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2 The effect of fluorine on reaction rim growth dynamics in the ternary CaO-MgO-

3 SiO₂ system

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Abstract

Growth of reaction rims is mainly controlled by a change in physical parameters such as pressure and temperature, a change in the chemical composition of the system and/or by the presence of volatiles. In particular, the effect of volatiles other than water on reaction rim growth remains poorly understood. In order to accurately model metamorphic and metasomatic processes, a quantification of the effect of volatiles on reaction-rim growth dynamics is necessary but hitherto missing.

In this study, reaction rims were experimentally grown in a series of piston cylinder experiments 14 15 in the ternary CaO-MgO-SiO₂ system at 1000°C and 1.5 GPa with 0-10 wt% F for 20 minutes. In the fluorine free system, a rim sequence of wollastonite (Wo) | merwinite (Mer) | diopside (Di) 16 17 | forsterite (Fo) | periclase (Per) formed, complying with the stable phase configuration at 18 water saturated conditions. As soon as 0.1 wt% F was introduced into the system, humite group 19 minerals (HGMs) and monticellite (Mtc) appeared, resulting in the multilayer rim sequence Wo 20 | Mer | Mtc | Fo + HGMs | Per. In experiments with fluorine concentrations ≥ 0.5 wt%, 21 cuspidine (Csp) appears in the layer sequence and represents the major fluorine sink. Our data 22 show that the addition of fluorine may stabilize the fluorine-bearing phases cuspidine and

23	HGMs to higher temperatures, which is in agreement with previous studies (Grützner et al.,
24	2017). However, the appearance of the nominally anhydrous minerals (NAMs) monticellite and
25	åkermanite (Ak) at this P-T-condition suggests that addition of fluorine may also affect the
26	stability of nominally fluorine free minerals. This may be explained by the effect of fluorine on
27	the Gibbs free energies of fluorine bearing phases, which in turn affects the relative Gibbs free
28	energies and thus the stabilities of all phases. An increase in absolute rim thickness from
29	11.8(21) to 105.6(22) μm (1 σ standard deviations in parentheses) in fluorine free and 10 wt% F
30	experiments respectively suggests that fluorine enhances absolute component mobilities and
31	thus results in faster rim growth rates. Additionally, a change in relative component mobilities
32	due to the presence of fluorine results in microstructural changes such as a phase segregation of
33	diopside and cuspidine at high fluorine (≥3 wt% F) concentrations.
34	These results not only imply that reaction rims may be used as a tool to infer the amount of
35	fluorine present during metamorphic reactions, but also that we need to consider the role of
36	fluorine for a correct interpretation of the P-T-t history of metamorphic and metasomatic rocks.
37	
38 39	<i>Keywords:</i> wollastonite, cuspidine, component mobilities, palisade microstructure, metasomatic, metamorphic, volatiles, grain boundary
40	
41	Introduction
42	Metamorphic coronas and reaction rims are examples of a non-equilibrium net-transfer
10	reaction in which are existing minoral phases react to now phases. The growth of reaction rims
43	reaction, in which pre-existing numeral phases react to new phases. The growth of reaction films
44	is mainly controlled by a change in physical parameters such as pressure and temperature, a
45	change in the chemical composition, and/or by the presence of volatile components, which

push the system to out-of-equilibrium conditions. As the system tends to equilibrate, the 46 47 interplay of reactions at the rim-reactant-interfaces and transport of chemical components 48 across the rim control overall rim growth (Abart and Petrishcheva, 2011). Reaction rims may 49 consist of several layers, whose sequence and texture depends on the relative diffusivity of the individual chemical components in each layer (Joesten, 1977). These component mobilities are 50 51 in turn affected by parameters such as temperature, pressure, chemical composition, and 52 rheological properties. (Milke et al., 2009; Joachim et al., 2019). This implies that an interplay of several parameters may directly influence the thickness of a reaction rim and its microstructure. 53 54 Consequently, if the effect of these parameters is guantified and constrained, reaction rims 55 have the potential to be used as a tool to gain insight into the setting and dynamics of complex 56 geological systems.

57 Growth kinetics of reaction rims were repeatedly investigated in a variety of binary systems and are reasonably well understood particularly at nominally dry conditions. Examples are the MgO-58 Al₂O₃ system where spinel grows between periclase and corundum (Rossi and Fulrath, 1963; 59 Whitney and Stubican 1971; Watson and Price, 2002; Götze et al., 2010; Keller et al., 2010) and 60 61 the system CaCO₃-SiO₂ where wollastonite grows between calcite and quartz (Milke and 62 Heinrich, 2002). Experimentally derived reaction rims were studied over a wide range of P-T 63 conditions in the MgO-SiO₂ (Yund 1997; Fisler et al., 1997; Milke et al., 2001; Milke et al., 2007; 64 Milke et al., 2009; Abart et al., 2004; Götze et al., 2010; Gardés et al., 2011), the Al₂O₃-MgO 65 system (Götze et al., 2010), and the ternary CaO-MgO-SiO₂ (CMS) system (Joachim et al., 2011; 66 Joachim et al., 2012; Joachim et al., 2019). Recent studies even started to experimentally 67 investigate reaction rims at high P-T conditions representative for Earth's lower mantle (Nishi et

al., 2013; Nagayoshi et al. 2016). However, the experimentally produced reaction rims in almost
all of these studies are limited to simplified chemical systems that produce a sequence of one or
maximum two monomineralic layers. In order to take the next step toward an understanding of
complex natural metamorphic and metasomatic processes, we require an experimental
approach that investigates the growth of multilayered rim sequences and includes volatiles.

73 Recent advances show that volatiles might have a major effect on the dynamics of net-transfer 74 reactions (Yund, 1997; Joachim et al., 2011; Gardés et al., 2012; Joachim et al., 2012; Joachim et 75 al., 2019; Remmert et al., 2018). The presence of water, for instance, enhances the bulk 76 diffusivity of MgO by multiple orders of magnitude in both the binary MgO-SiO₂ (Yund, 1997; 77 Milke et al., 2001; Gardés et al., 2012; Milke et al., 2013) and the ternary CMS system (Joachim 78 et al., 2011; Joachim et al., 2019), thus resulting in substantially greater rim thicknesses at 79 otherwise identical P-T-t-X conditions. The presence of small amounts of water might also affect the internal rim microstructure. For example, small amounts of surface water adsorbed on the 80 starting materials of powdered experimental charges lead to the segregation of a bimineralic 81 82 diopside + merwinite-single layered rim resulting in the formation of a merwinite – diopside – 83 merwinite multilayered rim grown between monticellite single crystals and wollastonite matrix 84 (Joachim et al., 2012). This reorganization of the rim microstructure can only be explained by a 85 change in the relative cation mobilities (Abart et al., 2012). Indeed, isotopic profiles confirmed 86 that the introduction of small amounts of water to the system increases the relative CaO/MgO 87 mobility ratio (Joachim et al., 2019). Thus, the relation between rim microstructures and relative 88 component mobility implies that rim microstructures may provide vital information about any 89 physico-chemical parameters that modify the relative mobilities of chemical components.

90 Grain boundaries may be considered as two-dimensional defects in the crystal structure that 91 have a high potential to host incompatible elements (Hiraga et al., 2004). It is reasonable to 92 assume that diffusion is faster along grain boundaries than through the volume of adjacent 93 crystals (Joesten, 1991). Examples of grain boundary diffusion-controlled rim growth is the presence of wollastonite reaction rims on chert nodules (Joesten and Fisher, 1988), and the 94 growth of the double forsterite and enstatite layers grown in between periclase and quartz 95 96 crystals (Gardés and Heinrich, 2011). Investigation of the role of water on grain boundary characteristics may therefore provide valuable information regarding reaction rim growth. The 97 98 effect of water on intergranular diffusivity can be categorized in at least four regimes, summarized as: (1) 'water-absent': the intergranular medium is lacking any hydrous 99 100 components. (2) 'water-undersaturated': a hydrous phase is incorporated in the crystal 101 structure or adsorbed to the grain boundary. (3) 'hydrous-saturated grain boundaries'; this regime is the first occurring at water-saturated conditions. (4) 'interconnected fluid-filled 102 103 porosity': the grain boundaries and pores are saturated with a hydrous species, creating an 104 interconnected network within the granular aggregate (Farver and Yund, 1995; Carlson, 2010; 105 Gardés et al., 2012). To the best of our knowledge, the classification above is solely ascribed to 106 the H_2O content and no other volatile components were to date considered.

107 Although extensive research has been done to elucidate the effects of H₂O and CO₂ on phase 108 relations and component mobilities (e.g. Sterner and Pitzer, 1994; Hirth and Kohlstedt, 1996), 109 much less is known about the role of other volatile compounds in the Earth's interior. In natural 110 systems, fluids present during metamorphic and metasomatic reactions may include several 111 other volatile components such as C, N, S, or halogens. Phase equilibrium experiments

112	demonstrate particularly the significance of fluorine for the stability field of fluorine-bearing
113	minerals, where their stability is exceeded beyond the stability field of their OH-counterparts
114	(Stalder and Ulmer. 2001; Giehl et al., 2014; Grutzner et al., 2017). Additionally, experiments in
115	the MgO-SiO ₂ -H ₂ O+F system showed that the fluorine salinity changes the stable humite group
116	minerals (HGMs) assemblage (Hughes and Pawley, 2019). These results demonstrate that
117	volatiles may not only affect component mobilities but can also change phase stabilities and
118	therefore the phase assemblage of a metamorphic rock.

119 In this study, we will investigate the effect of fluorine on the growth dynamics and 120 microstructure of a multi-layered reaction rim in the ternary CMS system and evaluate if 121 reaction rims can be used as a tool to quantify the fluorine content of metamorphic fluids.

122

Methodology

123 Starting materials

Reaction rims were grown between grains and cylindrical plates of quartz and wollastonite crystals and periclase matrix with the addition of 0-10 wt% fluorine using three different setups (Fig. 1). As starting materials, we used pure synthetic MgF₂ and MgO powders that were mixed thoroughly to produce a matrix with the desired fluorine fractions, natural quartz, and natural wollastonite stemming from Cziklewa near Orawitza (Banat, Romania) that was supplied by the Natural History Museum Vienna.

130 Capsule assembly

For assembly "a", clear quartz and wollastonite single crystals were crushed and individually handpicked in a grain size fraction of 500-1,000 μ m, rinsed with acetone and water and dried at

133 120°C for an hour. The starting material was placed in a platinum capsule (inner diameter 2.8 134 mm, outer diameter 3.0 mm, length 1 cm) in alternating quartz and wollastonite layers 135 surrounded by the powdered matrix (Fig. 1a). For assembly "b", cylindrical plates (2 mm in diameter and 500 to 1000 µm thick) were drilled from the quartz crystals parallel to the c-axis 136 137 and polished on both sides to create flat contact surfaces with the matrix (Fig. 1b). Unoriented wollastonite cylinders were prepared in a similar way for both, assembly "b" and "c". Assembly 138 "c" contained a combination of crushed wollastonite crystals and polished wollastonite cylinders 139 140 embedded in the powdered matrix (Fig. 1c). After loading, all capsules were dried in a 141 conventional oven at 400°C for 30 min and welded shut subsequently with a plasma welder to minimize adsorbed surface water. A detailed overview of the experimental conditions and bulk 142 143 fluorine concentrations is given in Table 1 and the composition of guartz and wollastonite 144 starting material is shown in Table 2.

145 **Piston cylinder experiments**

146 All experiments were carried out using a conventional end-load piston-cylinder apparatus. The Pt-capsule was surrounded by MgO powder and a talc-pyrex assembly served as pressure 147 148 medium. Run conditions for all experiments were 1000 °C and 1.5 GPa (Fig. 2). An S-type 149 thermocouple was used to monitor the temperature. The target temperature was reached with 150 a heating ramp of 30 K/min. All experiments were quenched after 20 minutes by cutting of the 151 power. After the run, the platinum capsule was retrieved and embedded in epoxy. Setup "a" 152 capsules were polished until grains with a diameter between 500-1,000 μ m were exposed to the surface. Setup "b" and "c" capsules were polished perpendicular to the flat surface of the 153 154 cylindrical plates until the centre of the respective cylinders were reached. Polished samples

155 were cleaned with ethanol and coated with a conductive carbon film prior to SEM and 156 microprobe analysis.

157 Analytical techniques

158 SEM & EMPA analyses. BSE images were obtained with a JEOL JSM-6010LV scanning electron 159 microscope. The rim thicknesses were determined by averaging 10 equally spaced 160 measurements over a total distance of at least 100 µm at places where the respective rim was 161 thinnest (Table 1). A JEOL JXA8100 electron probe equipped with 5 wave-length dispersive 162 spectrometers was used to determine phase compositions. Mineral phases in the reaction rims were analysed at 15 kV and 10 nA; starting materials were analysed at 15 kV and 50 nA. Well-163 164 known standards were used for EMPA calibration. Compositions are given in table 2 and 165 represent the average of at least five individual analyses per phase.

166 Raman spectroscopy. Raman spectroscopic analyses were performed at ambient conditions using a HORIBA JOBIN-YVON LabRam-HR800 spectrometer with a focal length of 800 mm to 167 168 identify the phases in the palisade microstructure at the wollastonite interface (Fig 3e-h) and to 169 distinguish HGMs in the outer layer of the reaction rim. All Raman spectra were obtained by 170 averaging 2 spectra acquired for a counting time of 40 sec. The analyzed areas were excited 171 using a green Nd-YAG laser with an excitation wavelength of 532.18 nm. Scattered light was 172 dispersed by an optical grating with 1800 grooves/mm resulting in a spectral resolution of 1.83 cm⁻¹, and collected with a cooled Andor[™] CCD collector. An Olympus 50x objective, a 173 174 confocal pinhole of 1000 μ m and a slit of 100 μ m was used to maximize the intensity at a lateral resolution of $\sim 5 \,\mu m^2$. Before the analyses, the spectral position of the Raman mode of a Si 175 176 standard wafer was measured against the position of the Rayleigh line, resulting in the expected

Raman shift of 520.7 cm⁻¹. Spectra were obtained in multi-window acquisition mode provided
by the *LABSPEC* (version 5.93.20) software package in the frequency range of 200-1200 cm⁻¹.
Background subtraction and the determination of band position were performed with the same
software.

181

Results

All experiments containing both, quartz and wollastonite grains or cylinders as starting materials, developed diopside layers at the original periclase-quartz interfaces. With wollastonite being the only Ca-source, this implies that the periclase-quartz interface is affected by presence of wollastonite in the sample. Consequently, separation of quartz and wollastonite grains would be required to investigate rim growth in the binary MgO-SiO₂ system. Therefore, we will focus in this study on the ternary CMS system

188 A series of 8 piston cylinder experiments containing up to 10 wt% fluorine at 1000°C and 1.5 189 GPa with a run duration of 20 minutes produced reaction rims with widths ranging between 190 11.8(21) and 105.6(22) μ m (Fig. 3 & 4). Rim thicknesses were measured at localities where the 191 total rim thickness was thinnest for geometrical reasons and isolated rim sections with clearly 192 visible irregularities were excluded from the dataset. The occurrence of larger cracks is likely related to differential dilation during cooling and depressurization (Fig. 3) (Gardés et al., 2012). 193 194 Smaller, micrometer sized voids are often present as dark patches at the phase boundaries in 195 the reaction rims (e.g. Fig. 3b, h). Phase assemblages and reaction rim widths are summarized in 196 Table 1, and detailed analyses of phase compositions are given in Table 2. Ternary diagrams 197 show the phase assemblage identified in rim sequences produced with 0, 0.1, 1.0, and 3.0-10 198 wt% F (Fig. 5).

In the fluorine-free system, a rim sequence of Wo | Mer | Di | Fo | Per is formed at the original
wo-per interfaces complying with phase stabilities at water saturated conditions (Fig. 3a; see
figure caption for mineral abbreviations). The reaction rim consists of two monomineralic layers
of forsterite and diopside with occasional lenses of merwinite.

203 The addition of 0.1 wt% fluorine to the matrix produced a rim sequence of Wo | Mer | Mtc | 204 HGMs + Fo | Per where diopside is sporadically present at the wollastonite interface (Fig. 3b). At 205 0.5 and 0.7 wt% F (Fig. 3c-d) cuspidine appears at the wollastonite interface in relatively small 206 quantities, becoming more pronounced as the fluorine content increases. Raman spectroscopy 207 analyses shows the absence and reappearance of HGMs in the 0.5 and 0.7 wt% experiments 208 respectively (Fig. 6a, b). At 1 wt% F, a rim sequence of Wo | Csp + Di + Ak | Mtc | HGMs + Fo | 209 Per is observed (Fig. 3e). The 1 wt% F experiment is the only experiment, in which akermanite is 210 observed and also marks the disappearance of merwinite from the layer sequence. In experiments with ≥ 1 wt% F, palisades of diopside and cuspidine are consistently present over 211 212 the entire rim (Fig. 3f-g & Fig. 6c). In experiments with \geq 3 wt% F, a layer sequence of Wo | Csp + 213 Di | HGMs | Per is produced. Forsterite disappeared from the rim sequence where HGMs are 214 the only phase present in the outer rim (Fig. 6d). The Di + Csp layer start to become more 215 irregularly oriented away from the wollastonite interface and show a mosaic instead of 216 palisades toward the rim-periclase interface. (Fig. 3f-h). Furthermore, a segregation of the 217 diopside-cuspidine palisades away from the reaction front is displayed in these reaction rims, 218 where diopside tends to be more pronounced closer to the HGMs layer.

219

Discussion

220 Phase configurations

221 In the fluorine-free system, reaction-rims between periclase and wollastonite develop the phase 222 sequence Per | Fo | Di | Mer | Wo with merwinite being present as isolated lenses between the 223 diopside layer and the wollastonite starting material. This phase sequence is in agreement with 224 the stable phase configuration in the CMS system at 1000°C, 1.5 GPa and water saturated 225 conditions (Holland and Powell, 2011; Fig. 2, 3a, 5a). As soon as 0.1 wt% F is introduced into the 226 CMS system, we observe a change in the layer sequence with the appearance of monticellite 227 and HGMs (Fig. 3b, 5b). Presence of HGMs may be explained by the fact that the stability field of 228 F-clinohumite extends to higher temperatures compared to its OH-counterpart (Stalder and 229 Ulmer, 2001; Grützner et al., 2017; Woodland et al., 2018), which may imply that the Gibbs Free 230 energy of F-clinohumite is lower compared to OH-clinohumite at identical P-T conditions. 231 However, this explanation does not hold for the presence of monticellite, which is a nominally 232 water and fluorine free mineral, indicating that the absolute Gibbs free energy of monticellite 233 should remain largely unaffected by the introduction of fluorine into the system. Nevertheless, 234 the addition of fluorine to the system may affect the Gibbs free energy difference of 235 monticellite relative to the fluorine bearing phases. This may result in stabilization and 236 consequently appearance of monticellite in the layer sequence.

Samples with 0.5 wt% bulk fluorine content mark the first appearance of cuspidine (Fig. 3c, 5c) while HGMs are absent (Fig. 6a). Similar to the appearance of HGMs in the experiment with 0.1 wt% F, the absolute Gibbs free energy of F-cuspidine is likely to be lowered with increasing fluorine content resulting in the appearance of this phase. Subsequently, the disappearance of HGMs between 0.1 and 0.5 wt% F may be caused by a change in relative Gibbs free energies of the potential fluorine bearing phases. Another explanation is that cuspidine as a major fluorine

sink leaves insufficient fluorine for HGMs to be formed. Both explanations would be in line with
the reappearance of HGMs at 0.7 wt% F (Fig. 3d, 5d, 6b).

245 A further increase in the fluorine content leads to the disappearance of merwinite at 1 wt% F, 246 followed by monticellite and akermanite at ≥ 3 wt% F (Fig. 3e-h, 5e-f). Simultaneously, the 247 amount of fluorine incorporated in cuspidine increases from 4.74(35) wt% F to 9.29(57) wt% F 248 with increasing bulk fluorine concentration (0.5 to 10 wt% F, Table 2). Again, it seems plausible 249 that the Gibbs free energies of the (F, OH) bearing phases decrease with increasing fluorine 250 content, whereas the absolute Gibbs free energies of nominally anhydrous minerals such as 251 merwinite, åkermanite, and monticellite, remain largely unaffected by the addition of fluorine. 252 Consequently, the decrease in the absolute Gibbs free energy of cuspidine and HGMs can only 253 affect the relative Gibb's Free energies of merwinite, åkermanite and monticellite with respect to cuspidine and HGMs. This provides an explanation for the stepwise disappearance of 254 255 merwinite at 1 wt% F and åkermanite and monticellite at 3 wt% F.

256 Microstructural changes

Nucleation of phases that plot on the tielines, which directly connect the starting materials wollastonite and periclase (monticellite and åkermanite; Fig. 5c), may be explained by the mobility solely of MgO or the combined mobility of CaO and SiO₂. In this study, a reaction rim consisting of monomineralic layers with the sequence Wo | Mer | Di | Fo | Per develops in the fluorine free system (Fig. 3a). Phases in this sequence deviate from the tieline that directly connects the starting materials periclase and wollastonite, which implies that additional component mobility must take place.

264 Several studies investigating rim growth dynamics in the binary MgO-SiO₂ and ternary MgO-265 CaO-SiO₂ system showed that it is the mobility of MgO that controls overall rim growth, while 266 SiO_2 remains largely immobile at low water contents (Milke et al., 2009; Gardés et al., 2012; 267 Joachim et al., 2012; Joachim et al., 2019). Experiments in this study were performed using 268 dried starting materials, so that we may safely assume that at least in the fluorine-free system 269 the mobility of MgO that controls overall rim growth. Deviation from the direct tieline 270 connection between periclase and wollastonite requires additional mobility of at least one 271 component. Consequently, with SiO_2 being most likely immobile, mobility of CaO is required to 272 explain the phase sequence in the fluorine-free system. The mobility of CaO alone cannot 273 contribute to overall rim growth as this would require additional mobility of SiO_2 (Fig. 5a) but 274 can explain the observed phase sequence. The reaction of wollastonite to merwinite at the Wo 275 | Mer interface in experiments with 0 and 0.1 wt% F can be written as:

276
$$2\text{CaSiO}_3 + \text{MgO}_m + \text{CaO}_m \rightarrow \text{Ca}_3\text{MgSi}_2\text{O}_8$$
 (1)

where "m" denotes a mobile component. The first appearance of cuspidine together with merwinite in the experiment with 0.5 wt% F requires additional fluorine mobility over the reaction rim, leading to the reaction:

$$4\text{CaSiO}_3 + \text{MgF}_{2,m} + 3\text{CaO}_m \rightarrow \text{Ca}_4\text{Si}_2\text{O}_7(\text{F})_2 + \text{Ca}_3\text{MgSi}_2\text{O}_8$$
(2)

In the sample that contains a bulk fluorine content of 0.7 wt% (Fig. 3d), a bimineralic cuspidine + diopside layer develops at the rim-wollastonite interface. At bulk fluorine concentrations of 1-3 wt%, this layer exhibits a palisade microstructure of alternating diopside and cuspidine lamellae that are oriented perpendicular to the reaction front (Fig. 3e-h). The reaction of wollastonite to

285 cuspidine + diopside requires the mobility of MgO and MgF₂ while the other components must 286 remain relatively immobile. Otherwise, monomineralic layers of cuspidine and diopside would 287 be formed instead of lamellae (Abart et al., 2012; Joachim et al., 2012). This is another 288 argument supporting the assumption that MgO is the mobile component and thus controls 289 overall rim growth; CaO and SiO₂ remain largely immobile relative to MgO because a combined 290 mobility of CaO + SiO_2 would result in a microstructure exhibiting monomineralic layers as 291 microstructure. The palisade growth of cuspidine and diopside at the rim-wollastonite interface 292 can therefore be explained according to:

293
$$6CaSiO_3 + MgO_m + MgF_{2m} \rightarrow Ca_4Si_2O_7(F)_2 + 2CaMgSi_2O_6$$
 (3)

with additional CaO mobility being required at the rim/reactant interface This demonstrates that overall rim growth in the fluorine rich systems of this study can be explained by long range diffusion of only MgO and MgF₂ across the reaction rim.

297 In experiments with ≥ 3 wt% F, BSE images show a segregation of the diopside-cuspidine 298 palisades toward the rim centre, where diopside tends to be more pronounced closer to the 299 HGMs layer and cuspidine is more pronounced at the wollastonite | rim interface (Fig. 3f-h). 300 Although it has been demonstrated that overall rim growth can be explained by MgO and MgF_2 301 mobility alone, segregation of diopside and cuspidine parallel to the reaction front requires 302 additional CaO mobility. A similar observation was made by Joachim et al. (2012) who showed 303 that the formation of a segregated multilayer type microstructure of merwinite and diopside 304 can be explained by increasing diffusivity of either CaO or SiO_2 , or both, relative to MgO. We 305 adopt this model to explain the cuspidine-diopside segregation observed in this study. Cuspidine

is consumed in the outer part of the rim closer to the HGMs layer to form additional diopside

307 according to:

308
$$Ca_4Si_2O_7(F, OH)_2 + MgO_m \rightarrow CaMgSi_2O_6 + 2CaO_m + CaF_{2m}$$
 (4)

309 The released calcium and fluorine components may migrate toward the inner part of the rim,

310 where the complementary reaction explains the formation of cuspidine at the rim-wollastonite

311 interface:

312
$$CaMgSi_2O_6 + 2CaO_m + CaF_{2m} \rightarrow Ca_4Si_2O_7(F, OH)_2 + MgO_m$$
 (5)

313 Note that F⁻ may be partially substituted by OH⁻ that was introduced into the sample as 314 adsorbed surface water (e.g. Joachim et al., 2012).

315 Growth kinetics and mass transport

Several experimental studies showed that presence of water has a major effect on rim growth rates (Yund, 1997; Milke et al., 2001; Joachim et al., 2011; Gardés et al., 2012; Milke et al., 2013; Joachim et al., 2019). This implies that a potential influence of any variations in water abundance on the results of this study must be excluded before we can discuss the effect of any other parameter on rim growth kinetics and mass transport.

A major constraint is the use of a matrix in powder form, which introduces, even if it is predried, a significant amount of adsorbed water to the sample (Joachim et al., 2012). These findings are supported by Joachim et al. (2017), who demonstrate that the amount of adsorbed water introduced to a dry setup varies between 0.03 and 0.18 wt% H_2O , depending on the hygroscopicity of the used starting materials. The water adsorbed to the powder matrix alone is likely sufficient to reach the water saturated grain boundary regime (Milke et al., 2013).

Moreover, the growth rate of the forsterite layer in the fluorine free system is $10^{-13.45(10)}$ m²/s. 327 328 which is in agreement with reported forsterite growth rates in the binary MgO-SiO₂ system that show an average of $10^{-13.98(16)}$ m²/s at a water content ranging from 0.11 to 0.5 wt% H₂O (Gardés 329 330 et al., 2012). The largest uncertainty in the determination of reaction rates is introduced through estimation of the rim thicknesses. At very dry conditions (i.e. in regime 1), we would 331 332 expect rim growth rates that are orders of magnitude slower (Gardés et al. 2012). Even when 333 acknowledging that we compare rim growth experiments in different chemical systems here, 334 this provides another argument that the grain boundaries of all experiments performed in this 335 study were water saturated (regime 3, Gardés et al., 2012).

However, it seems that once grain boundaries are water-saturated, significantly higher amounts of water of approximately 0.5 wt% H₂O are required to further affect overall component mobilities and thereby rim growth rates (regime 4, Gardés et al. 2012). We may safely assume that the amount of adsorbed surface water introduced into the samples of this study was below this threshold, which allows us to ascribe the difference in overall rim thickness solely to the effect of fluorine. This also implies that the effect of fluorine on component mobilities in a water-undersaturated regime cannot be evaluated in the framework of this study.

Results in this study show a positive correlation between overall rim thickness and fluorine content at otherwise identical P-T-t-X conditions (Fig. 4), which indicates that the bulk rock fluorine abundance directly affects component mobilities and thus rim growth rates. This also suggests that all fluorine-bearing experiments can be assigned to transport regime 4 (Gardés et al., 2012). Additionally, the presence of micrometer sized voids at the interfaces of adjacent phases (Fig. 3b-h) in all fluorine-bearing experiments are potential signs of fluid transport

through a network of interconnected pores, which is anticipated for regime 4 kinetics. However,
the absence of 3D imaging of the pore system limits our ability to definitively prove this
hypothesis.

352 It is important to note that even the addition of 0.1 wt% F immediately affects the overall rim 353 growth rate. In contrast, Gardés et al. (2012), who investigated enstatite rim growth between 354 forsterite and quartz, showed that the addition of water does not affect overall rim growth rates 355 in regime 3, which extends to a bulk water content of 0.5 wt% H_2O . One possible explanation for 356 these contrasting observations is that presence of fluorine already affects the grain boundary 357 properties and thus overall component mobilities at a lower bulk fluid content compared to water. Lee et al. (1991) showed that the presence of a chlorine-bearing fluid decreases the 358 359 wetting angle in low porosity silica aggregates, which in turn increases the degree of fluid 360 connectivity. If we assume that this is also valid for fluorine, this implies that the wettability of a 361 fluorine-bearing fluid might be responsible for decreasing the wetting angle, which in turn 362 lowers the fluid threshold necessary to create an interconnected fluid network compared to that of a pure water system. Another explanation might be that the grain and phase boundary 363 364 properties of the monomineralic enstatite rims and the multilayered rim sequences observed in 365 this study are not comparable. Both arguments illustrate that either the volatile content or the 366 bulk chemical composition or both may affect the physicochemical characteristics of grain and 367 phase boundaries. Therefore, it seems that the classification of intergranular mass transport in a 368 simplified water bearing system is not viable in a more complex fluorine bearing system. To gain 369 more insight into this problem, there is a need for rim-growth experiments with the addition of 370 small, defined amounts of other volatile components.

371 The relative increase of the overall rim growth rate with increasing fluorine bulk concentration 372 is strongest at low fluorine concentrations (≤ 1 wt%) and decreases as the fluorine content 373 reaches higher values (≥3 wt%, Fig. 4). Several explanations exist for this observation. [1] At high 374 bulk concentrations, fluorine is partially incorporated in fluorine-bearing phases such as 375 cuspidine and HGM's, which decreases the relative fluorine availability at the grain boundaries. 376 [2] Rims at 1 wt% bulk F show a lamellar type microstructure (Fig. 3e) while rims at 10 wt% F 377 show a mosaic microstructure (Fig. 3h). This change in microstructure leads to a reduction in the 378 grain boundary density normal to the reaction interface and may, as a consequence, lead to 379 lower overall rim growth rates as suggested in previous studies (Joachim et al., 2011; Gardés et 380 al., 2011). [3] The increase in bulk fluorine content is accompanied by a change in the rim layer 381 sequence (Fig. 3; see details above), which may affect grain and phase boundary properties, and 382 subsequently the potential effectivity of transport pathway for components through the 383 reaction rim.

384

Implications

Results of this study imply that fluorine may affect phase stabilities, component mobilities and
 the development of rim microstructures in the ternary CMS system.

Presence of fluorine significantly affects the reaction rim layer sequences and is responsible for the appearance of both, fluorine bearing minerals such as cuspidine and HGMs, and nominally fluorine free minerals such as monticellite and åkermanite. These findings demonstrate the potential limitation of utilizing current thermodynamic datasets for phase equilibrium modelling in fluorine bearing systems.

392 Absolute and relative component mobilities play a key role in net-transfer reactions because the 393 former control the absolute rim thickness and the latter the layer sequence and microstructural 394 features of reaction rims. This study shows that the presence of fluorine enhances the overall 395 MgO mobility resulting in faster rim growth rates but also changes relative component 396 mobilities in the CMS system resulting in microstructural changes such as the phase segregation 397 of diopside and cuspidine at high fluorine concentrations. Consequently, results of this study 398 emphasize the importance of taking fluorine and potentially other volatile components into 399 consideration to accurately reconstruct the P-T-t history of metamorphic rocks. Further 400 constraining and quantifying the effect of fluorine on phase stabilities and rim microstructures give natural reaction rims the potential to be used as a tool to estimate the fluorine content 401 402 during their formation.

403 In a broader context, this implies that many features of natural reaction rims, such as the overall 404 rim thickness, the layer sequence, the relative layer thicknesses and the internal microstructure 405 contain valuable information about the respective rim forming conditions, which include not only the P-T-t history of a metamorphic rock but in particular the fluid-composition in fluid-406 407 mediated metasomatic reactions. Consequently, results of this study show that natural reaction 408 rims have the potential to serve as "geofluidometers", which would be of great importance for 409 samples that have lost all direct clues such as fluid inclusions that usually allow us to unravel the 410 chemical composition of metasomatic fluids.

411

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- 415 (FWF) project P 31787. For the purpose of open access, the author has applied a CC BY public
- 416 copyright license to any Author Accepted Manuscript version arising from this submission.
- 417 References Abart, R., & Petrishcheva, E. (2011). Thermodynamic model for reaction rim growth: Interface 418 419 reaction and diffusion control. American Journal of Science, 311, 517–527. 420 Abart, R., Kunze, K., Milke, R., Sperb, R., & Heinrich, W. (2004). Silicon and oxygen self-diffusion 421 in enstatite polycrystals: The Milke et al. (2001) rim growth experiments revisited. 422 Contributions to Mineralogy and Petrology, 147, 633–646. 423 Abart, R., Petrishcheva, E., & Joachim, B. (2012). Thermodynamic model for growth of reaction 424 rims with lamellar microstructure. American Mineralogist, 97, 231–240. 425 Carlson, W. D. (2010). Dependence of reaction kinetics on H2O activity as inferred from rates of 426 intergranular diffusion of aluminium. Journal of Metamorphic Geology, 28, 735–752. Farver, J. R., & Yund, R. A. (1995). Grain boundary diffusion of oxygen, potassium and calcium in 427 428 natural and hot-pressed feldspar aggregates. Contributions to Mineralogy and Petrology, 429 118, 340-355. 430 Fisler, D. K., Mackwell, S. J., & Petsch, S. (1997). Grain boundary diffusion in enstatite. Physics and Chemistry of Minerals, 24, 264–273. 431 432 Gardés, E., & Heinrich, W. (2011). Growth of multilayered polycrystalline reaction rims in the 433 MgO-SiO2 system, part II: modelling. Contributions to Mineralogy and Petrology, 162, 37– 434 49. Gardés, E., Wunder, B., Wirth, R., & Heinrich, W. (2011). Growth of multilayered polycrystalline 435 reaction rims in the MgO-SiO2 system, part I: Experiments. Contributions to Mineralogy 436 437 and Petrology, 161, 1–12. 438 Gardés, E., Wunder, B., Marquardt, K., & Heinrich, W. (2012). The effect of water on 439 intergranular mass transport: New insights from diffusion-controlled reaction rims in the MgO-SiO 2 system. Contributions to Mineralogy and Petrology, 164, 1–16. 440 441 Giehl, C., Marks, M. A. W., & Nowak, M. (2014). An experimental study on the influence of 442 fluorine and chlorine on phase relations in peralkaline phonolitic melts. Contributions to
- 443 Mineralogy and Petrology, 167, 1–21.

- Götze, L. C., Abart, R., Rybacki, E., Keller, L. M., Petrishcheva, E., & Dresen, G. (2010). Reaction
 rim growth in the system MgO-Al2O3-SiO2 under uniaxial stress. Mineralogy and Petrology,
 99, 263–277.
- Grützner, T., Klemme, S., Rohrbach, A., Gervasoni, F., & Berndt, J. (2017). The role of Fclinohumite in volatile recycling processes in subduction zones. Geology, 45, 443–446.
- Hiraga, T., Andeson, I. M., & Kohlstedt, D. L. (2004). Grain boundaries as reservoirs of
 incompatible elements in the Earth's mantle. Nature, 427, 699–703.
- Hirth, G., & Kohlstedt, D. L. (1996). Water in the oceanic upper mantle: Implications for
 rheology, melt extraction and the evolution of the lithosphere. Earth and Planetary Science
 Letters, 144, 93–108.
- Holland, T. J. B., & Powell, R. (2011). An improved and extended internally consistent
 thermodynamic dataset for phases of petrological interest, involving a new equation of
 state for solids. Journal of Metamorphic Geology, 29, 333–383.

Hughes, L., & Pawley, A. (2019). Fluorine partitioning between humite-group minerals and
aqueous fluids: implications for volatile storage in the upper mantle. Contributions to
Mineralogy and Petrology, 174, 1–18.

Joachim, B., Gardés, E., Abart, R., & Heinrich, W. (2011). Experimental growth of åkermanite
reaction rims between wollastonite and monticellite: Evidence for volume diffusion
control. Contributions to Mineralogy and Petrology, 161, 389–399.

Joachim, B., Gardés, E., Velickov, B., Abart, R., & Heinrich, W. (2012). Experimental growth of
diopside + merwinite reaction rims: The effect of water on microstructure development.
American Mineralogist, 97, 220–230.

Joachim B, Stechern A, Ludwig T, Konzett J, Pawley A, Ruzié-Hamilton L (2017). Effect of water
on the fluorine and chlorine partitioning behavior between olivine and silicate melt.
Contributions to Mineralogy and Petrology. 172, 15.

Joachim, B., Heinrich, W., Höschen, C., & Abart, R. (2019). The effect of H2O fluid on relative
component mobilities in a bimineralic reaction rim in the system CaO–MgO–SiO2. European
Journal of Mineralogy, 31, 61–72.

Joesten, R. (1991). Grain-Boundary Diffusion Kinetics in Silicate and Oxide Minerals. In: Ganguly
J. (eds) diffusion, Atomic Ordering, and Mass Transport. Advances in Physical
Geochemistry, vol 8. Springer, New York, NY.

<sup>Joesten, R. (1977). Evolution of mineral assemblage zoning in diffusion metasomatism.
Geochimica et Cosmochimica Acta, 41, 649–670.</sup>

- Joesten, R., & Fisher, G. (1988). Kinetics of diffusion-controlled mineral growth in the Christmas
 Mountains (Texas) contact aureole. Bulletin of the Geological Society of America, 100, 714–
 732.
- Keller, L. M., Götze, L. C., Rybacki, E., Dresen, G., & Abart, R. (2010). Enhancement of solid-state
 reaction rates by non-hydrostatic stress effects on polycrystalline diffusion kinetics.
 American Mineralogist, 95, 1399–1407.
- Lee V.W., Mackwell S.J. & Brantley S.L. The effect of fluid chemistry on wetting textures in
 novaculite (1991). Journal of Geophysical Research, 96, 23–37.

Milke, R., Wiedenbeck, M., & Heinrich, W. (2001). Grain boundary diffusion of Si, Mg, and O in
enstatite reaction rims: A SIMS study using isotopically doped reactants. Contributions to
Mineralogy and Petrology, 142, 15–26.

488 Milke R, Heinrich, W. (2002). Diffusion-controlled growth of wollastonite rims between quartz
489 and calcite: comparison between nature and experiment. Journal of Metamorphic Geology,
490 20, 367-480.

Milke, R., Dohmen, R., Becker, H. W., & Wirth, R. (2007). Growth kinetics of enstatite reaction
rims studied on nano-scale, Part I: Methodology, microscopic observations and the role of
water. Contributions to Mineralogy and Petrology, 154, 519–533.

- Milke, R., Abart, R., Kunze, K., Koch-Müller, M., Schmid, D., & Ulmer, P. (2009). Matrix rheology
 effects on reaction rim growth I: Evidence from orthopyroxene rim growth experiments.
 Journal of Metamorphic Geology, 27, 71–82.
- Milke, R., Neusser, G., Kolzer, K., & Wunder, B. (2013). Very little water is necessary to make a
 dry solid silicate system wet. Geology, 41, 247–250.
- 499 Nagayoshi, M., Kubo, T., & Kato, T. (2016). Experimental investigation of the kinetics of the
 500 spinel-to-garnet transformation in peridotite: A preliminary study. American Mineralogist,
 501 101, 2020–2028.
- Nishi, M., Nishihara, Y., & Irifune, T. (2013). Growth kinetics of MgSiO3 perovskite reaction rim
 between stishovite and periclase up to 50 GPa and its implication for grain boundary
 diffusivity in the lower mantle. Earth and Planetary Science Letters, 377–378, 191–198.
- Remmert, P., Heinrich, W., Wunder, B., Morales, L., Wirth, R., Rhede, D., & Abart, R. (2018).
 Synthesis of monticellite–forsterite and merwinite–forsterite symplectites in the CaO–
 MgO–SiO2 model system: influence of temperature and water content on microstructure
 evolution. Contributions to Mineralogy and Petrology, 173, 1–17.
- Rossi, R.C., Fulrath, R.M. (1963). Epitaxial growth of spinel by the reaction in solid state. Journal
 of the American Ceramic Society, 46, 145-149.

- 511 Stalder, R., & Ulmer, P. (2001). Phase relations of a serpentine composition between 5 and 14 512 GPa: Significance of clinohumite and phase E as water carriers into the transition zone.
- 513 Contributions to Mineralogy and Petrology, 140, 670–679.
- 514 Sterner, S. M., & Pitzer, K. S. (1994). An equation of state for carbon dioxide valid from zero to 515 extreme pressures. Contributions to Mineralogy and Petrology, 117, 362–374.
- 516 Watson, E.B., Price, J.D. (2002). Kinetics of the reaction MgO-Al₂O₃ = 3MgAl₂O₄ and Al-Mg
- 517 interdiffusion in spinel at 1200-2000°C and 1.0 to 4.0 GPa. Geochimica et Cosmochimica 518 Acta, 66, 2123-2138.
- 519 Whitney, W. P., & Stubican, V. S. (1971). Interdiffusion studies in the system MgOAl2O3. Journal
- of Physics and Chemistry of Solids, 32, 305–312.
- 521 Woodland, A. B., Bulatov, V. K., Brey, G. P., Girnis, A. V., Höfer, H. E., & Gerdes, A. (2018).
- 522 Subduction factory in an ampoule: Experiments on sediment–peridotite interaction under
- 523 temperature gradient conditions. Geochimica et Cosmochimica Acta, 223, 319–349.
- Yund, R. A. (1997). Rates of grain boundary diffusion through enstatite and forsterite reaction
 rims. Contributions to Mineralogy and Petrology, 126, 224–236.

526 Table 1. Overview of the experimental conditions, assembly type, fluorine content, rim

527 sequence and average rim thickness. All experiments were performed at 1.5 GPa and 1000°C.

528 Uncertainties are given in terms of 1σ .

	No. of	Assembly	Fluorine	Rim sequence	Total rim thickness
	Experiment	type	content [wt%]		$\Delta x \ [\mu m]$
	1.8	а	0	Wo Mer Di Fo Per	11.8(21)
	1.9	а	10	Wo Di+Csp HGMs Per	105.6(22)
	2.1	b	1	Wo Di+Csp+Ak Mtc HGMs+Fo Per	61.6(21)
	2.2	а	0.1	Wo Mer+Di Mtc HGMs+Fo Per	16.1(16)
	2.3	а	5.0	Wo Di+Csp HGMs Per	77.0(34)
	2.6	с	0.5	Wo Mer+Csp Di Mtc Fo Per	30.0(25)
	2.9	с	0.7	Wo Csp Di+Mer Mtc HGMs+Fo Per	35.2(20)
	2.10	с	3.0	Wo Di+Csp HGMs Per	59.1(13)
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Table 2. Composition of starting materials and phases identified in each rim sequence. Values
 represent averages based on at least 5 EMP point analyses. Standard deviations are given in

549	terms of 1σ	$b_{1}d_{2} = below$	detection	limit)
545		D.u. – Delow	uelection	mmuj.

Sample	CaO (wt%)	MgO (wt%)	SiO ₂ (wt%)	F (wt%)	Total (wt%)
Forsterite/HGMs					
1.8	0.29(14)	58.2(14)	42.13(82)	b.d.	100.7(21)
2.2	0.79(42)	58.27(34)	38.5(10)	1.24(42)	98.77(69)
2.6	0.35(3)	58.28(28)	41.40(97)	0.13(0)	100.17(89)
2.9	0.88(15)	59.22(82)	38.9(13)	1.69(57)	100.7(12)
2.1	1.12(6)	59.8(12)	40.0(22)	1.85(54)	102.7(27)
2.10	1.2(10)	58.9(23)	29.2(30)	9.8(24)	99.19(83)
2.3	0.86(29)	58.95(31)	29.5(35)	11.0(32)	100.33(72)
1.9	1.03(15)	58.35(36)	34.22(68)	4.98(14)	98.59(93)
Monticellite					
2.2	35.2(11)	26.81(76)	37.73(24)	0.11(3)	99.84(74)
2.6	35.05(62)	26.28(63)	37.62(42)	0.09(5)	99.04(30)
2.9	35.21(21)	25.49(47)	37.86(57)	0.12(3)	99.68(98)
2.1	34.67(43)	26.51(58)	37.4(11)	0.16(3)	98.8(10)
Diopside					
1.8	26.21(13)	18.31(28)	54.62(55)	0.04(2)	99.17(67)
2.2	26.76(17)	18.38(9)	55.74(42)	0.04(4)	100.92(13)
2.6	26.50(7)	18.41(45)	54.87(40)	0.03(3)	99.82(82)
2.9	27.01(98)	18.49(46)	55.1(16)	0.06(2)	100.6(10)
2.1	26.49(26)	18.58(19)	52.96(39)	0.07(2)	98.09(30)
2.10	26.03(7)	18.63(24)	54.05(60)	0.12(2)	98.84(35)
2.3	26.17(13)	18.90(12)	55.31(43)	0.19(5)	100.57(52)
1.9	26.32(39)	18.74(34)	54.1(19)	0.17(16)	99.3(17)
Åkermanite					
2.1	41.36(21)	14.53(14)	43.58(92)	0.07(4)	99.5(12)
Merwinite					
2.2	51.86(9)	12.33(9)	36.39(23)	0.11(5)	100.69(19)
2.6	49.6(22)	14.0(18)	34.75(87	0.42(37)	98.80(96)
2.9	51.51(61)	12.60(15)	36.69(64)	0.03(2)	100.8(11)
Cuspidine					
2.6	58.67(68)	1.43(5)	31.34(27)	4.74(35)	96.16(65)
2.9	60.3(10)	1.4(12)	32.78(26)	7.4(11)	101.9(11)
2.1	58.0(12)	1.96(33)	31.0(16)	8.46(17)	99.42(82)
2.10	54.1(25)	4.3(13)	34.6(15)	8.46(50)	101.46(65)
2.3	50.1(42)	6.5(20)	38.3(27)	7.2(12)	102.02(78)
1.9	57.7(16)	2.30(59)	32.15(93)	9.29(57)	101.44(58)
Wollastonite					
	47.92(17)	0.05(1)	51.09(51)	0.01(1)	99.07(50)
Quartz					

551 Figure captions

Figure 1: Schematic figure of the Pt-capsule assemblies used in this study. (a) Assembly containing four alternating layers of quartz and wollastonite grains embedded in a MgO + MgF₂ powder matrix. (b) Assembly consisting of quartz and wollastonite cylinders embedded in a MgO

 $+ MgF_2$ powder matrix. (c) Wollastonite fragments embedded in a MgO + MgF_2 powder matrix.

556 Figure 2: Pseudo section showing the stability field of phases within the CMS ternary system at

557 water saturated conditions, which was created using Perple X and the TC-DS620 version of the

Holland and Powell database (Holland and Powell, 2011). The red dot marks the experimental

conditions of this study at 1000 °C and 1.5 GPa.

Figure 3: Scanning electron microscope (SEM) images, backscatter electron (BSE) image of 560 reaction rims grown between wollastonite and MgO $(+ MgF_2)$ matrix ordered by increasing bulk 561 562 fluorine content with (a) 0, (b) 0.1, (c) 0.5, (d) 0.7, (e) 1.0, (f) 3.0, (g) 5.0, and (h) 10 wt% F. All experiments were performed at identical P-T-t conditions of 1000°C and 1.5 GPa for 20 mins. 563 Rim thicknesses were always determined at the thinnest position to minimize the sectioning 564 effect caused by a potential inclination between the grain and the matrix (Table 1). Images a and f 565 566 were chosen as exemplarily visualizations of the internal rim texture and do not represent the minimum rim thickness of this specific experiment. Wo = wollastonite, Csp = cuspidine, Di = 567 diopside, Ak = akermanite, Mer = merwinite, Mtc = monticellite, Fo = forsterite, HGMs = humite568 group minerals. 569

Figure 4: Plot of the overall rim thickness (μ m) vs. bulk fluorine content (wt%). The obtained values are an average of 10 equally spaced measurements over a region of at least 100 μ m perpendicular to the reaction front. The grain boundaries in all experiments are most likely water saturated due to the use of a powdered matrix as starting material that introduces adsorbed

- surface water into the capsule (Joachim et al. 2017). Standard deviations in terms of 1σ are
- denoted in the figure if they exceed the size of the symbol.
- 576 Figure 5: Ternary plots for experiments with a fluorine content of (a) 0, (b) 0.1, (c) 1, (d) 3-10
- 577 wt% F showing the phase assemblage of the rim sequences. The red lines depict phases which are
- 578 in contact with each other in the respective reaction rim.
- 579 Figure 6: Representative Raman spectra of experiments with a fluorine content of 0.5 (**a**), 0.7 (**b**),
- 580 1 (c), 10 (d) wt% F. Spectra a, b, and d were taken in the outer layer of the respective rim
- sequence close to the rim | matrix interface. Spectrum c was obtained from the diopside-cuspidine
- 582 palisades bordering the wollastonite interface.
- 583
- 584





Figure 3



Figure 4





figure 6

