutions were prepared in order to test different aspects of the 109 diamond trap technique. Solubility measurements were carried out for quartz, forsterite-enstatite, 110 corundum, rutile and albite in water. The quartz was a very pure synthetic crystal from China (< 20 ppm) total impurities). Natural, inclusion-free forsterite-rich olivine (Fo₉₀) from San Carlos with a composition 111 112 similar to that used by Newton and Manning (2002), and enstatite $(En_{89}Fs_{09}Wo_{02}Ac_{00})$ from a metasomatic 113 vein in equilibrium with the peridotite also from San Carlos, were used for the forsterite-enstatite-water system. For corundum, we selected a synthetic, optical sapphire crystal that is very pure according to 114 115 Laser-Ablation Inductively-Coupled-Plasma Mass-Spectrometry (LA-ICP-MS) analyses (only measurable impurity 2600 ppm Si). Rutile was also a very pure synthetic crystal (main impurity up to 800 116 117 ppm Al). For albite, a natural inclusion-free crystal from Brazil, containing only 0.2 wt% K₂O and <0.05 118 wt% CaO, was selected. All the different crystals were crushed into fine powders, and for the forsterite-119 enstatite experiment, a mixture consisting of 15 wt. % olivine and 85 wt. % enstatite was prepared.

120 For partitioning experiments in the eclogite-water system, we used a K-free synthetic basalt with a 121 composition similar to the starting material of Kessel et al. (2005a) to reproduce an average mid ocean 122 ridge basalt (MORB). SiO₂, TiO₂, Al(OH)₃, Fe₂O₃, Mg(OH)₂, CaCO₃ and Na₂CO₃ were ground and mixed in an agate mortar under ethanol. The mixture was decarbonated in a Pt crucible at 1100 °C for 12 hours. 123 After cooling, the material was melted at 1600 °C for 80 minutes and quenched in distilled water to 124 prevent crystallization. The recovered glass was ground to a powder except for three pieces from different 125 126 portions of the crucible that were analyzed by LA-ICP-MS to assess the final composition and 127 homogeneity of the obtained starting material. In order to dope the trace elements into the MORB starting 128 material, two diopside composition glasses with different concentration of trace elements were 129 synthesized. To produce these doped diopside glasses, a procedure similar to that described above for the 130 MORB was used. In the forward experiments, the basaltic starting material was mixed with 0.4, 1 or 2 wt. 131 % of doped diopside glass in order to achieve different trace element concentrations. Circa 1 wt. % of 132 natural garnet seeds from Grytting (Norway) eclogite was also added to enhance garnet growth during the 133 experiments.

134 Saline aqueous solutions were used in some of the eclogite-fluid partitioning experiments. NaCl was directly added to distilled water to obtain 1, 5, 10 and 15 wt. % NaCl solutions. Also, in order to perform 135 reversed experiments, two trace element-doped solutions were prepared by mixing appropriate amounts 136 137 of ICP-MS calibration solution (containing 1000 ppm of each trace element in 5 % HNO₃). The resulting 138 solution was evaporated under an infrared lamp and the obtained solid residue was dissolved again in a 139 smaller amount of 5 % HNO₃ to increase the trace element concentration. The resulting milky solution 140 was left to rest for 1 month to allow the insoluble residue to sediment out. The top clear portion of the 141 solution was then separated and analyzed by ICP-MS. Compositions of the MORB glasses and of the 142 solutions for reversed experiments are reported in Rustioni et al. (2019).

A solution with known composition was prepared in order to test various analytical approaches. Two separate solutions were produced by dissolving CsOH and Na₂SiO₃ in distilled water in one case and

NaCl and KCl in in distilled water for the other solution. The final solution was then produced by mixing
the CsOH-Na₂SiO₃ solution with the NaCl-KCl solution to obtain the composition reported in Table 1.

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148 High pressure experiments

149 In all experiments, a cylindrical Au or Pt capsule with 10 mm length, 5 mm external diameter and 4.6 mm 150 internal diameter was used. A 2 mm thick layer of diamond powder (10-20 µm grain size) was placed in 151 the central part of the capsule in between two layers of solid starting material. Fluid was either completely 152 added before the solid starting material, or it was added in several steps during the filling of the capsules. In the second case, about 1/3 of the total fluid was added at the beginning, while the remaining fluid was 153 154 inserted after the diamond trap layer. This approach is particularly important when a fine-grained powder 155 is used, to prevent the solid starting material from being suspended and contaminating the diamond trap 156 layer during capsule preparation, which would cause an overestimation of solute content in the fluid phase 157 during LA-ICP-MS analysis after the experiments. About 1 mm of empty space was always left at the top 158 of the capsule to avoid fluid loss during the welding of the top lid. The weight of the capsule was always 159 checked before and after welding. Before high pressure experiments, the capsules were also left overnight in an oven at 130 °C and weighed again to test whether complete sealing was achieved. 160

161 High pressure and temperature experiments were conducted in an end-loaded piston cylinder apparatus 162 using ½ inch MgO-NaCl assemblies with a stepped graphite furnace. Pressure was calculated from the oil 163 pressure on the hydraulic ram, using a 5 % friction correction, as calibrated by the quartz-coesite transition and the density of synthetic fluid inclusions. Temperature was measured with a Pt/Pt-Rh (S-164 165 type) thermocouple and monitored by a Eurotherm controller. The temperature was raised at constant pressure after compression at a rate of 100 °C/min. Run durations varied depending on the complexity of 166 167 the system. For experiments on simple systems used in the solubility tests, the typical duration was 16-20 168 hours. In the eclogite-water \pm NaCl system, experiment duration varied from 2 to 7 days. Most of the runs

were quenched by shutting off the power at constant pressure before starting the decompression. In a few
 experiments conducted in the eclogite-water system, a cooling ramp of 100 °C/min was applied instead of
 the temperature quench.

In the eclogite-water ± NaCl experiments at 4 GPa and 800 °C, some of the Au capsules appeared very 172 173 deformed and contained small holes after the experiments. The extent of deformation could be reduced by 174 pre-shrinking the capsule inside a hydrothermal vessel pressurized to 200 MPa before the piston cylinder runs, in order to eliminate the empty space at the top of the capsules that was considered to be 175 mechanically weaker. However, this method did not particularly enhance the resistance of the capsule and 176 tiny holes were still observed after experiments. The problem was eventually solved by changing the 177 178 capsule material from gold to platinum and by slowly compressing and decompressing the sample over 16-20 hours at the beginning and the end of the experiments. Slow, continuous compression and 179 180 decompression was achieved using an automated hydraulic spindle press that continuously changed the 181 oil pressure on master ram and endload according to a pre-set program.

182 Another challenge in the eclogite-water experiments was to synthetize crystals (in particular omphacite) 183 large enough for LA-ICP-MS analysis. To overcome this problem, the initial fluid/solid starting material ratio in the capsule was increased from ~ 0.3 to ~ 0.4 . Moreover, temperature fluctuations of ± 30 °C 184 were applied in experiments to enhance grain growth by Ostwald ripening, i.e. the dissolution of smaller 185 186 crystals upon heating and the growth of larger crystals during cooling. Temperature cycling started after an initial equilibration at constant temperature for ~ 36 hours to nucleate the mineral assemblage stable at 187 800 °C. The temperature cycling was stopped ~ 24 hours before quenching to let the system equilibrate 188 189 again. Ramps in temperature (from 770 to 830 °C and vice versa) lasted 2 hours each, with dwell times at 190 both temperatures of 2 hours. A single temperature cycle thus lasted 8 hours in total, see Figure 1.

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192 Analytical methods

193 Several analytical approaches were tested, as described below. The best quality of data was obtained 194 when the fluid contained in the diamond trap was directly analyzed in frozen state by LA-ICP-MS 195 following a procedure similar to that described in Kessel et al. (2004). The capsules were cooled in liquid 196 nitrogen and then cut open longitudinally with a razor blade attached to an opening device. One half of 197 the frozen capsule was then quickly transferred to a LA-ICP-MS sample chamber equipped with a Peltier-198 cooling element to keep the sample frozen during the entire measurement. Tests with H₂O-ethanol mixtures revealed that the temperature within this sample chamber was ca. -30 °C. The LA-ICP-MS 199 200 measurements were performed with a 193 nm ArF GeolasPro laser ablation unit (Coherent, USA) 201 connected to an Elan DRC-e quadrupole ICP-MS unit (Perkin Elmer, Canada). The sample chamber was 202 flushed with He at a flow rate of 0.4 l/min, to which 5 ml/min H₂ was admixed on the way to the ICP-MS. Measured isotopes included ⁷Li, ⁹Be, ¹¹B, ²³Na, ²⁵Mg, ²⁷Al, ³⁰Si, ³⁵Cl, ³⁹K, ⁴³Ca, ⁴⁵Sc, ⁴⁹Ti, ⁵⁷Fe, ⁸⁵Rb, ⁸⁸Sr, 203 ⁸⁹Y, ⁹³Nb, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶³Dy, ¹⁶⁷Er, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁸¹Ta, ²⁰⁸Pb, ²³²Th, 204 and ²³⁸U, using a dwell time of 10 ms. The ICP-MS was tuned to a thorium oxide production rate of 0.05-205 206 0.10 % and a rate of doubly-charged Ca ions of 0.15-0.25 % based on measurements on NIST SRM 610 glass (Jochum et al. 2011). The diamond trap layer was analyzed first by moving the laser beam at 207 208 constant velocity along a transect perpendicular to the diamond layer in order to locate and subsequently 209 avoid eventual contaminations at the border of the diamond trap. A second transect, parallel to the 210 diamond layer, was measured in the central, homogeneous part of the diamond trap. To obtain the best 211 average of fluid composition, a large laser spot size of 50-70 µm and a repetition rate of 7 Hz were used. 212 The signals resulting from each transect (a typical example is shown in Figure 2) were divided into 3-6 213 separate integration intervals, for which element concentrations were calculated. The average composition of these intervals was considered to be representative of the fluid composition. The NIST SRM 610 glass 214 215 and a well-characterized, natural afghanite crystal (Seo et al. 2011) were used as external standards. Cesium and/or chlorine were used as internal standards, as these elements are expected to partition 216 217 strongly into the fluid in all the systems investigated in the present study. Internal standard concentrations

used for calculation were corrected considering the dilution effect due to major element dissolution intothe fluid during high pressure and temperature experiments.

220 After analysis of the diamond trap of the eclogite-fluid partitioning experiments, the capsules were left to 221 evaporate at room temperature and subsequently they were impregnated in epoxy resin and polished to expose minerals for LA-ICP-MS measurements. The largest suitable spot sizes to analyze single crystals 222 223 were typically in the range of 7-20 μ m. Special care was taken during the garnet measurements to only 224 analyze inclusion-free rim portions and to avoid the natural garnet seeds, which showed distinctively 225 different composition. Averages obtained from measurements of 4 to 7 separate crystals within the 226 capsule were used to calculate the compositions of garnet, omphacite and rutile. Kyanite crystals were 227 also analyzed, but trace element concentrations were always below the detection limits and thus were 228 considered irrelevant for partitioning calculation. To calculate bulk fluid/eclogite partition coefficients, 229 first the fluid/mineral partition coefficients for each mineral were calculated, and then the results 230 normalized to a representative eclogitic composition of 59 % omphacite, 39 % garnet and 2 % rutile.

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RESULTS AND DISCUSSION

233 Test of various analytical approaches

234 Simplified diamond trap experiments were carried out to understand which analytical approach provides 235 the most reliable data. Capsules were prepared following the procedure described above. Undoped 236 MORB glass was used as solid starting material, and an aqueous Na-Cl-Si-K-Cs solution of known 237 composition (see Table 1) was added to the capsules. Three experiments were conducted in a cold-seal 238 vessel at 200 MPa and room temperature for 1 hour in order to mechanically force the fluid into the pore space between the solid materials and the diamond trap without changing its composition. The retrieved 239 240 capsules were weighed to check that no fluid loss or gain occurred during experiments. After these experiments, three different procedures were used to analyze the diamond traps. One capsule was cut 241

open longitudinally and was allowed to evaporate at room conditions for three days (evaporation approach). The second was frozen in liquid nitrogen, cut open, and then transferred in frozen state into a Christ Alpha 2-4 LDplus freeze-drying apparatus with an ice condensation temperature of -85 °C, where the aqueous liquid sublimated over the course of 2 hours (freeze-drying approach). In both the evaporation and the freeze-drying approaches, after complete drying, one half of the capsule was impregnated in epoxy and polished for further analysis. For the third capsule, the procedure described in the "analytical methods" section was used (freezing chamber approach).

249 Results of these tests are shown in Figure 3 and Table 1, together with the original composition of the 250 fluid loaded into the capsule. Assuming that no major change in fluid composition occurred during the experiments, the most accurate and precise method for analysis is clearly the freezing chamber approach. 251 252 The concentrations of Na, K, and Cs are reproduced within a relative deviation of 3.6, 14, and 4.2 %. 253 Only for silica, the measured concentration is 25 % below the expected value. This could, however, 254 reflect adsorption of silica on the surface of the glass powder in the charge. While the data obtained with the freezing chamber are very stable and reproducible, both the evaporation and the freeze-drying method 255 256 give much more scattered results and even the averages sometimes deviate from the expected composition 257 by more than a factor of two (Table 1). Since none of the solute components in the fluid is expected to be 258 volatile near ambient temperature, the scatter is unlikely to be due to element loss during evaporation. However, some redistribution of elements inside the diamond trap during evaporation could very well 259 260 explain the scatter of the data. Consistent with the test results described above, only the freezing chamber 261 approach was used to analyze the samples from high-pressure experiments that are discussed in the following sections. 262

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264 Solubility measurements in known systems

Several test experiments were carried out to measure mineral solubilities in water for simple, well-studied systems, in order to compare the diamond trap method with data from literature. Results are shown in Figure 4 and Table 2.

Two experiments (SC05 and SC06) were performed at 1 GPa and 800 °C to test quartz solubility in water. 268 269 This system is very well studied and there is generally a rather good agreement between various 270 experimental data sets (e.g. Anderson and Burnham 1965, Fournier and Potter 1982, Manning 1994). At 271 the conditions of the experiments, SiO₂ concentration in the fluid is expected to be 7 wt. % (Manning 272 1994). The solubility measured in experiment SC05 is 7.2 ± 0.5 wt. %, consistent with literature data. On 273 the other hand, experiment SC06 gave a significantly lower solubility of 4.2 ± 0.5 wt. %. The experimental procedures for SC05 and SC06 were the same, also both diamond traps show relatively 274 275 homogeneous laser ablation signals along the analyzed transects, resulting in similar precision. Therefore, 276 the reason for the lower solubility obtained from experiment SC06 is not obvious. The slightly shorter run 277 duration of SC06 (16 hours) as compared to SC05 (18 hours) could have contributed to incomplete 278 attainment of equilibrium; however, the variation in the run durations is too small to account for the 279 observed differences in solubility.

The solubility of silica in the forsterite-enstatite-water system at 1 GPa and 800 °C was tested in 280 281 experiment SC02. The diamond trap approach yields well-reproducible data with an average of $0.94 \pm$ 282 0.03 wt. % for the SiO₂ concentration in the fluid. However, this value is significantly below the silica 283 solubility determined by Newton and Manning (2002), who report a value of 1.77 wt. % SiO₂ at the same 284 conditions. A possible reason for the observed low solubility could be incomplete equilibration or perhaps some error associated with the concentration of the Cs standard in the fluid. The run duration of 20 hours 285 286 is at the low end of those used by Newton and Manning (2002). However, in the latter study, a double 287 capsule technique was used in combination with single crystals, which should make attainment of 288 equilibrium more sluggish than in the present experiments. The high reproducibility in the diamond trap, 289 which reflects a homogeneous fluid and precipitate distribution in the capsule, is consistent with

equilibrium throughout the charge. Overall, the experiments in the quartz- H_2O and forsterite-enstatite-H₂O systems indicate that silica concentrations in fluids can be measured with a precision of about 10 % or better, but the accuracy of the measurements is likely lower, as they return the expected values only within a factor of two or better.

294 Corundum solubility tests yielded data with both low precision and low accuracy. The average value for Al_2O_3 concentration in the fluid for a diamond trap experiment (SC12) conducted at 2 GPa and 700 °C is 295 296 0.101 ± 0.009 wt. %. For these conditions, Tropper & Manning (2007) report a much lower corundum 297 solubility of 0.029 wt. %. The scatter in the measured concentrations in the diamond trap may be due to 298 inhomogeneous precipitation of solid materials either during the experiment or upon quench from high 299 temperature. Indeed, such effects are known from previous studies (e.g. Tropper and Manning 2007, Antignano and Manning 2008). Corundum solubility increases strongly with temperature and therefore, 300 301 minute temperature gradients inside a capsule may cause the dissolution and re-precipitation of corundum 302 crystals throughout the charge. Images of such "vapor-transport crystals" are shown by Tropper and 303 Manning (2007). They are likely responsible for the anomalously high apparent solubilities observed in 304 experiment SC12 and for similar order-of-magnitude differences in corundum solubilities reported in previous studies (e.g. Ragnasdottir and Walther 1985, Walther 1997). 305

306 Rutile solubility in water is known to be notoriously difficult to measure. Early single-crystal weight-loss 307 experiments in piston cylinder presses suggested very high solubilities up to 1.9 wt. % at 1 GPa and 1100 308 °C (Ayers and Watson 1993). These data were, however, very likely affected by dissolution and re-309 precipitation effects in a temperature gradient. In later studies, Tropper and Manning (2005) and 310 Antignano and Manning (2008) carefully reduced temperature gradients inside the piston cylinder 311 experiments and obtained solubilities that were orders of magnitude lower. Direct visual observation of 312 rutile dissolution and re-precipitation in an externally-heated diamond cell yielded even lower solubilities 313 in the range of 10 to 25 ppm at 900 to 1050 °C and 1 to 2.5 GPa (Audétat and Keppler 2005). As rutile 314 solubility may be strongly affected by temperature gradients, in experiment SC07 three separated

315 diamond traps were placed in the capsule to also test the temperature distribution. Therefore, in addition 316 to the diamond powder layer located at the center, one diamond trap was inserted at the bottom and one at the top of the capsule, with two rutile layers dividing the three diamond layers. TiO_2 concentrations 317 measured in the fluid with this approach are very inhomogeneous, with no systematic difference observed 318 319 between the three diamond traps. As in previous studies, the measured concentrations are likely affected 320 by dissolution and precipitation in a temperature gradient along the entire capsule. This process also leads to an overestimation of TiO₂ solubility, which at 2 GPa and 1000 ^oC is expected to be about 0.003 wt. % 321 (Audétat and Keppler 2005), while in our measurements it ranges between 0.017 and 0.042 wt. %. At face 322 value, these numbers would be more consistent with the rutile solubility model of Antignano and 323 324 Manning (2008), which predicts 0.026 wt. % TiO₂ under the run conditions. However, the scatter of the 325 data suggests that they are likely affected by some transport process in a thermal gradient.

Two experiments (SC03 and SC04) were conducted at 1.8 GPa and 800 °C in the albite-water system. At 326 these conditions a supercritical fluid should form (Shen and Keppler 1997), and therefore a single, 327 328 homogeneous fluid phase should fill the entire pore space in the capsule. The albite starting material was 329 thus directly mixed with diamond and the entire capsule was regarded as a single diamond trap for the fluid. The measured fluid composition turned out to be homogeneous along the entire capsule for both 330 331 experiments. As the fluid/solid ratio loaded in the two capsules was the same, the expected concentrations 332 in the fluid for both runs are 35.9 wt. % SiO₂, 10.9 wt. % Al₂O₃, and 6.0 wt. % Na₂O. The expected SiO₂ 333 concentrations are returned within 7 % relative or better in both experiments. In run SC03, Na₂O is reproduced within 13 % relative, while in SC04, the Na₂O content is overestimated by 77 %, i.e. by 334 335 almost a factor of two. Since there is no obvious difference between experiments SC03 and SC04, this 336 result is in line with the observations made in the silica-H₂O and forsterite-enstatite-H₂O systems, 337 indicating that the intrinsic accuracy of the method is such that it reproduces the true concentrations within a factor of two or better. 338

339 The measured Al_2O_3 concentrations in SC03 and SC04 are both less than half the expected value. This may be caused by a fractionation process. To understand the origin of this problem, we filled a smaller 340 platinum capsule (4 mm high and 4 mm in diameter; sample AbTest) with a mixture of diamond and 341 albite powder in a ratio of about 9:1 plus added water in a similar fluid/solid ratio as in the experiments 342 343 SC03 and SC04. The capsule was compressed in a cold-seal vessel at 200 MPa without any heating and 344 then analyzed in frozen state in the same way as SC03 and SC04. The SiO_2/Al_2O_3 ratio obtained from this 345 test is 7.5, which is close to that obtained in SC03 and SC04, but significantly different from the 346 theoretical SiO₂/Al₂O₃ weight ratio of 3.54 in albite. In contrast, LA-ICP-MS analyses on a larger 347 fragment of albite using the same laser settings returned the correct SiO_2/Al_2O_3 ratio. Note that the frozen 348 diamond trap ablates in a far less controlled fashion than solids, resulting in deep trenches that are 2-5 times wider than the used beam diameter. The uncontrolled ablation likely causes serious fractionation 349 effects, particularly for refractory elements like Al. We thus believe that the low Al₂O₃ values represent 350 351 an analytical artifact.

Overall, the data presented here suggest that the analytical precision of the diamond trap technique is high and that the accuracy is commonly within a factor of two or better, except in systems that are highly susceptible to dissolution and re-precipitation of solid phases in minor temperature gradients, such as the systems Al_2O_3 - H_2O and TiO_2 - H_2O .

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357 Tests in partitioning experiments in the eclogite–water ± NaCl system

Compositions of fluid and minerals, and trace element fluid/eclogite partition coefficients obtained from experiments in the eclogite-water ± NaCl system using the methods described here were reported by Rustioni et al. (2019). A frequent problem in such experiments is the difficulty to obtain crystals large enough for trace element analysis. While in a crystal-melt system this can usually be solved by very slow cooling and slow crystal growth from the melt, this is not possible for a system where crystals coexist

363 with an aqueous fluid only. However, we carried out some tests which suggest that periodic temperature 364 fluctuations can be used to enhance crystal growth through Ostwald ripening, i.e. the dissolution of smaller crystals during heating and the growth of larger crystals during cooling. Figure 5 shows a 365 comparison between an eclogite synthesized in an experiment conducted at constant temperature (a) and 366 367 one obtained with \pm 30 °C temperature fluctuations (b). Introducing temperature cycling effectively 368 enhanced omphacite and kyanite growth, while it did not particularly affect the size of garnet and rutile 369 crystals. Table 3 reports the average compositions of garnet and omphacite in two different experiments 370 (PC37 and PC38). Both experiments were conducted with pure water for a better comparison, but while in 371 PC38 the temperature was kept constant at 800 °C, in PC37 \pm 30 °C temperature cycling was used. The 372 resulting compositions of both garnet and omphacite from the two experiments are very similar, 373 indicating that although temperature cycling enhanced crystal growth, it did not affect the composition of 374 minerals. This observation also applies for trace element compositions. A comparison between trace 375 element D^{fluid/eclogite} between the same two experiments is shown in Figure 5c. Again, the measured 376 partition coefficients in PC37 and PC38 are the same within uncertainties. We therefore conclude that 377 temperature cycling can be a useful technique for enhancing crystal growth in fluid-mineral partitioning experiments without compromising the validity of the measured partition coefficients (see also da Silva et 378 379 al. 2017). A necessary prerequisite for applying this method is, however, that the amplitude of cycling is 380 within the stability range of the phase assemblage of interest. While in a few experiments even at constant 381 temperature sufficiently large crystals were obtained to allow LA-ICP-MS analyses of all phases, in 382 particular the omphacite crystals were often too small for measuring trace element compositions. In such 383 cases, temperature cycling was very efficient for increasing crystal sizes.

The effect of different cooling rates on measured trace element concentrations was tested by comparing experiment PC25, which was quenched from high temperature by shutting off the power resulting in a rapid cooling within 10-15 seconds, to experiment PC27, which was cooled at a constant rate of 100 °C/minute. All other parameters in the experimental procedure of PC25 and PC27 were the same. Figure 6

388 shows that the two different cooling rates did not have major effects on the measured partition
389 coefficients for most of the trace elements.

In all experiments, LA-ICP-MS signals obtained from the analysis of frozen fluid in the diamond trap were relatively constant in time for the measured isotopes (Figure 2). As the ablation was performed by moving along transects perpendicular and parallel to the diamond layer, this reflects a generally homogeneous distribution of elements inside the trap.

394 Kessel et al. (2005a) used a rocking multi anvil press to measure trace element partitioning in the eclogite-fluid system. Schmidt and Ulmer (2004) suggested that such a device is necessary in order to 395 396 suppress the formation of extreme chemical zoning (and therefore disequilibrium) in fluid-bearing multi 397 anvil experiments. However, while this technology may indeed offer an advantage for multi anvil 398 experiments, where temperature gradients may be rather large, we did not observe any zonation or other 399 evidence for disequilibrium in our piston cylinder experiments. Figure 7 shows electron microprobe 400 measurements of garnets that were located in different areas of a capsule recovered from one piston 401 cylinder experiment. The composition is constant throughout the entire length of the recovered charge; 402 moreover, garnet and clinopyroxene appear to be homogeneously distributed, without obvious phase 403 segregation in parts of the capsule. Accordingly, equilibrium was likely achieved throughout the entire 404 charge. We therefore conclude that fluid/mineral partitioning experiments can be carried out with a 405 simple piston cylinder device up to about 5 GPa; the use of a rocking multi anvil in this pressure range is 406 not required.

407 Unlike for the mineral solubilities in simple model systems, it is not possible to test the accuracy of the 408 data obtained in eclogite-fluid partitioning experiments against independent measurements. However, it 409 was possible to check attainment of equilibrium between mineral and fluid phases by reversed 410 experiments. While in "forward" experiments all the trace elements were doped in the solid starting 411 material, in reversed experiments all the trace elements, except for Ti, were added by means of the fluid 412 phase and an undoped MORB was used. In general, we obtained good agreement between results from 413 forward and reversed experiments, typically within a factor of two, demonstrating attainment of 414 equilibrium in our experiments. Figure 8 shows the effect of Cl on the fluid/eclogite partition coefficient 415 of europium. The enhancement of Eu solubility with addition of chlorine is the same for forward and 416 reversed experiments.

417 In order to be able to measure trace element concentrations in both fluid and solid phases, it may be 418 necessary to dope the starting material with a relatively high concentration of trace elements. At the same 419 time, to measure meaningful partition coefficients, the concentration of trace elements must be low 420 enough to not exceed the boundaries of Henry's law behavior. Figure 8 includes results from experiments 421 conducted with different initial concentrations of europium. The fact that all experiments produce a single 422 trend implies that the Eu concentrations used in our experiments fulfill Henry's law. Similar data on 423 reversed experiments and variable trace element concentration for other trace elements are given by 424 Rustioni et al. (2019).

Taken together, the good agreement between forward and reversed experiments and the independence of the measured partition coefficients on the bulk concentration of the trace elements suggests that in most cases, the diamond trap method yields reliable fluid/eclogite partition coefficients within a factor of two. However, the method can only be applied, if the system contains only one single mobile phase (fluid or melt), as in the eclogite-water±NaCl system at 4 GPa and 800 °C (Kessel et al. 2005 b). In the presence of both an aqueous fluid and a silicate melt, or in the presence of two coexisting fluids, distinguishing the compositions of these phases by analyzing the diamond trap would be very difficult or impossible.

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IMPLICATIONS

434 The systematic tests carried out in the course of this study show the potential and limitations of the 435 diamond trap technique for studying fluid compositions. In principle, the method is widely applicable for

436 both piston cylinder and multi anvil experiments, covering the entire pressure and temperature range of 437 the upper mantle. At least up to 5 GPa, partitioning and solubility experiments in fluid-bearing systems may be carried out with conventional piston cylinder devices; the use of a rocking multi anvil is not 438 required in this pressure range. Laser ablation ICP-MS analyses of the fluid in the diamond trap should 439 440 always be carried out in frozen state. The method is particularly suitable for measuring partition coefficients, which may vary by several orders of magnitude and thus do not require very high precision 441 442 or accuracy. However, particularly in chemically simple systems, measurements of mineral solubilities in fluids using the single-crystal weight-loss techniques, or by direct observation in diamond anvil cells, 443 may yield more accurate results than the diamond trap method. A severe problem can be the dissolution 444 445 and re-precipitation of solid phases already during the high-pressure and high-temperature experiment, which may lead to erroneously high fluid concentrations. Such effects are to be expected for phases like 446 corundum or rutile with solubilities that are highly temperature dependent, such that dissolution and re-447 448 precipitation may occur as a result of minor temperature gradients.

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Analytical Initial fluid					
approach	composition	Freeze-drying	Evaporation	Freezing chamber	
Na ₂ O (wt.%)	7.74	2.5 (7)	5.6 (3)	8.02 (6)	
SiO ₂ (wt.%)	3.12	7 (4)	6 (2)	2.35 (9)	
Cl (wt.%)*	7.62	7.62	7.62	7.62	
K ₂ O (wt.%)	2.69	1.3 (2)	3.7 (3)	2.30 (4)	
Cs (ppm)	120	110 (20)	148 (19)	115 (4)	

One standard deviation is reported in parentheses in terms of the least digit cited

*Cl concentration in the fluid is used as internal standard for calculations

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Table 2. Tests of mineral solubilities in known systems								
Experiment	Туре	Р	Т	Duration	SiO ₂	Al ₂ O ₃	Na ₂ O	TiO ₂
Experiment		(GPa)	(⁰ C)	(h)				
SC05	_	1	800	18	7.2 (5)			
SC06	Quartz			16	4.2 (5)			
SC02	Forsterite-enstatite	1	800	20	0.94 (3)			
SC12	Corundum	2	700	19		0.101 (9)		
SC07 (top)								0.023 (2)
SC07 (middle)	Rutile	2	1000	18				0.034 (1)
SC07 (bottom)								0.028 (6)
SC03	Albite-water	1.0	1.8 800	16	38.3 (7)	4.9 (2)	6.8 (3)	
SC04	supercritical fluid	1.0		16	37.0 (6)	3.0 (2)	10.6 (3)	

One standard deviation is reported in parentheses in terms of the least digit cited

Concentrations are expressed as wt. % in the fluid phase

554

Table 3. Effect of temperature cycling on mineral compositions in the eclogite-H₂O system at 4

GPa and 800 °C

Mineral	T cycling	SiO ₂	TiO ₂	Al ₂ O ₃	MgO	CaO	FeO	Na ₂ O
Compt	No	46.1 (12)	0.67 (2)	19.0 (9)	7.5 (2)	9.2 (7)	17.5 (4)	0.16 (5)
Gamet	Yes	46.3 (4)	0.71 (7)	19.2 (4)	8.1 (4)	8.3 (4)	17.4 (2)	0.32 (4)
Quality	No	59.3 (4)	0.55 (4)	14.2 (5)	7.5 (2)	13.4 (1)	5.1 (3)	6.73 (1)
Omphacite	Yes	61.4 (7)	0.45 (4)	14.6 (7)	7.3 (1)	11.8 (4)	4.5 (4)	6.88 (25)

One standard deviation is reported in parentheses in terms of the least digit cited

Concentrations are expressed as wt. %.

555

557 Figure captions

558

Figure 1. Example of temperature profile in a typical eclogite-water system experiment in which \pm 30 °C

temperature cycling was applied. On the left the entire experiment duration is shown. On the right is the

detail of a single temperature cycle with a total duration of 8 hours.

Figure 2. Representative LA-ICP-MS signal collected from the frozen fluid contained in the diamond
trap while moving along a transect parallel to the diamond layer from experiment PC39 conducted in the
eclogite-water system at 800 °C and 4 GPa. The fluid contained approximately 7 wt. % of Cl, 6 wt. % of
Na₂O, 27 wt. % of SiO₂, 1 wt. % Al₂O₃, 370 ppm of Ti and 6300 ppm of Cs.

Figure 3. Comparison between measurements of fluid compositions performed using three different
methods: "evaporation" (green triangles), "freeze drying" (red diamonds) and "freezing chamber" (blue
circles), as described in the text. The initial fluid composition is shown as a grey line.

569 Figure 4. Results of experiments to test mineral solubilities in known systems. Each graph gives the 570 results of a single experiment, and each point represents the integration of a segment of the laser ablation 571 transects performed on the diamond trap portions of the capsule. Expected concentrations in the fluid 572 from the literature are shown as a grey line. The data for quartz (experiment SC05) are from Manning (1994), for forsterite-enstatite (SC02) from Newton and Manning (2002), for corundum (SC12) from 573 574 Tropper and Manning (2007), and for rutile (SC07) from Audétat and Keppler (2005). For the albite-H₂O 575 system (SC03), the P, T conditions are beyond the critical curve (Shen and Keppler 1997) and therefore 576 the measured composition should equal the bulk composition of the charge.

Figure 5. Comparison of experimental results in the eclogite–fluid system at 4 GPa and 800 °C

578 conducted with and without temperature fluctuation. (a) Eclogite synthetized in an experiment run at

579 constant temperature. (b) Eclogite synthetized in an experiment where \pm 30 °C cycling was used. (c)

580	Comparison of trace element fluid/eclogite partition coefficient measured in two experiments conducted
581	at 4 GPa with pure water, one at a steady temperature of 800 °C and the other with temperature cycling.
582	Error bars correspond to one standard deviation.

583 Figure 6. Comparison of fluid/eclogite partition coefficients obtained from an experiment that was

rapidly quenched from high temperature, versus one that was cooled down at a rate of 100 °C/minute. In

general, variations in cooling rate were found to have little effect on the measured fluid compositions.

586 Error bars correspond to one standard deviation.

587 Figure 7. Garnet compositions measured along a single capsule from an experiment in the eclogite-fluid

588 system at 4 GPa and 800 °C. Red diamonds are iron, yellow triangles aluminium, blue squares calcium

- and green circles magnesium oxides.
- 590 Figure 8. Effect of the amount of chlorine dissolved in fluid on the fluid/eclogite partition coefficient of

591 europium. Green diamonds represent data obtained from forward experiments. Red circles are data

592 obtained from reversed experiments. Different shades of color represent different initial concentration of

trace elements in the solid starting material (green diamonds) or in the initial fluid (red circles) used in

594 experiments. Error bars correspond to one standard deviation.

Figure 1





Figure 3















