1 Revision 1

2 Limited channelized fluid infiltration in the Torres del Paine contact

- 3 aureole
- 4

5 Guillaume Siron^{1,2}, Robert Bodner¹, Lukas Baumgartner¹, Benita Putlitz¹, Torsten
6 Vennemann³

7 ¹ University of Lausanne, Institute of Earth Sciences, CH1015 Lausanne, Switzerland

8 ² WiscSIMS, Department of Geosciences, University of Wisconsin-Madison, Madison, WI53706, USA

9 ³ University of Lausanne, Institute of Earth Surface Dynamics, CH1015 Lausanne, Switzerland

10 Current email address: siron@wisc.edu

- 11
- 12

ABSTRACT

The metamorphic rocks from the Torres del Paine contact aureole (Patagonia, Chile) show 13 14 field, petrographic, and geochemical evidences for small amounts of igneous fluid infiltration 15 due to the solidification of the granite complex. Hydrogen isotope ratios (D/H) in the contact 16 aureole first decrease while approaching the intrusion and subsequently increase toward the granite contact. Initial decrease with metamorphic grade is due to preferential loss of the ²H 17 18 isotopes due to Rayleigh fractionation during prograde dehydration reactions. The infiltration of high δD fluids from the intrusion increases δD within the last 150 m. In contrast, ($^{18}O/^{16}O$) 19 20 ratios show no systematic changes, indicating that neither oxygen loss by Rayleigh 21 fractionation, nor oxygen exchange by fluid infiltration was significant enough to dominate original variations seen in the oxygen isotope ratio of the protolith. Calculated volume of 22 fluid using the position of the hydrogen isotope exchange front gives a relatively low time 23 integrated fluid flux of about $4m^3/m^2$ at the contact for the igneous fluid. These small 24 25 amounts of fluid flux are in agreement with whole rock oxygen isotope data that are not

26 affected in the contact aureole. Chlorine content of metamorphic biotite crystals, in contrast 27 to oxygen isotopes, supports infiltration of igneous fluids. Indeed, relatively high Cl 28 concentrations in biotite were measured in some samples close to the intrusion (up to 0.2 29 wt%), while chlorine concentrations in biotite are constant everywhere else in the entire 30 contact aureole, having low concentrations (0.01-0.06 wt%). The absence of a well-marked 31 Rayleigh fractionation trend in Cl concentrations with increasing metamorphism is surprising, since chlorine strongly fractionates into the fluid. This is best explained by slow 32 33 diffusive exchange of chlorine in biotite in the cooler outer aureole. Hence recrystallization 34 of biotite would be required to modify its Cl composition. Biotite grains from samples close 35 to the intrusion with high Cl content also have lower Ti content (0.4 p.f.u.) than biotite (0.5 36 p.f.u.) from other samples containing biotite with lower Cl content located at the same 37 distance from the contact. Since Ti content in biotite is a function of temperature, this is a 38 good indication that magmatic fluid infiltration started post peak, early during cooling of the 39 metamorphic rocks. Episodes of fluid-flow seemed to be nearly continuous during cooling as 40 evidenced by numerous retrogression textures such as secondary muscovite (above 470 °C) 41 or chlorite + muscovite intergrowth after cordierite or biotite (slightly below 470 °C). This 42 might be related to crystallization of subsequent batches of granites, or the onset of minor fluid convection during cooling of the aureole. Nevertheless, only minor secondary 43 44 muscovite has been found and fresh cordierite is present throughout the aureole confirming 45 small amounts of fluid infiltration.

The time integrated fluid flux computed from the hydrogen isotope exchange front is two orders of magnitude lower than values computed for metacarbonate in many other contact aureoles, suggesting low permeability of pelitic rocks. In conclusion, Cl content and hydrogen isotope composition of hydrous minerals provide a sensitive tool to identify small fluid-rock interaction events, much more sensitive than oxygen isotope compositions of thewhole rock or minerals.

- 52
- 53

INTRODUCTION

54 Fluid-rock interaction is one the most important process on Earth. It plays an important role 55 in mass and heat transport during metamorphism (Ferry 1986, Baumgartner and Rumble 56 1988, Baumgartner and Valley 2001, Cui et al. 2001, Gerdes et al. 1998), influences the stable mineral assemblages (Ferry 1986, Baumgartner and Ferry 1991, Cartwright and Buick 57 58 1996, Ferry 2000) and can drive partial melting at temperatures close to the granite solidus 59 for metapelitic rocks (Goranson 1983, Tuttle and Bowen 1958, Luth et al. 1964, Holness and 60 Clemens 1999) or even lower temperatures in metacarbonates as demonstrated by recently 61 for example by Floess and Baumgartner, 2015.

62 Stable isotopes are one of the most common tool used to track fluid-rock interaction, 63 especially through the measurement of oxygen isotope compositions in metacarbonates and 64 marls (Labotka et al. 1988, Cook et al. 1997, Baumgartner et al. 1989, Holness 1997, Roselle et al. 1999), but they have been rarely used in metapelites. This is partly due to the smaller 65 66 differences in terms of oxygen isotopic compositions between metapelites and typical 67 igneous fluids. Oxygen isotopes require large amounts of fluids to register and change the large amount of oxygen contained in minerals, while hydrogen isotope compositions can 68 69 trace small amounts of water infiltration, as rocks contain much smaller amounts of hydrogen 70 (e.g., Baumgartner and Valley, 2001). The position of stable isotopes fronts has also been 71 used to compute the amount of fluid that infiltrated a rock using transport theory 72 (Baumgartner and Rumble 1988, Baumgartner and Valley 2001, Bickle and Naker 1990, 73 Bowman et al. 1994, Nabelek and Labotka 1993).

74 A more recent tracer for fluid-rock interaction is Cl content in hydrous phases. To this date, it 75 is mostly used in magmatic/hydrothermal systems and has not been extensively used in metamorphic petrology. The chlorine concentration in these minerals is directly linked to the 76 77 HCl° activity of the fluid and the Cl solubility in silicate melts (Zhu and Sverjensky 1991, 1992, Icenhower and London 1997, Webster et al. 2015). For example, chlorine 78 79 concentrations have been used to track fluid infiltration in high grade terrains using biotite Cl-contents (Higashino et al. 2013). During crystallization of magmas, chlorine becomes 80 81 progressively enriched in the melt due to its incompatibility in most minerals (Speer 1984; 82 Candela 1986, 1997). Thus, a fluid expelled during the very late stage evolution is generally 83 enriched in chlorine. Interpreting its concentration in biotite, a major igneous or metamorphic 84 mineral, is further controlled by crystallographic constraints, either due to Fe-Mg octahedral 85 composition, i.e. known as the Mg-Cl avoidance rule (Munoz 1984), or the tetrahedral Al 86 composition (Henry and Daigle 2018). Finally, Cl content in biotite seems to be very 87 refractive and slow to exchange between biotite and fluid at medium temperatures, as 88 highlighted recently (Siron et al. 2018a).

Here we use the Torres del Paine contact aureole (Patagonia) to compare the usefulness and sensitivity of these three different proxies to study fluid-rock interactions in metapelitic dominated contact aureoles. The Torres del Paine intrusive complex is one of the best natural laboratories to study fluid flow due to its 3D outcrop exposures (Baumgartner et al. 2007), precise geochronology and geochemical constraints on its magmatic history (Michel et al. 2008, Leuthold et al. 2012, Leuthold et al. 2013).

- 95
- 96

GEOLOGICAL SETTING

97 The Torres del Paine intrusive complex (TPIC) is located in the southernmost Andes in
98 Patagonia (Chile). It consists of three major granite laccoliths, a mafic stock and a composite

99 mafic laccolith. They intruded the Cretaceous turbidites between 12.60 and 12.43 Ma (Michel 100 et al. 2008; Leuthold et al. 2012). The intrusion is elongated in West-East direction with a total length of about 12 km and a North-South extension of roughly 8 km (Fig. 1a). The 101 102 major feeder zone of the TPIC is situated at the western end of the laccolith (Michel et al., 2008; Leuthold et al. 2013). A small, well defined contact aureole was formed in the 103 104 Cretaceous Punta Barrosa and Cerro Toro Formations. These formations are mainly 105 composed of pelites, psammites and sandstone, with minor thick (>10 m) conglomerate 106 layers in the Cerro Toro formation (Wilson 1991; Hubbard and Schultz 2008; Fildani 2005). 107 They also contain some minor carbonate layers with a thickness of a few centimeters to a few 108 decimeters. This Cretaceous sequence is a thick sequence of turbidites, shed from the west 109 into the foreland trench of the Andes (Fildani et al. 2007; Hubbard et al. 2008). The intrusion 110 was emplaced at ca. 750 bars (Putlitz et al. 2001); pressure estimates are based on the 111 stability of prehnite in metacarbonates, the presence of fayalite in miarolitc cavities for 112 temperature information, as well as fluid inclusion data. For this work, a total of 5 profiles 113 were sampled in the host rocks around the intrusion to reflect the different parts of the 114 intrusion exposed. All samples were collected within the dark grey to black, oxide and 115 graphite rich metapelites of the Cerro Toro Formation. Two profiles were collected above the 116 intrusion, two at the side and one below. The different profiles are located on the map in 117 Figure 1a (black stars). The profiles in the roof of the pluton were collected at the Cuerno 118 Principal (CPa, Fig. 1b) and another at the Cerro Fortaleza (F, Fig. 1c). The profile on Monte 119 Almirante Nieto comes from the side of the intrusion (A, Fig. 1d). Three more samples from 120 the Monte Almirante Nieto (Fig. 1d) were taken on a ridge which is located about 500 m to 121 the East than the rest of this profile (dotted line in Fig. 1d, A* in table A-1). They are treated together with the rest of the Mte. Almirante Nieto profile. The other profile located at the side 122

- 123 of the intrusion is from the Eastern ridge of the Co. Paine Principal, in Valle Frances (VF,
- 124 Fig. 1e). A profile below the intrusion is from the Cuerno Principal (CPb, Fig. 1b).
- 125
- 126
- 127

METHODS

128 Laser fluorination

The oxygen isotope composition of bulk rocks was determined using a CO₂ laser-fluorination 129 130 technique at the stable isotope laboratory of the University of Lausanne, using a method adapted after Lacroix and Vennemann (2015). Oxygen isotope ratios are given in the 131 132 standard δ -notation, expressed relative to VSMOW in permil (‰). Several aliquots of the in-133 house quartz standard (LS-1) were measured during each analytical session. Reproducibility 134 for the analyses of the LS1 quartz is typically better than 0.1‰ (1SD) for two or three 135 standards analyzed with each sequence of 12 samples.

136

137 Thermal conversion elemental analyzer (TC/EA)

Hydrogen isotope compositions were analyzed using a Thermal Conversion Elemental 138 139 Analyzer (TC/EA), coupled to a Finnigan Thermo Delta Plus XL; for details on the procedure 140 used in Lausanne see Bauer and Vennemann (2014). In-house standards (kaolinite K17 and 141 biotite G1) were analyzed repeatedly during the sessions for normalization. Reproducibility 142 for δD analyses of the standards is typically better than 2‰ (1SD).

143

Electron Microprobe Analysis (EMPA) 144

Major and minor element analyses of minerals were obtained with a JEOL 8200 Superprobe 145 146 equipped with 5 wavelength dispersive spectrometers. The concentration of the elements Si,

147 Al, Ti, Fe, Mg, Mn, K, Na, Ca, F and Cl were measured. The operating conditions were 15

148 kV, a beam current of 15 nA, with a spot size of 5 µm. Counting times were set for most 149 elements to 15 seconds for background before and after peak and 30 seconds on the peak. 150 Counting times were reduced for Na and K to 10 seconds on the background and 20 seconds 151 on the peak. Fluor-phlogopite (F), scapolite (Cl), albite (Na), wollastonite (Ca), orthoclase (Si, K), andalusite (Al), fayalite (Fe), forsterite (Mg) and MnTi oxide (Mn, Ti) were used as 152 153 reference standards. The data were reduced with the CITZAF matrix correction routine of 154 Armstrong (1989). Structural formulae for biotite and muscovite were normalized to 44 155 charges or 22 equivalent oxygens, 8 oxygens for feldspars and 18 oxygens for cordierite. All iron was assumed as Fe²⁺, no Fe³⁺ corrections were attempted. Cl detection limit for biotite 156 157 grains were about 40 ppm weight.

- 158
- 159
- 160

RESULTS

161 Petrography

The metapelites of the Cerro Toro Formation in the far field of the intrusion are characterized 162 163 by abundant clastic minerals. Minerals preserved are plagioclase, K-feldspar, quartz, biotite, 164 and muscovite intermingled with newly formed clay minerals, chlorite, kaolinite, and pyrite 165 crystallized during the Anchizone metamorphism (Süssenberger et al. 2017). The detrital grains originated from the erosion of the Patagonian Batholith and its metamorphic host 166 167 rocks. The sediments were deposited on the shelf and deltas on the eastern side of the Andean 168 orogeny and material was transported into the deep-sea trench by turbidites (Fildani et al. 169 2007; Hubbard et al. 2008). The outermost parts of the contact aureole are characterized by 170 formation of hydrated minerals from these clastic precursors.

171 The first well defined reaction is the breakdown of chlorite (Chl), reacting with muscovite

172 and quartz, to produce biotite (Bt) and cordierite (Crd). This evolution is typical for the low-

173 pressure chlorite dehydration reaction. Cordierite is poikiloblastic and usually contains biotite 174 and quartz inclusions. Biotite grain size is on the order of 10 µm; biotite crystals appear often in clusters and randomly distributed in the rocks. Metamorphic muscovite shows similar 175 176 textural characteristics. Any remaining muscovite breaks down at higher metamorphic grade, 177 reacting with biotite, to form K-feldspar (Kfs) and additional cordierite. Again, the 178 disappearance of muscovite together with appearance of K-feldspar and newly formed cordierite is typical for the very low-pressure dehydration reaction of muscovite. Despite the 179 180 aluminous character of these host rocks, no aluminosilicates have been found anywhere in the 181 aureole of the TPIC. Hence, the TPIC contact aureole is typical for a very low-pressure 182 environment corresponding to the 1a bathozone of Pattison and Tracy (1991). Here we will 183 refer to the muscovite + cordierite + biotite zone as the cordierite zone and the K-feldspar + 184 cordierite + biotite as the K-feldspar zone. The lower grade rocks that are still part of the 185 contact aureole are referred to the chlorite zone since it is the primary mineral of these rocks. 186 The Torres del Paine contact aureole shows a decrease in grain size approaching the contact 187 for most of the minerals involved in metamorphic reactions with the important exception of

biotite (see below). Large detrital quartz grains can be found in the outer aureole (Fig. 2a),
even within the cordierite zone where it is consumed by the chlorite breakdown reaction.
Quartz and plagioclase have a more homogeneous grain size distribution at the thin section

191 scale for rocks that experienced muscovite breakdown. Detrital muscovite can be found in the 192 cordierite zone as coarse grains, coexisting with small, newly grown, metamorphic muscovite 193 (Fig. 2b). These variations in mineral texture with increasing grade indicate a 194 recrystallization of the rock matrix including the reactants when muscovite reacts out at 195 higher temperature to form K-feldspar.

Rocks far from the intrusive contact have larger cordierite grains (Fig. 2a) than rocks close tothe contact (Fig. 2f), which have typically a larger modal amount of cordierite. This indicates

198 that the textures reflect mostly the original reaction textures, with minor recrystallization of 199 the product mineral cordierite.

In contrast, biotite grain size has an opposite trend, exhibiting coarsening with increasing metamorphic grade. In the cordierite zone, biotite crystals are very small, e.g. less than 10 μ m, often in clusters (Fig. 2b and 2c). In the K-feldspar zone, biotite grains are bigger (10-25 μ m) and distributed in the rock much more homogeneously (Fig. 2d and 2e).

The Torres del Paine contact aureole rocks also show different stages of retrogression. Newly grown muscovite after K-feldspar is present in several samples (Fig. 2e), they are distinct from prograde metamorphic muscovite since they are larger in grain size. Even if cordierite is usually well preserved in the Torres del Paine contact aureole, many samples show evidence of destabilization of cordierite, e.g. it locally altered at the grain boundary (Fig. 2d), but more commonly cordierite is completely replaced by muscovite and chlorite intergrowth. Biotite can also be replaced by muscovite and chlorite (Fig 2f).

211

212 Chemical compositions of metamorphic minerals

To discuss the evolution of the compositions of metamorphic minerals in the Torres del Paine contact aureole, we will focus on the metamorphic gradient in a profile below Cuerno Principal peak. It is located underneath the intrusion. The profile is referred to as CPb. It is the most complete profile sampled, mineral assemblages can be found in supplementary material. Nevertheless, the evolution of mineral compositions is very similar for all profiles.

Muscovite. White micas in the CPb profile are very close to the muscovite end-member compositions with a small amount of phengite component (i.e. FeO content ranging from 0.99 to 2.03 wt% and MgO content between 0.52 and 1.46 wt%; see Table 1). This corresponds to a low phengite component (calculated using ${}^{VI}R^{2+}/({}^{VI}R^{2+} + {}^{VI}R^{3+})$) from 0.052 to 0.126. The two lowest grade samples (07TP55 and 07TP56), located at a distance of

respectively 400 m and 300 m from the contact with the intrusion have the highest $^{VI}R^{2+}$ content. There is no correlation between paragonite content and distance from the intrusion. F and Cl contents are very low, with 0.04-0.08 wt% (0.018-0.030 p.f.u.) for F content and mostly below detection limit for Cl content, i.e. \approx 0.004 wt% (below 0.001 p.f.u.). At these levels, no trend was observed in the contact aureole with the precision of EMPA.

228 **Feldspars.** Plagioclase is present in all samples from the CPb profile, usually with two 229 distinct compositions due to the peristerite gap at these temperatures (470-600 °C, see Table 230 2). Metamorphic albite is in equilibrium with an oligoclase of decreasing X_{An} (calculated as Na / (Na + Ca + K)) with increasing peak temperature, with $X_{An} = 0.270$ at 300 m and $X_{An} =$ 231 232 0.166 at 150 m, respectively. Close to the contact with the intrusion there is only one 233 plagioclase composition, with $X_{An} = 0.217$. In contrast, Sample 07TP63 (at 10 m) has two very distinct populations of plagioclase of $X_{An} = 0.359$ and $X_{An} = 0.786$. These are 234 235 completely different from the rest of the profile. This sample also exhibits clinozoisite-rich 236 epidotes, calcite grains showing the influence of the second part of the thin section, which is 237 a meta-carbonate.

K-feldspar is present as sedimentary relicts at lower metamorphic grades up and into the cordierite zone as well as a product of the muscovite dehydration reaction in the K-feldspar zone. The X_{Ab} (Na / (Na + Ca + K)) component is comprised between 0.154 and 0.222 (Table 2). The compositions of these two different generations are not different.

Biotite. Biotite compositions have high octahedral Al (^{VI}Al), as often in low pressure metamorphic rocks (see Table 3). The X_{Mg} and Ti contents have two opposite trends with increasing temperature for most samples. The X_{Mg} decreases toward the contact with the intrusion and Ti content increases. The X_{Mg} range from 0.389 at 400 m to 0.355 at 5 m and the Ti content (based on 44 charges or 22 equivalent oxygens formulae) from 0.161 p.f.u. at 400 m to 0.463 p.f.u. at 5 m (Fig. 3a). Both X_{Mg} and Ti contents show a large range along this

248 trend, especially visible for sample 07TP58 (grey squares, Fig. 3a). Two samples fall clearly 249 off this trend, i.e. 07TP63 (at 10 m) and 10TP57 (at 1 m). Interestingly, the only difference 250 between these two samples and the rest of the samples is their Cl content (Fig. 3b), they both 251 have higher Cl concentrations, i.e. 0.16-0.18 wt% (0.041-0.046 p.f.u.) versus 0.01-0.02 wt% 252 (0.002-0.004 p.f.u.) for the other samples. F content was difficult to determine because of the 253 Fe interference when using a large crystal (LDE1) for the determination of fluorine 254 concentrations with EPMA. F contents in amphibolite facies biotite grains from contact 255 aureoles are usually about 0.2-0.4 wt% (Sisson 1987, Siron et al. 2018a).

Cordierite. As for the biotite of the CPb gradient, cordierite shows a decrease in X_{Mg} toward the contact with the intrusion, from 0.539 to 0.505, except close to the intrusion where sample 10TP54 has a slightly higher XMg of 0.52 (see Table 4). Cordierite does not contain measurable amounts of Cl, either below or slightly above the detection limit (0.004 wt%).

260

261

262 Thermodynamic modelling

Pseudosections were computed using version 6.6.6 of the Perple X software (Connolly 263 264 2009). Due to the small variations in bulk rock composition of the Torres del Paine samples 265 (see Fig. 4), sample 07TP56 was chosen for pseudosection calculations, since its composition 266 is typical for the metapelites of the TPIC contact aureole. The composition used for 267 thermodynamic modelling comes from XRF analyses, oxide composition can be found in the 268 supplementary materials. Ti has been excluded from the composition by projection through 269 ilmenite (i.e. associated Fe moles were subtracted from the bulk rock composition), no 270 correction for Ti in biotite was attempted since it is usually low (below 0.5 p.f.u.). Since graphite is present in most samples, C was set as a saturated component and fluid 271 272 compositions were calculated using the equation of state (EoS) by Connolly and Cesare

273 (1993, EoS 10 in Perple X). An X_0 of 1/3 was set to impose a saturated H₂O rich fluid (see 274 Connolly and Cesare (1993) for a discussion of this variable). This choice was made since the 275 fluid produced from the successive dehydration reactions is mostly H₂O. Hence, water-rich 276 conditions most likely prevailed during contact metamorphism of metapelites in the Torres 277 del Paine contact aureole. The choice of a reduced water activity using this fluid EoS instead 278 of imposing a pure H₂O fluid phase using the CORK equation of state from Holland and 279 Powell (1991) results in a small shift of the dehydration reactions towards lower temperatures 280 (less than 20 °C).

281 Even if bulk rock compositional variations are very small, this could still translate into large 282 differences for calculated locations of the reactions, depending on the sensitivity of each 283 individual reactions to variations of composition. The most important component in the case 284 of metapelite is the bulk rock Fe/(Mg+Fe) ratio. Fig. 5a shows the impact of Fe/Mg 285 variations for the composition of a typical rock from the aureole (07TP56). Interestingly, 286 temperatures do not change much for the X_{Mg} range of 0.36-0.5, which represents the extend 287 of bulk rock variations for the rocks of the Torres del Paine contact aureole. Both isograds, the crd-in (field 1) and kfs-in (field 3), are only slightly displaced in temperature (<10 °C) 288 289 with changes in X_{Mg} . The temperature for the bt-in isograd (field 2) is not affected by 290 changes in bulk rock composition (Fig. 5a). This agrees well with the appearance of 291 cordierite at approximately the same distance from the intrusion in all pelitic compositions, 292 allowing to readily map the isograd (Fig. 5a).

Pressure has been estimated based on assemblages in meta-marls to be 75MPa (Putlitz et al., 2001; Baumgartner et al., 2007). This is consistent with the absence of aluminosilicate, which also indicates very low-pressure metamorphism. Figure 5b shows a phase diagram calculated for the composition of the representative pelite sample, 07TP56. The temperatures are 470 °C for crd-in isograd and 520 °C for kfs-in isograd (Fig. 5b).

Figure 5c shows the calculated volume percent of the major phases in the rock, in good agreement with the observed mineralogical evolution in the aureole. Even if cordierite is stable at slightly lower temperature than biotite, the major episode of cordierite growth is related to the chlorite breakdown reaction with cordierite and biotite as products of this reaction (Fig. 5c). The second episode of growth for cordierite occurred during the muscovite breakdown reaction, where metamorphic K-feldspar is produced. Fe and Mg of cordierite is obtained from biotite, resulting in a minor consumption of biotite (Fig. 5c).

305

306 Field observations of fluid flow

307 The Torres del Paine intrusion has abundant miarolitic cavities in all granitic and most mafic 308 intrusive rocks. Cavities are more abundant towards the borders of the intrusion and modal 309 abundance of cavities can reach up to 20-30% in the most external parts of the oldest granite, 310 the granite I, also called Almirante granite (Michel et al., 2007; Baumgartner et al., 2007; 311 Leuthold et al., 2013). These rocks are fined-grained and have graphic quartz-feldspar 312 intergrowths. The cavities are typically isolated, but they can form in some rare cases interconnected tube-like structures surrounded by granite grus. These cavities mark igneous 313 314 fluid exsolution upon cooling and solidification of the granite. The cavities are filled mainly 315 with euhedral quartz and feldspars, as well as with fayalite, tourmaline, chlorite, pyrite, 316 zeolites and carbonates (Bégué et al. 2018). Some miaroles are completely filled with coarse 317 quartz, forming pods up to one meter in size. These textures indicate a granite melt with near-318 eutectic composition, which was highly water saturated. At a pressure of 75 MPa – the likely 319 emplacement pressure (see above) water saturation of a granitic magma is reached at ca. 3 320 wt% of water (Holtz et al. 1995).

Fluid infiltration textures – veins, or bleaching zone, skarns, etc. – are rarely visible in the
host rocks, despite the fact that the contact is extremely well exposed (see Fig. 1). The only

323 obvious features are small bundles of veins which continue on strike from the dyke tips 324 emanating into the host rocks (Bégué et al. 2018). Numerous dykes emanate from the 325 intrusion into the host rock on the Eastern end of the intrusion, as well as on the North and 326 South side of the intrusion. These dykes are similar to ring dykes in that they emanate from 327 the rim of the intrusion about vertically from the contact, dipping towards the center of the 328 intrusion (Fig. 6a). Their spacing is a few hundred meters in the roof. They start from within 329 the intrusion and can be followed for tens and up to a hundred meters into the host rock. They 330 explode into a myriad of dyklets about halfway along their length. Each dyklet is continued 331 by a fissure-like vein, which sometimes produces pyrite-amphibole veins surrounded by 332 bleached zones in the metacarbonates and metapelites. The veins are maximum several 333 millimeters wide, surrounded by a bleaching zone of a few centimeters' width (Fig. 6b). The 334 bleaching zone is due to the oxidation of the organic matter present in the sedimentary rocks. 335 Fluid infiltration is localized along these veins. Similar bleaching zones can be found in the 336 metasediments close to the contact. The zone is typically less than 1 meter wide, and only 337 visible locally.

338

339 Stable isotope compositions

340 Oxygen and hydrogen isotope compositions of the Torres del Paine igneous complex. Whole rock oxygen isotope compositions range for mafic rocks from 5.5% to 7.8% for 341 gabbronorites, gabbros, and diorites, with the diorites having the lowest δ^{18} O values 342 (Leuthold 2011). Granite oxygen isotope ratios vary between 7.1 to 9.1‰. Oxygen isotopes 343 344 range from 9.1 to 9.9‰ for quartz and 5.1 to 6.0‰ for biotite (Table 5). These values fall into the field characteristic for A-type granitic plutons (Sheppard 1986). Quartz in miarolitic 345 cavities shows a slightly wider range in δ^{18} O values of 8.8 to 11.1‰ (Table 5), but they 346 347 overlap with the quartz values of the granites. Oxygen isotope thermometry on favalite-quartz

pairs from miarolitic cavities give a temperature of 750 ± 30 °C (Putlitz et al. 2001). The pressure derived from the solidus for a haplogranitic melt at this temperature is about 750 bar (Luth 1964). This is in good agreement with available estimates based on meta-marls (Putlitz et al. 2001). Quartz-biotite pairs from the granites give 600 to 640 °C. The fact that biotite is a fast diffuser for oxygen (e.g. Eiler et al., 1993) and that solidus temperature at these pressures are much higher ($\approx 730-750$ °C, Johannes and Holtz, 1996), indicates that these are most likely closure temperatures and not crystallization temperatures.

Hydrogen isotope values of magmatic biotite from the different granites of the Torres del Paine complex span a narrow range of -97 to -83‰ (Table 5). Indeed, only one sample has a δD value of -126‰. The biotite grains of Almirante granite (granite I, Michel et al. 2008) have values between -97 and -95‰, which are slightly lower than those for Cathedral granite (Granite III, Michel et al., 2008), with biotite values between -88 and -83‰ (Table 5) typical for granite derived biotite. The granite I values are depleted in D relative to typical δD values for granites (e.g., Sheppard 1986).

362

Oxygen and hydrogen isotope composition of the host rock. Bulk rock oxygen and hydrogen isotopes ratios have been determined for the profiles above and below the Cuerno Principal, as well as for the profiles at Co. Fortaleza and at the Mte. Almirante Nieto. Several samples far from the contact aureole have also been analyzed in order to evaluate the initial heterogeneity of the protolith. They are plotted schematically on the right-hand side of the diagrams of Figure 7.

Host rock oxygen isotopes. Within each profile, bulk rock oxygen isotope compositions were found to be homogeneous at the scale of about 1‰ (Table 6 and Figure 7a). However, comparison of the different profiles shows differences. Especially, the profile below the intrusion at Cuerno Principal has oxygen isotope values which are approximately 1‰ higher

373 than in other profiles, between 13.9 and 15.1‰, compared to 12.8 to 14.1‰ for other profiles, respectively. But taking into account all profiles, the δ^{18} O values still overlap with 374 initial heterogeneity (between 12.7 to 15.1%), i.e. protolith values of the samples outside the 375 376 aureole (dashed lines in Fig. 7a). Only three samples (two from the profile above Cuerno Principal and one from the Monte Almirante profile) have oxygen isotopes composition 377 378 which is distinct from the rest. They are found at distances of 155, 215 and 250 m from the 379 intrusion. A microscopic inspection reveals that these samples are texturally different, 380 containing coarse clasts (>1 mm) of quartz and feldspar. The presence of larger feldspar and quartz clasts identify them as aluminium-rich, immature psammites, while the other samples 381 382 had a fine-grained protolith with only small clasts (<200 µm). Hence, we suggest that the low 383 isotopic values reflect different protolith compositions for these samples.

Two additional samples have low δ^{18} O values between 9.8 to 10.0‰. They were collected very close to the intrusion (<1 m away from the contact). They lost their organic carbon and are bleached (see fig. 6b).

387 Host rock hydrogen isotopes. The hydrogen isotope data show a clear pattern on the aureole 388 scale, in contrast to the oxygen isotope compositions (Table 6 and figure 7b). This is best 389 seen in two profiles; one below the intrusion (Cuerno Principal below) and one above the 390 granite (Monte Almirante Nieto; Fig. 7b). In these two profiles, the δD values decrease first 391 towards the intrusion up to about 150 m from the contact, where a value as low as -104‰ 392 was measured in the Monte Almirante profile. Subsequently, the hydrogen isotope ratios 393 increase again closer to the intrusion, to reach a maximum at the contact, with values of -394 82‰. The hydrogen is mainly carried by biotite, thus in the samples close to the intrusion it 395 can be directly compared to values of the granites, where the main hydrogen carrier is also 396 biotite. They are very similar to the values of the granites, in which biotites vary between -97 397 and -83‰ (see above).

398

399 Chlorine content in igneous and metamorphic biotites

400 Chlorine content in igneous biotites. The chlorine content of biotite of four samples from 401 the granitic complex varies between 0.3 and 0.8 wt%. This corresponds to a Cl content of 402 0.08-0.22 p.f.u. and a molar fraction $X_{C1} = 0.02-0.05$. These somewhat high chlorine 403 concentrations are consistent with a progressive enrichment of the Magmatic Volatile Phase 404 (MVP) due to the incompatibility of Cl with the crystallizing minerals. The biotite has a high 405 iron content in these granites, with X_{Mg} between 0.15 and 0.32.

406

Chlorine content in metamorphic biotite. Figure 8 shows the chlorine content in biotite for 407 408 each profile collected in the contact aureole. Chlorine concentrations are almost always very 409 low, i.e. below 0.05 wt% (0.015 p.f.u.). Chlorine concentration is sample dependent, but it 410 also varies within each sample. In contrast to hydrogen isotopes, no systematic variations 411 with the distance from the intrusion are found on the large scale. Nevertheless, four samples 412 collected just next to the intrusion have higher Cl contents in biotite than the rest of samples.

413 Chlorine concentrations in biotite in the distal aureole varies between 0.01-0.06 wt% (Fig. 414 8f). while chlorine concentrations in biotite close to the contact can reach values of up to 0.18 415 wt% (0.05 p.f.u.). Indeed, four samples have high chlorine concentrations. They are samples 416 from three different profiles: two samples from the profile below the granite at Cuerno 417 Principal (Fig. 8a), one sample from the Valle Frances side profile (Fig. 8e), and one sample 418 from the profile above the granite at Mte. Almirante Nieto (Fig. 8c). They all are from the 419 immediate proximity of the granite, less than 20 m away from the contact. These high values 420 are 3 to 10 times higher than those observed in distal host rocks.

Figure 9 reveals no correlation between Cl content and X_{Mg} biotite grains. This is true for 421 422 biotite grains from different samples within a specific profile, as well as between profiles.

423 Indeed, in the Cuerno Principal below profile, the two samples with a high Cl content have 424 both higher X_{Mg} than the samples with low Cl content. In addition, no correlation between 425 Al^{iv} or Ti content has been found.

426

427

428 **DISCUSSION**

429 Both bulk rock hydrogen isotope compositions and chlorine content in biotite change close to 430 the contact between intrusive rocks and surrounding metamorphic rocks. Characteristic are 431 higher δD values (whole rock) and a higher Cl content in biotite in some samples. These data 432 provide good evidence that the Torres del Paine contact aureole experienced igneous fluid 433 infiltration. Oxygen isotope compositions do not show significant trends. In the distal 434 aureole, hydrogen isotope compositions again show a clear trend with a marked decrease in 435 δD values approaching the contact. In contrast, neither chlorine concentrations nor oxygen 436 isotope ratios show any trend in the distal aureole. The following section discusses the 437 different behavior of these three potential markers of fluid-rock interactions in terms of 438 equilibrium vs disequilibrium processes and scale of equilibration vs time integrated fluid 439 flux.

440

441 Significance of bulk rock δD variations

Hydrogen is present in biotite in the K-feldspar zone, and in biotite and muscovite in the cordierite zone. Hydrogen can also be stored in the channels of cordierite in both zones, but in much lesser amount compared to muscovite and biotite. At lower temperature, most of the hydrogen is bound in chlorite and muscovite. Trace amounts of apatite are present in some rocks in the Torres del Paine contact aureole; but its fraction is too small to have a significant effect on the hydrogen balance. Since kinetics of isotopic exchange by recrystallization is orders of magnitude faster than by diffusion (Baumgartner and Valley 2001; Putnis et al.
2007), hydrogen isotopes in the Torres del Paine should monitor fluid-rock interactions most
efficiently, since all of the major hydrous phases are involved in dehydration reactions.

Indeed, the different hydrogen isotope profiles of the Torres del Paine do vary in the contact aureole (Fig. 7b), showing a decrease of the δD values when approaching the intrusion in the outer part of the aureole (>150 m from the intrusion) and an increase in the inner part of the aureole. We interpret these two trends as being the consequence of two very different processes of fluid-rock interaction: (i) metamorphic dehydration reactions and (ii) magmatic fluid infiltration. The two processes are described below.

The decrease of the δD value in the chlorite and cordierite zones is interpreted to reflect Rayleigh fractionation due to dehydration reactions. At these temperatures, water is enriched in deuterium with respect to hydrous silicates (Suzuoki and Epstein, 1976). Hence, water removed from the rocks takes up a disproportionately high amount of deuterium. The remaining hydrogen bound in the mineral structures contains a disproportionately low amount of deuterium.

463 The calculation below assumes that the removed water was in isotopic equilibrium with biotite. Assuming a temperature of 480 °C, corresponding to the temperature of the chlorite 464 465 breakdown (see Fig. 3) it can be estimated that about 40% of the water contained initially in the hydrous silicates needs to be removed to produce the ca. 20% change in δD values (α_{bt} -466 $_{\rm H20}$ = 0.95453, Suzuoki and Epstein, 1976). At a temperature of 520 °C approximately 45% of 467 468 the water has to be removed. The overall amounts of removed hydrous fluids agrees with the 469 actual water loss estimated from phase petrology calculations. Given the sharpness of the 470 isograds, one would expect from these estimates a step-like decrease in δD . The relatively smooth decrease is expected if reaction kinetics is sluggish, so that the individual reactions 471 occur over a temperature range of ca. 50 °C or if the initial profile is changed by small 472

473 amounts of diffusion, dispersion, and fluid flow. Crystal size analysis and thermal modelling by Bodner et al. (2013) suggest that, indeed, reaction progress can span several tens of °C. 474 Furthermore, the presence of larger, detrital grains of biotite or quartz is a good indication 475 476 that large amount of textural disequilibrium exists in the Torres del Paine contact aureole. Also, in other contact aureoles, evidences for sluggish reaction kinetics are well established. 477 Inconsistencies between isograd locations (Waters and Lovegrove 2002; Pattison and 478 479 Tinkham, 2009) or thin section scale heterogeneity for Cl and F contents in biotite (Siron et 480 al. 2018a) are common in metapelitic contact aureoles. Heterogeneity within samples for 481 oxygen isotope compositions (Ferry et al. 2013) or calcite-dolomite thermometry (Müller et 482 al. 2008) have been shown for metacarbonate contact aureoles. Both evidences are good 483 indications that metamorphic reactions do not progress according to the equilibrium paradigm 484 in contact aureoles.

485 Close to the contact (at about 150 m) the δD values increase and become similar to those of biotite in the granites. This is interpreted as the result of magmatic fluid infiltration. A rough 486 estimate of fluid flux can be obtained using the distance of the δD -front (demarking the most 487 488 notable change in values) from the contact with the intrusion, which is assumed to be the 489 source of the fluids. Maximum estimates of the amount of fluid flow needed are computed, in 490 order to determine the potential effect of fluid flow on contact metamorphism in the Torres 491 del Paine. Additional details on these estimates can be found in Baumgartner and Rumble 492 (1988) and Baumgartner and Valley (2001).

For the stable isotope transport theory, the isotopic exchange front lags behind the actual fluid front. The difference in front speed between fluid and tracer (here bulk rock δD) is termed the retardation factor and can be described by the relation:

496
$$\frac{v_f \cdot t}{v_\delta \cdot t} = \kappa \tag{1}$$

497 where κ represents the retardation factor, v_f is the velocity of the fluid front, v_{δ} the velocity of 498 the isotope front and t stands for time. The combination $v_i \cdot t$ represents the distance of front i 499 (i = isotope (δ) or fluid (f)) from the intrusion. The retardation factor κ can be approximated 500 by the equilibrium constant K_D between fluid and rock,

501
$$\kappa \approx K_D = \alpha \frac{\beta_s \overline{V}_f}{\beta_f \overline{V}_s}$$
(2)

Here, β is the stoichiometry of hydrogen in the solid (s) and the fluid (f), α the fractionation factor from Suzuoki and Epstein (1976), and \overline{V} the molar volume of the respective phases, i.e. 52 cm³ · mol⁻¹ for a fluid composed of pure water and 153 cm³ · mol⁻¹ for biotite. Equation (2) is valid for small porosities only (Baumgartner and Rumble, 1988). A contact temperature of 550 °C is used, along with a typical modal abundance of 10% by volume of biotite in the rock. This results in a K_D of 3.6. Using the largest distance of the isotope front of 150 m (Fig. 7b), a time integrated fluid flux of roughly 4m³/m² is obtained.

509 This value shall be compared with values from the literature. Bowman et al. (1994) calculated about 500 m^3/m^2 based on oxygen isotope compositional changes in siliceous 510 dolomite around the Alta stock. Similarly, Nabelek and Labotka (1993) obtained 720 m^3/m^2 511 512 to produce the oxygen isotope composition in the Notch Peak contact aureole. Hence, the 513 value registered by the rocks in the Torres del Paine is very small, ca. 100 times less, 514 compared to other contact aureoles. Such small amounts of fluid infiltration might be typical 515 for metapelite dominated aureoles, where the host rocks have a relatively small permeability 516 when compared to metacarbonate dominated aureoles.

517

518 Lack of δ^{18} O fronts in the aureole

Rayleigh fractionation effects have been shown to be very small for a major element like oxygen, since only a very small fraction of oxygen is accessible for fast isotopic equilibration during dehydration reactions of a typical metapelite. In addition, the fractionation between oxygen in the fluid phase and metamorphic minerals is relatively small compared to hydrogen (maximum several permille). As a consequence, the oxygen isotope composition typically is not changed by Rayleigh fractionation alone (Bumgartner and Valley, 2001).

The absence of an oxygen isotope infiltration front in the Torres del Paine contact aureole can 525 526 be explained by two factors: 1) The fluid expelled from the intrusion has a composition 527 similar to a fluid in equilibrium with the minerals in the metapelites. This is in contrast to 528 metacarbonate rocks, where a difference between host rock and fluid expelled from the 529 intrusion can be as high as 15‰. 2) Oxygen being a major element within minerals, a small 530 amount of infiltrated fluid, even when reacting with the minerals, cannot produce a well recognizable infiltration front for δ^{18} O because of simple mass balance constrains. In addition 531 532 to that, using the time integrated fluid flux determined from hydrogen isotopes, the position 533 of the oxygen isotope infiltration front would lie within the first meter of the contact. The 534 sampling strategy chosen for this study does not allow a spatial resolution of 1 m or less, 535 which would be required to characterize a 1 m oxygen isotope front. The fact that some samples have very low δ^{18} O values at the contact could support infiltration of a small amount 536 of fluid. Nevertheless, the high background-variability of δ^{18} O values for the 537 538 metasedimentary rocks also does not allow well-defined oxygen isotope depletion zones to be 539 present in the Torres del Paine contact aureole.

540

541 **Cl content in biotite**

542 The third tracer used to investigate fluid flow is the chlorine content of biotite. Figure 9 543 illustrates that the Cl content is not correlated with X_{Mg} and hence not constrained by

544 variations of the crystal lattice in the aureole. It follows that the higher Cl contents close to 545 the contact are most probably due to fluid infiltration. Cl content of hydrous minerals are linked to the HCl° activity in the fluid (Zhu and Sverjensky 1991, 1992). The HCl° activity is 546 547 a function of two major variables, the pH of the fluid (Eugster and Baumgartner 1987) and 548 the total Cl dissolved in the fluid (Zhu and Sverjensky 1991). Thus, any change in the 549 mineral assemblage in equilibrium with the fluid will result in a change in pH and HCl° activity, and by consequence Cl content in hydrous minerals. Therefore, changes in Cl 550 551 content of hydrous minerals can be either the result of the appearance or disappearance of a 552 metamorphic mineral due to metamorphic reactions or change in the total Cl dissolved in the 553 fluid due to the infiltration of an external fluid, dilution/desiccation of the residual fluid.

554 Recently, Siron et al. (2018a) have documented the slow kinetics of exchange for the O(4) 555 site of biotite during contact metamorphism, especially for Cl. It seems that the Cl content 556 does not change during contact metamorphism, unless biotite grains recrystallize, when they 557 can exchange with a fluid of different chlorinity or under different pH conditions, if such a 558 fluid is present at that moment. This may account for the absence of a trend in Cl 559 concentrations of biotite within the cordierite zone. In contrast to hydrogen isotopes, the Cl 560 content in biotite does not record Rayleigh fractionation, even though Cl fractionates strongly 561 into the fluid, and hence Cl is incompatible with biotite. Thus, Cl should be strongly depleted 562 by Rayleigh fractionation. Such discrepancy between the expected behavior and the actual 563 measurements requires an explanation.

564 Disequilibrium might be an appropriate explanation. If Cl only exchanges for the part that 565 reacts, Cl cannot be depleted in the whole crystal; hence no Rayleigh fractionation occurs. 566 Such a disequilibrium behavior is not unexpected in the case of the Torres del Paine contact 567 aureole, since various examples of disequilibrium can be found, i.e. presence of clastic 568 minerals, even in the cordierite zone (Fig. 2a and 2b), as well as large variations in the X_{Mg} 569 and Ti content of biotite (Fig. 3a).

570 The biotite grains that have high Cl content close to the intrusion are clearly larger, with a 571 well-defined habitus compared to the patchy, small, biotite grains observed in the cordierite 572 zone. This provides good evidence that the large biotite crystals recrystallized and were thus 573 able to exchange their composition with a fluid of different HCl° activity. The fact that not all 574 samples from the K-feldspar zone have a high Cl content in biotite is a good argument 575 against a potential pH influence. If the high Cl contents in biotite were the result of a change 576 in pH due to the shift from muscovite to K-feldspar for the KCl° buffer, all samples close to 577 the contact should be affected, not only a few. Together, these arguments allow the 578 interpretation that the high Cl content in biotite – as well as the bulk rock hydrogen isotope 579 compositions - are the result of the infiltration of igneous fluid. Moreover, since only a few 580 samples have these relatively high Cl contents, the infiltration seems to have been 581 channelized and does not represent a major percolation of fluids. This interpretation is 582 consistent with the very low time integrated fluid flux computed from hydrogen isotopes 583 compositions in the contact aureole.

The sample 07TP63 is slightly different since it is in contact with a carbonate layer. This sample provides evidence of CO_2 infiltration, i.e. clinozoisite-rich epidotes, calcite grains, higher X_{An} composition of plagioclases. In this case the high Cl content in biotite might be due to fluid immiscibility, well known in the case of H₂O-CO₂-NaCl fluids (Aranovich 2010), instead of igneous fluid infiltration. Nevertheless, since only this sample was close to a metacarbonate layer, this does not change the overall interpretation of high Cl content in biotite resulting from igneous fluid infiltration.

591

592 **Timing of fluid infiltration**

Fluid infiltration can have a major effect on heat and mass transport. It is important to understand the timing of fluid infiltration because it could, for example, increase peak metamorphic temperatures if infiltration occurs close to the peak metamorphism in the contact environment, or promote short cooling times (e.g. Cook and Bowman 1994, Hanson 1995). Below is an attempt to identify the relative timing of fluid infiltration in the Torres del Paine contact aureole.

The granites of the Torres del Paine laccolith are typical A-type granites (Michel et al. 2008), which can be hot and relatively dry (King et al. 2001). These dry granites become water saturated at the very end of cooling, after a substantial degree of crystallization. This is supported by the quartz-fayalite temperatures of 750°C measured in the miaroles of the granite I. This would imply that fluid expulsion occurred at a late stage of granite crystallization.

The major element composition of metamorphic biotite shows that biotite grains with high Cl 605 606 content have slightly lower Ti contents compared to biotite from samples located at the same 607 distance (or close) to the intrusion. Since the Ti content is strongly linked to the temperature (Henry and Guidotti 2002, Henry et al. 2005), this indicates that the biotite grains with a high 608 609 Cl content have recrystallized in equilibrium with the high salinity fluid from the intrusion 610 during the onset of cooling. While post peak, fluid infiltration must have occurred above the lower stability limit of biotite, which is about 470 °C (Fig. 5). Ti-in-biotite for samples from 611 612 the Torres del Paine contact aureole are very different than temperatures deciphered from 613 mineral assemblages, sometimes even more than 100 °C (Table 3). This can be either due to 614 disequilibrium or the fact that aluminosilicates are not present, and hence, the Torres del 615 Paine metamorphic rocks have a different buffer assemblage than what was used to constrain 616 this geothermometer. Nevertheless, the overall trend of decreasing temperature with distance 617 to the contact for low Cl content samples is also observed for Ti-in-biotite temperatures.

618 Similarly, high Cl contents biotite grains have lower Ti-in-biotite temperatures than low Cl619 contents located at similar distance from the contact.

Retrograde muscovite after K-feldspar provides evidence of fluid infiltration during cooling of the surrounding rocks, at a still relatively high temperature, i.e. between the K-feldspar-in isograd (520 °C) and the biotite and cordierite isograd (470 °C). Chlorite-muscovite alteration of cordierite or biotite represent fluid infiltration at temperatures below 470 °C.

Figure 10 sketches the interpretation of the temperature-time evolution for a metapelite at the 624 625 contact between the intrusion and the surrounding rocks. Overall time for cooling of the 626 Torres del Paine intrusion can be estimated using simple 1-d thermal models (e.g. Spear, 627 1993). The time span shown corresponds to about 20 ky for the cooling of an 800 m 628 intrusion. Since the three different markers of fluid infiltration, i.e. a high chlorine content, a 629 δD infiltration front, and the retrograde muscovite and finally chlorite + muscovite intergrowth after cordierite and biotite, occur within a 15 ky window, it is very unlikely that 630 631 they represent three distinct fluid infiltration events but rather the nearly continuous 632 emplacement/crystallization of the different pulses of granites of the Torres del Paine 633 laccolith.

634

635 **IMPLICATIONS**

The comparison of these three different tracers for fluid rock-interactions shows the need to carefully evaluate which one is appropriate in the environment to be studied. In the case of metapelites, low concentration tracers are easier to exchange, and hydrogen isotopes or Cl content in hydrous minerals will be more sensitive to fluid-rock interactions than oxygen isotope compositions. This might open the possibility to reassess the extend of fluid flow in metapelite dominated aureoles, where clear evidences of igneous fluid flow has so far not been commonly observed. Using chlorine in hydrous minerals provides an exciting avenue 643 for studying fluid-rock interaction in this kind of environment. Nevertheless, the fact that Cl 644 content in hydrous minerals, such as biotite, exchange very slowly at low to medium 645 temperatures requires carefull petrologic studies to identify newly crystallizing phases or re-646 crystallization of pre-existing phases.

Additionally, the observation of a Rayleigh fractionation trend for hydrogen isotope during 647 648 chlorite breakdown reaction show the potential of this tracer to study fluid-rock interactions during internal fluid production where the fluid isotopic composition is in equilibrium with 649 650 the rock composition. Fluid-rock interactions during dehydration reactions is a key 651 component to understand porosity creation and is necessary to obtain connected pores 652 (Plumper et al. 2017) and slip events created due to fluid overpressure (Taetz et al. 2018). To 653 date, only a few studies have focused on hydrogen isotopes from metamorphic minerals 654 during prograde metamorphism. However, all of these studies used mineral separates and 655 never analyzed the hydrogen isotope composition of metamorphic minerals within the 656 context of their textural positions. The recent development of new SIMS reference materials 657 (Siron et al. 2018b, Luisier et al. 2019) will promote the use of hydrogen isotopes and water 658 content since these can know be measured in-situ in micas.

659

660

661 ACKNOLEDGEMENTS

We thank Darrell Henry and Simon Harley for extensive comments on an earlier version of the manuscript. Funding was provided for this project to L.P. Baumgartner by SNF grants 200021_153094 and 200020_140974 and the KIP 6, PCI CASA, grant are gratefully acknowledged.

666

668 REFERENCES

- 669 Armstrong J.T. (1989) CITZAF: Combined ZAF and Phi-Rho (Z) Electron Beam Correction
- 670 Program, California Institute of Technology, Pasadena, CA.
- 671 Bauer, K.K., and Vennemann, T.W. (2014) Analytical methods for the measurement of
- 672 hydrogen isotope composition and water content in clay minerals by TC/EA. Chemical
- 673 Geology, 363, 229–240.
- 674 Baumgartner, L. P. and Rumble, D. (1988) Transport of stable isotopes: I: Development of a 675 kinetic continuum theory for stable isotope transport. Contributions to Mineralogy and 676 Petrology, 98, 417-430.
- 677 Baumgartner, L. P., Gieré, R., Trommsdorff, V., and Ulmer, P. (1989) Field guide for the
- 678 Southern Adamello. in Guidebook for the excursion to the Central Alps, Bergell and
- 679 Adamello, Consiglio Nazionale delle Ricerche, Sienna, Italy, 91-115.
- 680 Baumgartner, L. P., and Ferry, J. M. (1991). A model for coupled fluid-flow and mixed-
- volatile mineral reactions with applications to regional metamorphism. Contributions to 681 682 Mineralogy and Petrology, 106, 273–285.
- 683 Baumgartner, L. P., Michel, J., Putlitz, B., Leuthold, J., Müntener, O., Robyr, M. and Darbellay, B. (2007) Field guide to the Torres del Paine Igneous Complex and its contact 684 685 aureole. in Field guide book GEOSUR 2007, vol. 185.
- Baumgartner, L. P. and Valley, J. W. (2001) Stable Isotope Transport and Contact Metamor-686 687 phic Fluid Flow. Reviews in Mineralogy and Geochemistry, 43, 415–467.
- 688 Bégué, F., Baumgartner, L.P., and Ewing, T. (2018) Density instabilities, melt remobilization
- 689 and their relationship to volatile exsolution; Torres del Paine igneous complex (Patagonia,
- 690 Chile). EGU General Assembly Conference Abstracts 20, 12739.
- Bickle, M. and J. Baker (1990) Migration of reaction and isotopic fronts in infiltration zones: 691 692 assessments of fluid flux in metamorphic terrains. Earth and Planetary Science Letters, 98, 1– 693 13.
- 694 Bodner, R., Baumgartner, L. P., and Foster, C. T., Jr. (2013). Cordierite nucleation and
- 695 growth rates in the Torres del Paine contact aureole. Goldschmidt 2013 Conference

- 696 Abstracts, 724.
- 697 Bowman, J. R., Willett, S. D. and Cook, S. J. (1994) Oxygen isotopic transport and exchange 698 during fluid flow: one-dimensional models and applications. American Journal of Sciences, 699 294, 1-55.
- 700 Candela, P.A. (1986) Toward a thermodynamic model for the halogens in magmatic systems:
- 701 an application to melt-vapor-apatite equilibria. Chemical Geology, 57, 289–301.
- 702 Candela, P. A. (1997). A review of shallow, ore-related granites: Textures, volatiles, and ore 703 metals. Journal of Petrology, 38, 1619–1633.
- 704 Cartwright, I., and Buick, I. S. (1996) Determining the direction of contact metamorphic fluid

705 flow: an assessment of mineralogical and stable isotope criteria. Journal of Metamorphic

706 Geology, 14, 289–305.

- 707 Connolly, J.A.D. (2009) The geodynamic equation of state: What and how. Geochemistry, 708 Geophysics, Geosystems, 10, Q10014.
- 709 Connolly, J. A. D., and Cesare, B. (1993) C-O-H-S fluid composition and oxygen fugacity in 710 graphitic metapelites. Journal of Metamorphic Geology, 11, 379–388.
- 711 Cook, S. J., & Bowman, J. R. (1994). Contact metamorphism surrounding the Alta stock:
- Thermal constraints and evidence of advective heat transport from calcite + dolomite 712
- 713 geothermometry. American Mineralogist, 79(5-6), 513-525.
- 714 Cook, S. J., Bowman, J. R. and Forster, C. B. (1997) Contact metamorphism surrounding the Alta Stock; finite element model simulation of heat- and ¹⁸O/¹⁶O mass-transport during 715 716 prograde metamorphism. American Journal of Science, 297, 1–55.
- Cui, X. J., Nabelek, P. I., and Liu, M. (2001). Heat and fluid flow in contact metamorphic 717
- 718 aureoles with layered and transient permeability, with application to the Notch Peak aureole,
- 719 Utah. Journal of Geophysical Research, 106, 6477-6491.
- 720 Eiler, J.M., Valley, J.W., and Baumgartner, L.P. (1993) A new look at stable isotope 721 thermometry. Geochimica et Cosmochimica Acta, 57, 2571–2583.
- 722 Ferry, J. (1986) Reaction Progress: A Monitor of Fluid-Rock Interaction during

- 723 Metamorphic and Hydrothermal Events. in Fluid—Rock Interactions during Metamorphism,
- 724 ed. by J. Walther and B. Wood, Springer New York, vol. 5 of Advances in Physical
- 725 Geochemistry, 60–88.
- 726 Ferry, J.M. (2000) Patterns of mineral occurrence in metamorphic rocks. American
- 727 Mineralogist, 85, 1573–1588.
- 728 Ferry, J.M., Winslow, N.W., and Penniston-Dorland, S.C. (2013) Re-evaluation of 729 Infiltration-driven Regional Metamorphism in Northern New England: New Transport 730 Models with Solid Solution and Cross-layer Equilibration of Fluid Composition. Journal of 731 Petrology, 54, 2455-2485.
- Floess, D., Baumgartner, L.P., and Vonlanthen, P. (2015) An observational and 732 733 thermodynamic investigation of carbonate partial melting. Earth and Planetary Science 734 Letters, 409, 147–156.
- 735 Fildani, A. (2005). Stratigraphic record across a retroarc basin inversion: Rocas Verdes-736 Magallanes Basin, Patagonian Andes, Chile. Geological Society of America Bulletin, 737 117(11), 1596.
- Fildani, A., Schultz, M. R., Graham, S. A., and Leier, A. (2007). A deep-water amalgamated 738
- 739 sheet system, Punta Barrosa Formation, Marina's cliff, chile.
- 740 In: Nilsen T., Shew R., Steffens G. & Studlick J. (eds.), Atlas of deep-water outcrops. AAPG
- 741 Studies in Geology, vol. 56, p. 125-127.
- 742 Gerdes, M. L., Baumgartner, L. P., and Person, M. (1998). Convective fluid flow through 743 heterogeneous country rocks during contact metamorphism. Journal of Geophysical 744 Research: Solid Earth, 103, 23983–24003.
- 745 Goranson, R.W. (1983) Silicate-water systems phase equilibria in the NaAlSi₃O₈-H₂O and
- 746 KAlSi₃O₈-H₂O systems at high temperatures and pressures. American Journal of Science, 35,
- 747 71–91.
- 748 Hanson, R. B. (1995) The hydrodynamics of contact metamorphism. Geological Society of 749 America Bulletin, 107, 595–611.
- 750 Henry, D.J., and Guidotti, C.V. (2002) Titanium in biotite from metapellitic rocks:

- 751 Temperature effect, crystal-chemical controls, and petrologic applications. American
 752 Mineralogist, 87, 375–382.
- Henry, D. J., Guidotti, C. V. and Thomson, J. A. (2005) The Ti-saturation surface for low-tomedium pressure metapelitic biotites: Implications for geothermometry and Ti-substitution
 mechanisms. American Mineralogist, 90(2-3), 316–328.
- 756 Henry, D.J., and Daigle, N.M. (2018) Chlorine incorporation into amphibole and biotite in
- high-grade iron-formations: Interplay between crystallography and metamorphic fluids.
 American Mineralogist, 103, 55–68.
- 759 Higashino, F., Kawakami, T., Satish-Kumar, M., Ishikawa, M., Maki, K., Tsuchiya, N., et al.
- 760 (2013) Chlorine-rich fluid or melt activity during granulite facies metamorphism in the Late
- 761 Proterozoic to Cambrian continental collision zone—An example from the Sør Rondane
- 762 Mountains, East Antarctica. Precambrian Research, 234, 229–246.
- 763 Holland, T.J.B., and Powell, R. (1991) A Compensated-Redlich-Kwong (CORK) equation
- for volumes and fugacities of CO_2 and H_2O in the range 1 bar to 50 kbar and 100-1600°C.
- 765 Contributions to Mineralogy and Petrology, 109, 265–273.
- Holness, M. B. (1997). Fluid flow paths and mechanisms of fluid infiltration in carbonates
 during contact metamorphism: the Beinn an Dubhaich aureole, Skye. *Journal of Metamorphic* Geology, 15(1), 59–70.
- 769 Holness, M. B., and Clemens, J. D. (1999). Partial melting of the Appin Quartzite driven by
- fracture-controlled H 2 O infiltration in the aureole of the Ballachulish Igneous Complex,
 Scottish Highlands. Contributions to Mineralogy and Petrology, 136, 154–168.
- Holtz, F., Behrens, H., Dingwell, D.B., and Johannes, W. (1995) H₂O solubility in
 haplogranitic metls compositional, pressure, and temperature-dependance. American
 Mineralogist, 80, 94–108.
- Hubbard, S. M., Romans, B. W., and Graham, S. A. (2008). Deep-water foreland basin deposits
- of the Cerro Toro Formation, Magallanes basin, Chile: architectural elements of a sinuous
- basin axial channel belt. Sedimentology, 55(5), 1333–1359.

- 778 Icenhower, J.P., and London, D. (1997) Partitioning of fluorine and chlorine between biotite
- and granitic melt: experimental calibration at 200 MPa H. Contributions to Mineralogy and
- 780 Petrology, 127, 17–29.
- Johannes, W., Holtz, F. (1996) Petrogenesis and experimental petrology of granitic rocks.
- 782 Springer-Verlag Berlin Heidelberg.
- 783 King, P. L., Chappell, B. W., Allen, C. M., & White, A. (2001). Are A-type granites the high-
- temperature felsic granites? Evidence from fractionated granites of the Wangrah Suite.
- 785 Australian Journal of Earth Sciences, 48(4), 501–514.
- 786 Kretz, R. (1983) Symbols for rock-forming minerals. American Mineralogist, 68, 277–279.
- Labotka, T.C., Nabelek, P.I. and Papike, J.J. (1988) Fluid infiltration through the Big Horse
 Limestone Member in the Notch Peak contact-metamorphic aureole, Utah. American
 Mineralogist, 73, 1302–1324.
- Lacroix, B., and Vennemann, T. (2015) Empirical calibration of the oxygen isotope
 fractionation between quartz and Fe-Mg-chlorite. Geochimica et Cosmochimica Acta, 149,
 21–31.
- Leuthold, J. (2011) Geometry, petrology and growth of a shallow crustal laccolith : the
 Torres del Paine Mafic Complex (Patagonia). Thesis, Université de Lausanne.
- Leuthold, J., Müntener, O., Baumgartner, L.P., Putlitz, B. and Chiaradia, M. (2013) A
 Detailed Geochemical Study of a Shallow Arc-related Laccolith; the Torres del Paine Mafic
 Complex (Patagonia). Journal of Petrology, 54, 273–303.
- Leuthold, J., Müntener, O., Baumgartner, L.P., Putlitz, B., Ovtcharova, M. and Schaltegger,
 U. (2012) Time resolved construction of a bimodal laccolith (Torres del Paine, Patagonia).
 Earth and Planetary Science Letters, 325-326, 85–92.
- Luisier, C., Baumgartner, L., Siron, G., Vennemann, T., and Robyr, M. (2019) H 2O Content
 Measurement in Phengite by Secondary Ion Mass Spectrometry: A New Set of Reference
 Materials. Geostandards and Geoanalytical Research, 43, 635–646.
- Luth, W. C., Jahns, R. H., and Tuttle, O. F. (1964) The granite system at pressures of 4 to 10
 kilobars. Journal of Geophysical Research, 69, 759–773.

- Michel, J., Baumgartner, L. P., Putlitz, B., Schaltegger, U. and Ovtcharova, M. (2008)
 Incremental growth of the Patagonian Torres del Paine laccolith over 90 k.y. Geology, 36,
 459–462.
- 809 Müller, T., Baumgartner, L. P., Foster, C. T. and Roselle, G. T. (2008) Forward modeling of
- 810 the effects of mixed volatile reaction, volume diffusion, and formation of submicroscopic
- 811 exsolution lamellae on calcite-dolomite thermometry. American Mineralogist 93, 1245–1259.
- 812 Munoz, J.L. (1984) F-OH and Cl-OH Exchange in Micas with Applications to Hydrothermal
- 813 Ore Deposits. Reviews in Mineralogy and Geochemistry, 13, 469–493.
- 814 Müntener O., Ewing T. A., Baumgartner L. P., Manzini M., Roux T., Pellaud P. and Alleman
- 815 L. (2018) Source and fractionation controls on subduction-related plutons and dike swarms in
- southern Patagonia (Torres del Paine area) and the low Nb/Ta of upper crustal igneous rocks.
- 817 Contribution to Mineralogy and Petrology, 173, 1–22.
- Nabelek, P. I. and Labotka, T. C. (1993). Implications of geochemical fronts in the Notch
 Peak contact metamorphic aureole, Utah, USA. Earth and Planetary Science Letters. 119,
 539–559.
- 821 Newton, R. C., Charlu, T. V., & Kleppa, O. J. (1980). Thermochemistry of the high structural
- state plagioclases. *Geochimica et Cosmochimica Acta*, 44(7), 933-941.
- 823 Pattison, D.R.M., and Tracy, R.J. (1991) Phase equilibria and thermobarometry of
- 824 metapelites. Reviews in Mineralogy and Geochemistry, 105–206.
- 825 Pattison, D. R. M., and Tinkham, D. K. (2009). Interplay between equilibrium and kinetics in
- 826 prograde metamorphism of pelites: an example from the Nelson aureole, British Columbia.
- S27 Journal of Metamorphic Geology, 27(4), 249–279.
- 828 Powell, R., & Holland, T. (1999). Relating formulations of the thermodynamics of mineral
- solid solutions; activity modeling of pyroxenes, amphiboles, and micas. American
- 830 *Mineralogist*, 84(1-2), 1-14.
- 831 Putlitz, B., Baumgartner, L.P., Oberhänsli, R., Diamond, L. and Altenberger, U. (2001) The
- 832 Torres del Paine Laccolith (Chile); intrusion and metamorphism. LPI Contribution, abstract
- 833 no. 3534.

- 834 Roselle, G.T., Baumgartner, L.P. and Valley, J.W. (1999) Stable isotope evidence of
- heterogeneous fluid infiltration at the Ubehebe Peak contact aureole, Death Valley National
- 836 Park, California. American Journal of Science, 299, 93–138.
- 837 Sheppard, S.M.F. (1986) Characterization and isotopic variations in natural waters. Reviews
- in Mineralogy and Geochemistry, 16, 165–184.
- 839 Siron, G., Baumgartner, L.P., and Bouvier, A.-S. (2018a) Significance of OH, F and Cl
- 840 content in biotite during metamorphism of the Western Adamello contact aureole.
- 841 Contributions to Mineralogy and Petrology, 173, 1–19.
- 842 Siron, G., Baumgartner, L.P., Bouvier, A.-S., and Vennemann, T. (2018b) Accurate
- Measurements of H 2O, F and Cl Contents in Biotite Using Secondary Ion Mass
 Spectrometry. Geostandards and Geoanalytical Research, 363, 229–16.
- 845 Sisson V. B. (1987) Halogen chemistry as an indicator of metamorphic fluid interaction with
- 846 the Ponder pluton, Coast Plutonic Complex, British Columbia, Canada. Contribution to
- 847 Mineralogy and Petrology, 95, 123–131.
- 848 Smye, A.J., Bickle, M.J., Holland, T.J.B., Parrish, R.R., and Condon, D.J. (2011) Rapid
- 849 formation and exhumation of the youngest Alpine eclogites: A thermal conundrum to
- Barrovian metamorphism. Earth and Planetary Science Letters, 306, 193–204.
- 851 Spear, F.S. (1993) Metamorphic Phase Equilibria and Pressure-Temperature Paths,
- 852 *Mineralogical Society of America, Washington D.C.*, 799 p.
- Speer, A.J. (1984) Micas in Igneous Rocks. Reviews in Mineralogy and Geochemistry, 13,
 299–356.
- 855 Süssenberger, A., Schmidt, S.T., Wemmer, K., Baumgartner, L.P., and Grobety, B. (2017)
- 856 Timing and thermal evolution of fold-and-thrust belt formation in the Ultima Esperanza
- 857 District, 51°S Chile: Constraints from K-Ar dating and illite characterization. Geological
- 858 Society of America Bulletin, 130, 975–998.
- Suzuoki, T. and Epstein, S. (1976) Hydrogen isotope fractionation between OH-bearing
 minerals and water. Geochimica and Cosmochimica Acta, 40, 1229–1240.
- 861 Tajčmanová, L., Connolly, J.A.D., and Cesare, B. (2009) A thermodynamic model for

- 862 titanium and ferric iron solution in biotite. Journal of Metamorphic Geology, 27, 153–165.
- Tuttle, O. F., and Bowen, N. L., 1958, Origin of granite in the light of experimental studies in 863
- 864 the system NaAlSi3O8-KAlSi3O8-SiO2-H2O: Geological Society of America Memoir 74,
- 865 153 p.
- Waldbaum, D. R., & Thompson, J. B. (1968). Mixing Properties Of Sanidine Crystalline 866
- 867 Solutions .2. Calculations Based On Volume Data. American Mineralogist, 2000-2017.
- 868 Waters, D. J., and Lovegrove, D. P. (2002). Assessing the extent of disequilibrium and
- overstepping of prograde metamorphic reactions in metapelites from the Bushveld Complex 869
- 870 aureole, South Africa. Journal of Metamorphic Geology, 20, 135-149.
- 871 Webster, J.D., Vetere, F., Botcharnikov, R.E., Goldoff, B., McBirney, A., and Doherty, A.L.
- 872 (2015) Experimental and modeled chlorine solubilities in aluminosilicate melts at 1 to 7000
- 873 bars and 700 to 1250 °C: Applications to magmas of Augustine Volcano, Alaska. American
- 874 Mineralogist, 100, 522-535.
- Wilson, T.J. (1991) Transition from back-arc to foreland basin development in the southern-875 876 most Andes: Stratigraphic record from the Ultima Esperanza District, Chile. Geological 877 Society of America Bulletin, 103, 98–111.
- 878 White, R. W., Pomroy, N. E., & Powell, R. (2005). An in situ metatexite-diatexite transition 879 in upper amphibolite facies rocks from Broken Hill, Australia. Journal of Metamorphic 880 Geology, 23(7), 579-602.
- 881 Zhu, C. and Sverjensky, D.A. (1991) Partitioning of F-Cl-OH between minerals and 882 hydrothermal fluids. Geochimica Et Cosmochimica Acta, 55, 1837–1858.
- Zhu, C., and Sverjensky, D.A. (1992) F-Cl-OH partitioning between biotite and apatite. 883 884 Geochimica et Cosmochimica Acta, 56, 3435–3467.
- 885
- 886

APPENDIX

- 887
- 888 All pseudosections were computed using the 2002 version of the Holland and Powell (1998)

- 889 thermodynamic database (hp02ver in Perple X). Activity-composition models used for each 890 mineral for thermodynamic modelling are as follow: 891 Biotite: Bio(TCC), Tajcmanova et al. (2009) _ 892 White mica: Mica(SGH), Smye et al. (2011) -Plagioclase: Pl(h), Newton et al. (1980) 893 -894 Orthoclase: San, Waldbaum and Thompson (1968) _ 895 Chloritoid: Ctd(SGH), Smye et al. (2011) _ Cordierite: hCrd, White et al. (2005) 896 -897 Chlorite: Chl(SGH), Smye et al. (2011) -898 Staurolite: St(HP), Powell and Holland (1999) _ 899 900 901 902 **Figure Captions**
- 903

904 Figure 1: (a) Geological map of the Torres del Paine Intrusion (TPI); The TPIC has a west-905 east and a North-South extension of about 12 and 8 km, respectively. The TPI is a bimodal 906 laccolith which consists of three older granitic (12.59-12.50 Ma, Michel et al. 2008; Leuthold 907 et al., 2012), an older mafic unit (12.6Ma) and three youngers mafic (12.5-12.43 Ma, 908 Leuthold et al. 2012) pulses. It intruded into the sediments of the Punta Barrosa and Cerro 909 Toro formations. The investigated localities are situated in the Cerro Toro formation (black 910 stars). (b) A profile above and below the intrusion was investigated at the Cuerno Principal, 911 at the south end of the TPI. The thickness of the contact aureole is indicated by the 912 perpendicular white line. It is 400 and 150 m below and above the intrusion, respectively. (c) 913 The thickness of the contact aureole at the investigated profile on the Cerro Fortaleza is larger 914 than what was collected, because the summit still contains cordierite. The thickness from the

915 upper contact to the summit is 260 m. At the Fortaleza the intrusion is thicker than at the 916 other profile localities. It is at least 1.5 km thick; the bottom of the intrusion is not exposed. 917 (d) The Monte Almirante is situated at the east end of the laccolith. This represents the front 918 end of the magma injection (Baumgartner et al., 2007). One profile above the intrusion was 919 investigated. The contact aureole thickness is 200 m. (e) The profile in the Valle Frances is 920 situated at the side of the intrusion. The thickness of the contact aureole is approximately 921 200m, measured perpendicular to the subvertical contact. (b)-(e) Abbreviations: CPa (Cuerno 922 Principal above), CPb (Cuerno Principal below), F (Fortaleza), A (Almirante) and VF (Valle 923 Frances).

924

925 Figure 2: BSE images of different samples of the Torres del Paine contact aureole showing 926 textural change during metamorphism and fluid infiltration; a) big grains of detritic quartz 927 (qtz) and metamorphic cordierite (crd). The sample 07TP56 is located at 300m from the 928 contact; b) detritic muscovite in sample 07TP55 at 400m from the contact; c) The decrease in grain size of cordierite and quartz is well shown in this image from sample 07TP58 at 150m 929 from the contact; d) Altered cordierite, which is dissolved along grain boundaries (crd') is 930 931 shown in this image from sample 12P22, located at the contact. Abundant retrogression of cordierite and biotite to chlorite + muscovite (chl+ms) is shown. Plagioclase (pl) and quartz 932 933 (qtz) are equigranular and homogeneously distributed in the rock; e) retrograde muscovite is 934 present in sample 10TP57 collected at the contact with the intrusion. Note that biotite from 935 this sample has the highest Cl content. Biotite has well defined, straight grain boundaries and 936 is more homogeneously distributed at the thin section scale; f) chlorite + muscovite intergrowth in sample 10TP54, collected at 1m from the contact. Note that this sample 937 938 contains low chlorine content biotite. Mineral abbreviations after Kretz (1983).

940 Figure 3: Biotite compositions from the profile below the intrusion at the Cuerno Principal 941 location; a) There are two different Ti vs X_{Mg} different trends defined by the data: biotites with low Cl content show relatively low X_{Mg} -values, while samples close to the contact have 942 943 higher X_{Mg} values. In either case, the X_{Mg} values decrease with increasing Ti with increasing 944 temperature, and the high Cl content at higher X_{Mg}; b) Cl content in biotite plotted against the 945 distance from the intrusion. No trend in chlorine content is observed for most samples. Only 946 two samples in the immediate vicinity of the intrusion show high chlorine concentrations 947 reflecting igneous fluid infiltration.

948

Figure 4: AFM triangular plot of all the bulk rock composition from the Torres del Paine contact aureole (n=71). The diagram was constructed by projecting from muscovite, quartz, and fluid. The FeO content was corrected for ilmenite, the major Ti oxide phase found in these rocks. White symbol represents the bulk rock composition (sample 07TP56) chosen for thermodynamic modeling.

954

955 Figure 5: a) T-X_{Mg} pseudosection was calculated for the bulk composition of sample 07TP56 by keeping the measured sum of FeO+MgO constant, but varying X_{Mg}. The dark grey range 956 957 outlines the variation of composition for the Torres del Paine rocks. The hatched area 958 represent the stability field of andalusite; b) P-T pseudosection for the composition of 959 07TP56, x-axis is shared with c); a) and b) are projected through ilmenite and graphite, fields 960 correspond to 1) Chl + Ms + Crd, 2) Chl + Ms + Crd + Bt, 3) Ms + Crd + Bt + Kfs; c) Modes 961 for the major minerals in the Torres del Paine contact aureole at 750 bars, the major isograds 962 are highlighted in grey (crd+, bt+, Chl-, Kfs+ and Ms-).

964 Figure 6: Fluid infiltration textures seen in the field are restricted to localized fractures and 965 dykes. a) Many dykes emanate from the roof and the distal parts of the Torres del Paine intrusion. Here an image of a typical dyke emanating from the frontal part into the host rocks 966 967 in the Co. Almirante Nieto area. Note that the dykes split up into a myriad of dyklets. Each 968 dykelet transitions into a veinlet, which can be followed for about 10m. These horse-tail like 969 dykes are common around the intrusion. See also Müntener et al. (2018). b) Bleaching zones 970 at the contact and surrounding dyklets are common. They are typically only a few 10's of 971 centimeters wide.

972

Figure 7: Bulk rock isotopic measurements are shown, with symbols keyed to the different profiles. a) Oxygen isotope compositional variations are small, and do not show any conclusive trends with respect to distance to the intrusion b) Hydrogen isotope vary systematically as a function to the distance of the intrusion in all profiles. Compositions first decrease towards the intrusion and slightly increase towards the contact. See text for more details.

979

Figure 8: Cl content in metamorphic biotite from the contact aureole plotted against distance 980 981 from the intrusion for the 5 studied profiles; a) Cuerno Princiapl below (CPb) profile; b) 982 Cuerno Principal above (CPa) profile; c) Mte. Almirante profile; d) Fortaleza profile; e) Valle Frances profile; f) Average Cl content distribution in the contact aureole for the 5 profiles 983 studied, symbols are the same as in panels a), b), c) d), e). Note that chlorine concentration is 984 985 low in the far-field of the aureole in all samples, while some samples show elevated concentrations of chlorine close to the contact. Note however, that not all samples in the 986 987 proximity of the contact are elevated.

Figure 9: Cl content in metamorphic biotite in the contact aureole plotted against X_{Mg} composition for the 5 studied profiles; a) Cuerno Princiapl below (CPb) profile; b) Cuerno Principal above (CPa) profile; c) Mte. Almirante profile; d) Fortaleza profile; e) Valle Frances profile; f) Average Cl content vs X_{Mg} for all profiles, symbols are the same as in panels a), b), c) d), e). No correlation between X_{Mg} and Cl content in biotite can be found, in contradiction with the Mg-Cl avoidance rule.

995

996 Figure 10: Schematic temperature-time evolution diagram showing the fluid infiltration 997 events for samples located close to the contact of the intrusion. The suggested relative fluid 998 infiltration events are shown with bold lines. Note that high salinity fluids from the intrusions 999 infiltrated the metapelites post-peak, but still in the stability field of biotite and likely K-1000 feldspar. Subsequent infiltration produced first retrograde, coarse muscovite, then fine 1001 grained muscovite and chloride in the pinitized cordierites. While fluid infiltration is shown 1002 as discrete events, fluid infiltration might have been continuous in time, but localized in 1003 space.

	Muscovite				
	07TP55	1sd	07TP56	1sd	07TP58
SiO ₂	49.79	(5.66)	49.01	(1.51)	47.19
TiO ₂	0.1	(0.17)	0.16	(0.09)	0.34
Al_2O_3	32.82	(5.39)	32.66	(2.06)	36.15
FeO	1.87	(1.19)	2.03	(0.47)	0.99
MgO	1.42	(1.45)	1.46	(0.38)	0.52
MnO	0.01	(0.02)	0.01	(0.01)	0.01
CaO	0.08	(0.17)	0.13	(0.31)	0.02
K ₂ O	8.84	(1.19)	8.74	(0.61)	9.41
Na ₂ O	0.54	(0.39)	0.79	(0.61)	0.48
F	0.06	(0.08)	0.05	(0.02)	0.04
Cl	b.d.l.		b.d.l.		b.d.l.
O = F	0.02	(0.03)	0.02	(0.01)	0.02
Total	95.51	(1.48)	95.02	(0.7)	95.14
Al ^{tot}	5.076	(0.854)	5.091	(0.633)	5.617
Si	6.531	(0.626)	6.481	(0.363)	6.219
IVΔI	1.469	(0.626)	1.519	(0.363)	1.781
Sum	8	, , , , , , , , , , , , , , , , , , ,	8		8
VIAL	3.607	(0.323)	3.572	(0.285)	3,836
Fo	0.206	(0.133)	0.224	(0.107)	0.11
Μσ	0.200	(0.133)	0.224	(0.107)	0.11
Mn	0.278	(0.287)	0.289	(0.132)	0.102
Ti	0.001	(0.002)	0.001	(0.003)	0.001
Sum	4.102	(0.175)	4.102	(0.176)	4.082
			=.		
K	1.48	(0.218)	1.474	(0.209)	1.583
Na	0.069	(0.049)	0.101	(0.156)	0.062
Ca	0.011	(0.023)	0.019	(0.087)	0.003
Sum	1.559	(0.225)	1.594	(0.072)	1.648
F	0.025	(0.033)	0.023	(0.02)	0.018
Cl	b.d.l.		b.d.l.		b.d.l.
X _{Ma} ^a	0.549	(0.165)	0.559	(0.08)	0.48
$^{VI}R^{2+} / (^{VI}R^{2+} + ^{VI}R^{3+})$	0.118	(0.097)	0.126	(0.060)	0.052

Table 1: major element compositions of mucovite from the Cuerno Principal below gradient, Structural formulae are computed using 44 charges or 22 equivalent oxygens.

Distance (m)	400	300	150
Estimated T (°C) ^b	470	490	510

^a compute as follow : $X_{Mg} = Mg / (Mg + Fe)$

^b Estimated from phase petrology and distance from the contact

b.d.l. : below detection limit

determined by electron microprobe.

1sd	10TP54	1sd	10TP57	1sd
(1.33)	49.83	(6.37)	47.43	(1.14)
(0.31)	0.04	(0.05)	0.03	(0.1)
(0.7)	34.87	(5.76)	35.76	(1.23)
(0.2)	1.26	(0.28)	1.29	(0.48)
(0.12)	0.63	(0.09)	0.91	(0.28)
(0.01)	0.02	(0.02)	0.02	(0.02)
(0.02)	0.02	(0.02)	0	(0.01)
(0.69)	8.95	(2.1)	10.22	(0.26)
(0.04)	0.54	(0.33)	0.48	(0.05)
(0.03)	0.06	(0.09)	0.08	(0.05)
	b.d.l.		b.d.l.	
(0.01)	0.02	(0.04)	0.03	(0.02)
(1.24)	96.2	(1.35)	96.18	(2.13)
(0.2)	5.332	(0.934)	5.536	(0.087)
(0.225)	6.46	(0.704)	6.221	(0.046)
(0.225)	1.54	(0.704)	1.779	(0.046)
	8		8	
<i>.</i>				<i>.</i>
(0.085)	3.792	(0.246)	3.756	(0.065)
(0.047)	0.137	(0.027)	0.152	(0.034)
(0.049)	0.122	(0.017)	0.181	(0.066)
(0.002)	0.002	(0.002)	0.002	(0.002)
(0.062)	0.004	(0.005)	0.003	(0.011)
(0.05)	4.057	(0.211)	4.094	(0.026)
(0.000)	4 400	(0,000)	4 700	(0.055)
(0.239)	1.483	(0.386)	1.703	(0.055)
(0.011)	0.068	(0.04)	0.062	(0.003)
(0.005)	0.003	(0.002)	0.001	(0.002)
(0.235)	1.554	(0.351)	1.765	(0.053)
(0 024)	በ በ1ዩ	(0 030)	0 03	(0 017)
(0.024)	6.018 h d l	(0.039)	0.03 h d l	(0.017)
	D.U.I.		D.U.I.	
(0.048)	0.472	(0.042)	0.543	(0.044)
(0.022)	0.065	(0.013)	0.082	(0.023)

5	1	
590	600	

	Plagioclases					
	071	⁻ P56	071	P58	07T	P63
	low X _{An}	high X _{An}	low X _{An}	high X _{An}	low X _{An}	high X _{An}
SiO ₂	68.81	61.03	66.69	64.50	59.60	49.16
TiO ₂	0.02	0.01	0.01	0.01	0.00	0.02
Al ₂ O ₃	19.97	23.93	20.92	22.40	25.49	32.68
MgO	0.00	0.01	0.00	0.00	0.00	0.00
FeO	0.27	0.25	0.27	0.28	0.28	0.29
CaO	0.31	5.76	2.08	3.56	7.52	16.11
K ₂ O	0.03	0.06	0.14	0.17	0.06	0.06
Na ₂ O	11.92	8.58	10.77	9.80	7.39	2.40
Total	101.33	99.62	100.88	100.71	100.35	100.76
Si	2.974	2.726	2.910	2.831	2.652	2.235
Al	1.017	1.260	1.076	1.159	1.337	1.751
Sum	3.992	3.985	3.985	3.990	3.989	3.985
Na	0.999	0.743	0.911	0.834	0.638	0.212
Са	0.014	0.276	0.097	0.167	0.359	0.785
К	0.002	0.003	0.009	0.010	0.004	0.003
Sum	1.015	1.022	1.017	1.011	1.000	0.999
X _{An} ^a	0.014	0.270	0.096	0.166	0.359	0.786
X _{Ab} ^b	0.984	0.727	0.896	0.825	0.638	0.212
X _{Or} ^c	0.002	0.003	0.008	0.010	0.004	0.003
Distance (m)	300	300	150	150	10	10
Estimated T (°C) ^d	480	480	510	510	560	560

Table 3: representative major element compositions of feldspars from the Cuerno Principal below gradie

^a Compute as follow: Ca / (Na + Ca + K)

^b Compute as follow: Na / (Na + Ca + K)

^c Compute as follow: K / (Na + Ca + K)

^d Estimated from phase petrology and thermodynamic modelling

ent, determined by EPMA.

	K-feldspars		
10P54	07TP58	10TP54	10TP57
62.84	65.16	65.18	65.18
0.03	0	0	0
23.01	18.45	18.44	18.59
0.01	0.0612	0.0084	0.0145
0.22	0.4052	0.3017	0.1368
4.70	0.0127	0.0261	0.028
0.19	11.99	13.85	14.05
9.25	2.45	1.74	1.83
100.25	98.5396	99.5485	99.8904
2.782	3.006	3.001	2.994
1.200	1.003	1.001	1.007
3.982	4.009	4.001	4.001
0.794	0.219	0.155	0.163
0.223	0.001	0.001	0.001
0.011	0.765	0.882	0.893
1.028	0.985	1.039	1.058
0.217	0.001	0.001	0.001
0.772	0.222	0.149	0.154
0.011	0.777	0.849	0.845
Г	150	F	4
5	150	5	T
570	510	590	600

	Biotite				
	07TP55	1sd	07TP56	1sd	07TP58
SiO ₂	35.92	(3.81)	35.06	(1.1)	35.15
TiO ₂	1.4	(0.2)	1.98	(0.58)	2.75
Al ₂ O ₃	20.08	(1.24)	19.68	(0.95)	20.08
FeO	21.58	(0.96)	21.94	(0.76)	21.41
MgO	7.71	(0.43)	7.45	(0.53)	6.93
MnO	0.06	(0.03)	0.07	(0.03)	0.07
CaO	0.03	(0.1)	0.03	(0.06)	0.16
K ₂ O	7.86	(0.52)	7.77	(0.64)	8.27
Na ₂ O	0.13	(0.06)	0.19	(0.2)	0.1
F	0	(0)	0	(0)	0
Cl	0.01	(0.01)	0.01	(0.01)	0.02
O = F	0	(0)	0	(0)	0
Total	94.79	(1.25)	94.18	(1.36)	94.94
Al ^{tot}	3.612	(0.301)	3.578	(0.136)	3.621
Si	5.477	(0.414)	5.409	(0.104)	5.378
^{IV} AI	2.523	(0.414)	2.591	(0.104)	2.622
Sum	8		8		8
^{VI} AI	1.09	(0.139)	0.987	(0.136)	0.999
Fe	2.754	(0.179)	2.831	(0.132)	2.74
Mg	1.753	(0.135)	1.715	(0.129)	1.581
Mn	0.008	(0.004)	0.009	(0.004)	0.01
Ti	0.161	(0.026)	0.231	(0.069)	0.316
Sum	5.765	(0.187)	5.773	(0.141)	5.646
к	1.53	(0.132)	1.53	(0.12)	1.614
Na	0.019	(0.01)	0.028	(0.029)	0.015
Са	0.006	(0.016)	0.006	(0.009)	0.027
Sum	1.555	(0.139)	1.563	(0.12)	1.656
F	0	(0)	0	(0)	0
Cl	0.002	(0.001)	0.003	(0.003)	0.004
X _{Mg} ^a	0.389	(0.009)	0.377	(0.015)	0.366
Distance (m)	400		300		150

Table 3 : major element compositions of biotite from the Cuerno Principal below gradient, $d_{\rm i}$

Ti-in biotite T (°C) ^b	512	593	648
Estimated T (°C) ^c	470	490	510

^a compute as follow : $X_{Mg} = Mg / (Mg + Fe)$

 $^{\rm b}$ Computed from biotite composition using the Ti-in biotite geothermometer from Henry et

^c Estimated from phase petrology and distance from the contact

etermined by electron microprobe.

1sd	07TP63	1sd	10TP54	1sd	10TP57	1sd
(1.42)	35.92	(0.55)	35.67	(0.77)	35.84	(1.56)
(1.39)	1.71	(0.18)	4.04	(0.81)	3.39	(0.62)
(1.11)	17.51	(0.77)	18.48	(0.57)	18.57	(1.34)
(1.13)	21.03	(0.4)	21.83	(0.67)	20.52	(0.9)
(0.71)	9.9	(0.75)	6.74	(0.63)	7.85	(0.41)
(0.03)	0.18	(0.03)	0.1	(0.03)	0.19	(0.09)
(1.22)	0.07	(0.09)	0.05	(0.11)	0.01	(0.02)
(0.46)	9.16	(0.34)	9	(0.28)	9.36	(0.25)
(0.05)	0.11	(0.06)	0.16	(0.33)	0.1	(0.04)
(0)	0	(0)	0	(0)	0.03	(0.08)
(0.01)	0.16	(0.02)	0.01	(0.01)	0.18	(0.02)
(0)	0	(0)	0	(0)	0.01	(0.04)
(2.12)	95.76	(0.88)	96.09	(0.9)	96.03	(1.07)
(0.18)	3.155	(0.131)	3.317	(0.099)	3.328	(0.218)
(0.111)	5.491	(0.059)	5.434	(0.076)	5.448	(0.146)
(0.111)	2.509	(0.059)	2.566	(0.076)	2.552	(0.146)
	8		8		8	
(0 233)	0.646	(0 124)	0 751	(0 125)	0 775	(0 209)
(0.255)	0.040	(0.124)	0.751	(0.123)	0.775	(0.205)
(0.161)	2.689	(0.061)	2.781	(0.094)	2.609	(0.149)
(0.176)	2.257	(0.169)	1.531	(0.152)	1.779	(0.114)
(0.004)	0.023	(0.004)	0.013	(0.004)	0.024	(0.011)
(0.157)	0.197	(0.022)	0.403	(0.092)	0.388	(0.074)
(0.141)	5.612	(0.040)	5.559	(0.122)	5.570	(0.092)
(0.077)	1.786	(0.062)	1.75	(0.055)	1.816	(0.066)
(0.008)	0.017	(0.01)	0.023	(0.047)	0.015	(0.007)
(0.204)	0.012	(0.015)	0.007	(0.017)	0.002	(0.003)
(0.201)	1.815	(0.058)	1.78	(0.035)	1.833	(0.066)
(0)	0	(0)	0	(0)	0 001	(0 004)
(0) (2) (0)	0 041	(0,005)	5 200 0	(0 002)	0.046	(0.004)
(0.003)	0.041	(0.005)	0.000	(0.002)	0.040	(0.000)
(0.033)	0.456	(0.021)	0.355	(0.022)	0.405	(0.013)
	10		5		1	

575	706	686
580	590	600

al. (2005)

	07TP55	07TP56	07TP58	10TP54
SiO ₂	49.53	48.47	48.92	48.59
TiO ₂	0.02	0.01	0.03	0.01
AI_2O_3	31.89	32.43	32.92	32.66
MgO	6.71	6.79	6.5	6.62
FeO	10.25	10.43	11.35	10.88
MnO	0.24	0.24	0.21	0.28
CaO	0.08	0.05	0.02	0.02
Na ₂ O	0.34	0.28	0.18	0.18
K ₂ O	0.05	0.04	0.03	0
Cl	0	0	0.01	0.01
Total	99.11	98.73	100.17	99.26
Ci .	5 102	5 024	5 012	5 017
ΔI	3 873	3 961	3 976	3 97/
	5.075	5.501	5.570	5.574
Mg	1.031	1.049	0.993	1.019
Fe	0.883	0.904	0.973	0.939
Mn	0.021	0.021	0.018	0.025
Са	0.009	0.005	0.002	0.003
Na	0.067	0.056	0.036	0.036
К	0.006	0.005	0.004	0
Cl	0	0	0.001	0.002
X., ^a	0 520	0 527		
Mg	0.339	0.007	0.303	0.52
Distance (m)	400	300	150	5
Estimated T (°C)	470	490	510	590

Table 5: Representative cordierite major element compositions (wt%) from lower profile of Cuerno Principal (CPb)

^a Compute as follow : $X_{Mg} = Mg / (Mg + Fe)$

^b Estimated from phase petrology and distance from the contact

Table 5: Isotopic compositions for whole rock granites, quartz and biotites from granite and quartz from miaroles

		¹⁸ O	δD
Granites	Whole rock	7.1 - 9.1 ‰	
	Quartz Biotite	9.1 - 9.9 ‰ 5.1 - 6.0 ‰	-97 to -95 ‰
Quartz fror	n cavities	8.8 - 11.1 ‰	-88 to -83 ‱

Sample	Profile	distance	¹⁸ O (‰)	δD (‰)
09TP6	А	1	9.73	-90.38
09TP9	А	3	12.83	-93.31
09TP11	А	35	13.63	-81.84
09TP13	А	75	13.31	-86.69
09TP14	А	100	13.65	-95.39
09TP15	А	120	12.89	-103.29
09TP18	А	150	13.28	-101.26
09TP19	А	180	13.56	-93.34
09TP22	А	250	11.13	-82.39
10P55	A*	40	-	-95.24
0770.00	0.51	10	40.00	00.40
071P63	CPb	10	13.92	-82.13
07TP60	CPb	50	14.67	-85.13
07TP59	CPb	120	14.53	-89.21
07TP58	CPb	150	14.43	-85.93
07TP56	CPb	300	14.51	-78.72
07TP55	CPb	400	15.02	-76.92
07TP54	CPb	520	14.61	-
07TP45	CPb	520	15.06	-79.74
07TP53	CPb	600	14.74	-71.92
07TP48	CPb	670	14.79	-75.71
07TP52	CPb	700	14.49	-73.11
10P103	СРа	2	11.94	-85.83
10P105	CPa	2	12.98	-94.15
10P111	СРа	2	9.92	-110.76
10P84	СРа	2	13.11	-97.24
10P72	СРа	10	13.02	-94.49
10P78	СРа	10	13.8	-90.01
10P91	СРа	23	14.09	-85.49
10P95	СРа	30	13.36	-84.47
10P86	СРа	80	-	-98.14
10P99	СРа	155	10.77	-90.92
10P101	СРа	215	11.21	-91.08
			_	
10P144	F	1	23.11	-97.32
10P142	F	8	13.15	-95.41
10P140	F	26	13.22	-94.4
10P138	F	40	13.18	-101.72
10P134	F	80	12.21	-102.78
10P130	F	130	13.14	-93.39

Table 6: bulk rock isotopic measurements in the Torres del Paine aureole

10P120	F	200	13.75	-90.01
10P118	F	230	13.38	-85.54
10P114	F	265	13.42	-96.73
L5	S	>1500	15.08	-80.77
L2A	S	>1500	14.86	-86.64
L17	S	>1500	12.68	-75.41
L12	S	>1500	13.27	-88.33
L20	S	>1500	13.47	-78.94
L23	S	>1500	13.44	-89.32
L31	S	>1500	13.15	-78.03
L40	S	>1500	-	-75.08

Profiles: A = Almirante; A* = Almirante samples with a small offset from regular profile; CPb = Cuerno Principale below; CPa = Cuerno Principale above; F = Fortalezza

N





Ε

Figure 2























