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# Halogen (F, CI, Br, I) behaviour in subducting slabs: a study of lawsonite blueschists in western Turkey

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2	Halogen (F, Cl, Br, I) behaviour in subducting slabs: a
3	study of lawsonite blueschists in western Turkey
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#### 31 Abstract

32 We examined the F, Cl, Br and I abundance of minimally retrogressed lawsonite 33 blueschists from the Tavsanli Zone in northwest Turkey to evaluate the behaviour of 34 halogens in subduction zones, and to determine the role coexisting high pressure minerals 35 may play in transporting the halogens to the Earth's mantle. The blueschists contain sodic 36 amphibole and lawsonite, with variable amounts of phengite and chlorite, and minor 37 apatite. A positive correlation between Cl, Br and I contents in bulk rocks suggests their 38 overall coherent behaviour in subduction zones, although high ratios of I/Cl and Br/Cl 39 compared to altered oceanic crust indicate that Cl is preferentially lost relative to Br and I 40 before or during blueschist metamorphism. Iodine and F are enriched relative to altered 41 oceanic crust, suggesting incorporation from marine sediments. In situ analyses of 42 minerals in thin sections reveal F preferentially concentrates in apatite (avg. 3.13 wt%), 43 over phengite (482 ppm), lawsonite (avg. 413 ppm) and Na-amphibole (257 ppm). 44 Chlorine also preferentially resides in apatite (138 ppm), followed by equal partitioning 45 between phengite (59 ppm) and Na-amphibole (56 ppm), and lower concentrations in 46 lawsonite (27 ppm). Upon apatite decomposition at a depth of ~200 km, F may 47 redistribute into lawsonite and phengite in slabs, whilst Cl is likely expelled to the 48 overlying mantle wedge. Given the stability of lawsonite and phengite to a depth of 280-49 300 km in cold subduction zones, they may transport F beyond subarc depths, 50 contributing to the high F in magmas derived from the deep mantle. 51

### 52 Keywords

53 Subduction; Halogens; Fluorine; Lawsonite; Phengite; Deep mantle

55 **1. Introduction** 

56 Halogens are predominantly concentrated in the Earth's surface reservoirs, including 57 seawater and sediments. Their concentrations are low in the primitive mantle, with 58 current estimates of 18 ppm F, 1.4 ppm Cl, 0.0036 ppm Br and 0.001 ppm I (Lyubetskaya 59 & Korenaga 2007). As halogens are not compatible with mantle minerals, they are 60 preferentially removed from the mantle during partial melting, and as such their 61 concentrations are even lower in the depleted MORB mantle (DMM). Despite having low 62 concentrations in the mantle, halogens are abundant in mantle-derived magmas, and are 63 continuously discharged from volcanoes of a variety of settings. For example, F and Cl 64 are the most abundant constituents of volcanic gases discharged from arc volcanoes after 65  $H_2O$ ,  $CO_2$  and S species (Symonds et al. 1994). The key mechanism responsible for 66 volcanic outputs is the recycling of elements from surface reservoirs to the mantle 67 through subduction. Many studies have primarily focused on Cl in subduction zones, 68 using it as a proxy for the other halogens (e.g. Scambelluri et al. 2004; Marschall et al. 69 2009). 70 During subduction, aqueous fluids released from the slab move upward to the overlying 71 mantle wedge, which leads to partial melting of the interior of the hot mantle wedge for 72 arc magmatism. The depth of fluid release is related to the geothermal gradient of the 73 subduction zone and the stability of hydrous minerals. As halogens are soluble in aqueous

fluids, their behaviour is expected to follow that of water, but the stability of hydrous

75 minerals differs widely, and hydrous minerals have varying ability to accommodate fluid-

76 mobile elements, including halogens. Therefore, the composition of fluids released from

77 slabs is likely to change with increasing depth. Furthermore, some hydrous minerals, 78 such as serpentine (~13wt% H<sub>2</sub>O), lawsonite (~11wt% H<sub>2</sub>O) and phengite (~4wt% H<sub>2</sub>O), 79 are stable to depths of 200-300 km in cold subduction zones (Schmidt & Poli 1998), far 80 beyond the depths beneath arcs. This suggests that these minerals are able to transport not 81 only water, but also fluid-mobile elements, to the deeper mantle. 82 Recent work has documented the importance of serpentinite in the transport and 83 fractionation of the halogens in subduction zones (e.g. John et al. 2011; Kendrick et al. 84 2013), with their findings suggesting Br and I are preferentially released relative to Cl 85 and F during serpentine phase transition and decomposition. However, there are few 86 studies documenting the abundance of halogens in other hydrous minerals. This paper 87 reports the abundance of halogens in lawsonite-bearing blueschists from the Tavsanli 88 Zone in northwestern Turkey using a variety of analytical techniques, and discusses the 89 behaviour of halogens, particularly F, in subduction zones and the implications for global 90 halogen recycling.

91

#### 92 2. Geological Setting

93 Turkey is comprised of several continental fragments that assembled during the Tertiary 94 collision of Laurasia and Gondwana. In western Turkey, the Izmir-Ankara-Erzincan 95 suture marks the collision of the southern and northern terranes. Prior to the collision, the 96 margin of the southern continent, the Anatolide-Tauride Block, was subducted to a depth 97 of 80 km by 80 Ma in an intra-oceanic subduction zone and was metamorphosed in 98 blueschist facies (Sherlock et al. 1999; Okay & Whitney 2010). The resulting blueschist 99 belt, known as the Tavsanli Zone, is exposed immediately south of the suture (Fig. 1). It

is primarily comprised of Paleozoic-Mesozoic metabasites and metasedimentary rocks
representing the subducted continental margin, in addition to tectonically overlying
oceanic accretionary complex and peridotite. The east-west trending Tavsanli Zone is 5060 km wide and approximately 250 km long (Okay & Whitney 2010). It is one of the
most extensive and well-preserved blueschist belts in the world with little retrogression
(Okay 1980).

106 In the western part of the Taysanli Zone, the Orhaneli Group blueschists are divided into 107 three units. The base is the quartz-mica-pelitic schists of the Kocasu Formation (Okay 108 2002), which gradually changes to the overlying Inönü Marble. The mica schist consists 109 of quartz, phengite, jadeite, chloritoid, Na-amphibole, lawsonite, and chlorite. The 110 assemblage constrains the peak metamorphic conditions to  $24 \pm 3$  kbar and  $430 \pm 30$  °C, 111 corresponding to a low geotherm of 5°C/km (Okay 2002). The uppermost unit, the 112 Devlez Formation, is composed of metabasite (>80 vol%) with minor metasedimentary 113 rocks metamorphosed under similar blueschist facies conditions (Okay 1980). The 114 metabasites contain euhedral lawsonite laths in a matrix of foliated sodic amphibole with 115 variable amounts of phengite and chlorite. Rb-Sr phengite ages of  $78.5 - 79.7 \pm 1.6$  Ma 116 likely reflect the age of metamorphism in the region (Sherlock et al. 1999). These 117 metabasites are the focus of this study.

- **Figure 1**: Simplified geological map of the Tavsanli Zone in northwestern Turkey
- 120 (modified from Okay & Whitney 2010). Sample outcrop locations are numbered and
- 121 marked with stars.



# 122

# 123 **3. Samples**

- 124 Lawsonite-rich metabasites were collected from three outcrops of the western Tavsanli
- 125 Zone (Fig. 1). All samples contain idioblastic lawsonite laths (< few mm in length) with
- 126 varying abundance of blue amphibole (**Table 1**). Samples are characterized by prograde
- 127 mineral assemblages with very little retrograde products (e.g. no secondary calcic
- amphibole, and only minor epidote and albite).
- 129 Samples TUR12 and TUR14 are blueschists collected in the Orhaneli region, near the
- town of Deliballar (Okay & Whitney 2010). TUR12 contains an intergrowth of prismatic
- 131 lawsonite (< 0.5 mm) and Na-amphibole grains (< 0.5 mm), with minor chlorite (**Fig.**

132 2a). Lawsonite contains inclusions of quartz, Na-amphibole and titanite. There are 133 interstitial quartz, apatite, Na-Ca pyroxene and minor epidote throughout the sample. 134 Large (up to 4 mm) euhedral lawsonite of TUR14 are highly fractured and contain 135 inclusions of Na-amphibole and minor quartz. They are set in a matrix of fibrous Na-136 amphibole prisms (and some larger grains up to 0.5 mm), in addition to fibrous chlorite 137 and minor rutile. Phengite grains are larger than in other samples (up to 0.3 mm), and are 138 often found in clusters (Fig. 2b). Blueschists from this region have been previously 139 described by Okay (2002). 140 One sample (TUR23) was collected from a blueschist outcrop near Harmancik (southeast 141 of Orhaneli). It contains clusters of idioblastic lawsonite laths (~ 1 mm length) along with 142 minor Na-amphibole needles (<0.2 mm) and minor titanite set in fine-grained aggregates 143 of phengite and chlorite (Fig. 2c). The surrounding dark matrix is composed of fine-144 grained actinolite, chlorite, titanite, apatite and pyrite. 145 The remaining samples (TUR30, 31, 32, 33) were collected from the Devlez Formation 146 near the village of Ketenlik, farther east along the Tavsanli Zone (Fig. 1). Sample TUR30 147 is characterized by elongated lawsonite laths surrounded by Na-amphibole, phengite, 148 quartz, minor apatite and minor titanite (Fig. 2d). The lawsonite laths of TUR31 vary in 149 size (up to 1 mm) and contain inclusions of quartz and titanite. They are surrounded by 150 green Na-amphibole, chlorite, interstitial quartz and disseminated albite and phengite 151 (Fig. 2e). Wide (up to 5 mm) quartz veins are also present in the sample. TUR32 shows 152 foliation defined by fibrous Na-amphibole and lawsonite laths (Fig. 2f). Na-amphibole is 153 compositionally zoned with Al-rich cores and Fe-rich rims. There is also minor chlorite, 154 quartz and titanite throughout the sample. Generally, TUR32 is more fine-grained than

155	the other three	samples from this area.	TUR33 contains	veins composed	l of large
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- 156 lawsonite laths (up to 5 mm), which are fractured and contain inclusions of Na-
- amphibole, apatite and magnetite, similar to those of TUR14. Lawsonite is surrounded by
- a matrix of fine-grained fibrous Na-amphibole, iron oxides, apatite, titanite, phengite and
- 159 minor chlorite (**Fig. 2g**). Some phengite forms aggregates up to 0.5 mm. Blueschists from
- this outcrop have been previously described by Okay (1980) and sampling locations are
- 161 described in the field trip guidebook by Okay & Whitney (2010).
- 162
- 163 **Table 1**: Summary of sample mineralogy of Tavsanli Zone blueschists in northwest
- 164 Turkey.

Outcrop No.	Sample	Mineralogy	7
in Figure 1	ID	Major	Minor
1	<b>TUR12</b>	Lws, Na-Amp, Chl, Jd, Ttn	Qtz, Ap, Ep
1	TUR14	Lws, Na-Amp, Ph, Chl	Qtz, Ttn, Rt, Ap
2	TUR23	Lws, Chl, Ph, Ttn	Na-Amp, Ap, Py
	TUR30	Lws, Na-Amp, Ph, Qtz, Chl	Ap, Ttn, Rt
2	<b>TUR31</b>	Lws, Chl, Ph, Qtz	Ap, Ttn, Ab
3	<b>TUR32</b>	Lws, Na-Amp, Qtz, Ab	Chl, Ttn, Ap
	<b>TUR33</b>	Lws, Na-Amp, Ph, Ap, Ttn	Fe-oxides, Chl

165

- 167 Figure 2: Photomicrographs of lawsonite blueschist samples from the Tavsanli Zone,
- 168 northwest Turkey. (a) TUR12, (b) TUR14, (c) TUR23, (d) TUR30, (e) TUR31, (f)
- 169 TUR32 ad (g) TUR33. Chl: chlorite, Cpx: clinopyroxene, Lws: lawsonite, Na-amp: Na-
- amphibole, Ph: phengite.



# 171

- 172 4. Analytical Methods
- 173 *4.1 Bulk-rock chemistry*
- 174 Bulk rock major and minor element composition was determined by ALS Global (North
- 175 Vancouver, Canada) using X-ray fluorescence (XRF) after fusion of rock powder with
- 176  $50/50 \text{ Li}_2\text{B}_4\text{O}_7/\text{LiBO}_2$ , and trace element composition was determined at the same facility
- 177 by ICP-MS following digestion of rock powder by concentrated HF-HNO<sub>3</sub>-HClO<sub>4</sub>-HCl.

#### 179 4.2 Halogen extraction: pyrohydrolysis + IC/ICP-MS

180 Amphibole-rich and lawsonite-rich fractions were separated from four samples (TUR14, 181 30, 32, 33) by hand under a binocular microscope. A phengite-rich fraction was also 182 collected from TUR14. The remaining samples were too fine-grained for separation. 183 Halogens were extracted from the mineral-rich fractions and bulk rock samples using a 184 modified pyrohydrolysis technique after Muramatsu et al. (2007) and references therein. 185 Method details are in Appendix A. 186 Analysis for F and Cl was carried out at the University of Ottawa using a Dionex Model 187 2100 Ion Chromatograph equipped with KOH eluent generator. Instrumental detection 188 limits  $(3\sigma)$  for F and Cl were 0.017 ppm and 0.034 ppm in solution, respectively. 189 Analysis for Br (79Br) and I (127I) was carried out at the University of Ottawa using an 190 Agilent 7700 ICP mass spectrometer. Instrumental detection limits  $(3\sigma)$  for Br and I were 191 0.022 and 0.041 ppb, respectively. Standard deviations  $(1\sigma)$  for duplicate or triplicate 192 analyses of samples are in the range 0.3-15 % for F, 1.7-36 % for Cl, 2.3-25% for Br, and 193 2.0-29% for I. Accuracy of the pyrohydrolysis technique is based on the analysis of four 194 international reference materials (BCR-2, JB-1, JB-3 and MRG-1). Precent yield ranges 195 from 76-93 % for F, 85-106 % for Cl, 66-111 % for Br, and 110-156 % for I (refer to

196 Table S1 in supplementary files for details).

#### 198 *4.3 Mineral chemistry*

199 4.3.1 Electron microprobe analysis (EPMA)

200 Na-amphibole, lawsonite and phengite were analyzed for Si, Ti, Al, Mg, Fe, Ca, Na, K,

- 201 Mn, Cr and Ni at the University of Ottawa with a JEOL 8230 electron microprobe using a
- 202 wavelength dispersive spectrometer. A 5 µm diameter 20 nA beam accelerated to 20 kV
- 203 was used. Peak counting times were 10s per element for the  $K\alpha$  lines of Fe, Mn, Cr and

204 Si, 20s for K, Ca, P, Al, Ti, Na and Mg, and 50s for Ni. Instrument calibration used

sanidine (Si, Al, K), diopside (Ca, Mg), albite (Na), hematite (Fe), tephroite (Mn), San

206 Carlos olivine (Ni), rutile (Ti), chromite (Cr) and apatite (P).

207 Mineral formulae of Na-amphibole grains were calculated using 23(O), and ferric and

208 ferrous iron contents were determined on the basis of stoichiometric composition after

209 normalizing to 8 Si atoms. For lawsonite, all iron was assumed to be  $Fe^{3+}$ , and mineral

210 formulae were determined using 8(O). Mineral formulae of phengite and the amount of

- 211  $Fe^{3+}$  were calculated based on stoichiometric composition and charge balance using
- 212 11(O).
- 213 The analytical conditions for apatite were 10 kV accelerating voltage, 4 nA beam current,

and 10 µm diameter beam size as recommended by Goldoff et al. (2012) for optimal

- analysis of fluor-chlorapatites. Each grain was analyzed in 1-3 spot(s), depending on
- 216 grain size. Peak counting times were 10s per element for Si ( $K\alpha$ ), Fe ( $K\alpha$ ), Mg ( $K\alpha$ ), K

217 (K $\alpha$ ), S (K $\alpha$ ), Ce (L $\alpha$ ), La (L $\alpha$ ) and As (L $\alpha$ ), 20s for Al (K $\alpha$ ), Ca (K $\alpha$ ), Na (K $\alpha$ ), P (K $\alpha$ ),

- 218 Sr ( $L\alpha$ ) and Cl ( $K\alpha$ ), and 50s for F ( $L\alpha$ ). Instrument calibration used sanidine (Si, Al, K),
- hematite (Fe), diopside (Mg), apatite (Ca, P, F), albite (Na), celestine (S, Sr), CePO<sub>4</sub>
- 220 (Ce), LaPO<sub>4</sub> (La), and GaAs (As). The apatite standard contains 3.53 wt% F. An LDE1

- 221 diffraction crystal was used to enhance the count of F. Apatite mineral formulae were
- 222 calculated based on normalizing to 13 (O, OH, F, Cl).

#### 223 4.3.2 Ion microprobe analyses by secondary ion mass spectrometer (SIMS)

224 Grains for *in situ* analyses were selected from EPMA-analyzed samples. Grains were

- cored from polished thin sections using a diamond-tipped drill bit, mounted in indium-
- filled Al holders, and gold-coated. Fluorine, Cl and H<sub>2</sub>O were measured by SIMS using a
- 227 Cameca 4f instrument at the Edinburgh Ion Microprobe Facility (EIMF), University of
- Edinburgh. A 5-nA primary beam of negative <sup>16</sup>O ions accelerated to 14.5 kV was used.
- 229 Pit diameter was *ca.* 15  $\mu$ m, depth of the analysis pits was <2  $\mu$ m. Total counting times
- 230 were 30s per isotope per analysis. Water and Cl were calibrated using an in-house
- 231 basaltic glass standard (St81-A9; Lesne et al. 2011). Fluorine was calibrated using T1-G
- 232 glass (Guggino and Hervig, 2010). Reproducibility for all elements, as determined by
- repeat measurements of glass standards, is better than 10% for all elements.
- The use of glass standards may introduce a bias due to matrix effects. Therefore,
- amphibole standards of known  $H_2O$ , F and Cl contents were used to calibrate the matrix
- effects associated with Fe-Mg hydrous silicates. Correction factors of 1.4 for F and 1.9
- for Cl were ascertained and applied to the analysis of Na-amphibole and phengite. No
- 238 matrix-induced fractionation was observed for H<sub>2</sub>O. Due to a lack of suitable standards
- for lawsonite, F and Cl contents of this mineral were calibrated using basaltic glass
- standards. Calibration curves can be found in supplementary material (**Fig. S1**).

#### 242 **5. Results**

#### 243 5.1 Bulk rock chemistry

244 Most samples have a basaltic chemical composition (44.4-52.1 wt% SiO<sub>2</sub>; Table S2 of 245 supplementary files). Sample TUR31 has a slightly higher SiO<sub>2</sub> content (58.0%), 246 reflecting the abundant quartz veinlets in thin section. Although the overall composition 247 is similar to that of tholeiitic basalts, the samples show some variations in major element 248 abundance due to the coarse-grained nature of the samples. Samples have variable CaO 249 (3.9-12.7 wt%) due to the presence of coarse-grained lawsonite, and moderate bulk-rock 250 Mg# (0.49-0.74). TiO<sub>2</sub> content of most samples (0.5-2.1 wt%) is consistent with a ridge 251 basalt protolith rather than an arc basalt (White & Klein 2014), and the presence of 252 phengite in most samples corresponds to elevated  $K_2O$  (0.34-0.82 wt%) relative to typical 253 N-MORB values. Two samples have very low bulk  $K_2O$  (<0.06%), and as a result 254 contain only a very minor amount of phengite. High  $P_2O_5$  (up to 0.67 wt%) in most 255 samples is consistent with the presence of apatite. Overall, major element data of the 256 Tvasanli Zone blueschists are consistent with their origin as basaltic rocks of the Izmir-257 Ankara Ocean.

258

#### 259 5.2 Mineral chemistry

260 5.2.1 Na-Amphibole

All amphiboles are sodic following the classification of Leake et al. (2003), with Na

- dominating the B-site ( $\geq$  1.50 pfu; Table S3; **Fig. 3**). Other than minor K (<0.01 pfu), the
- A-site is vacant in all samples except for TUR31 which has high Na (<1.92 pfu). Most

- samples are characterized by high  $Fe^{3+}$  (0.242 1.80 pfu) in the C-site. Amphibole
- 265 composition is similar to previous reports of blueschist amphiboles in this region (e.g.
- 266 Okay 2002, Davis & Whitney 2006) and other HP belts (e.g. Schliestedt 1986, Spandler
- 267 et al. 2003; **Fig. 3**).
- 268

- 269 Figure 3: Composition of amphiboles from lawsonite blueschists of the Tavsanli Zone,
- 270 northwestern Turkey. Classification based on B-site (B<sub>2</sub>) occupancy according to Leake
- et al. (2003). Modified from Hawthorne & Oberti (2006). For comparison, the
- 272 composition of other blueschists in Turkey (e.g. Okay 2002, Davis & Whitney 2006),
- 273 Greece (Schliestedt 1986) and New Caledonia (Spandler et al. 2003) are plotted.



<sup>275</sup> *5.2.2 Lawsonite* 

The lawsonite grains have near-ideal chemical composition with minimal variation
among different grains, and among different samples (Table S4). Total Fe content is
elevated, up to 2.3 wt%, compared to other lawsonites in blueschists worldwide (e.g.

279	Spandler et al. 2003), but the values are similar to those of lawsonite of the Sivrihisar
280	Massif in the eastern part of the Tavsanli Zone (Davis & Whitney 2006).
281	5.2.3 Phengite
282	Phengite is common in TUR14, TUR30 and TUR33, and is a minor constituent of
283	TUR23 and TUR31. In the latter, grains are small (< 100 $\mu m$ ) and often intergrown with
284	chlorite, making precise composition analysis difficult. Phengite composition in the
285	Deliballar outcrop sample (TUR14) covers a narrow range ( $Si = 3.4-3.5$ pfu; Table S5),
286	similar to previous reports for white mica in other lawsonite blueschists in the world (e.g.
287	Spandler et al. 2003; Davis & Whitney 2006; Bebout et al. 2007). A wider spread in Si
288	content (3.4-3.9 pfu) is observed for two samples from the Ketenlik outcrop (TUR30,
289	TUR33). From the same outcrop, phengite in TUR31 has low Si (3.2-3.4 pfu) and K/Na
290	(< 30; Fig. 4), suggesting this sample may have re-equilibrated at low temperatures.

**Figure 4:** Composition of phengite from lawsonite blueschists of the Tavsanli Zone,

293 northwestern Turkey. Atomic ratios of K/Na increases with increasing Si atoms per

294 formula unit (pfu). The compositions are similar to phengite in blueschists from other

- terranes, including New Caledonia (Spandler et al. 2003), the Catalina Schist, California
- 296 (Bebout et al. 2007), Mariana forearc (Pabst et al. 2012), and the Sivrihisar Massif of the
- 297 eastern Tavsanli Zone (Davis & Whitney 2006).



298

299 *5.2.4 Apatite* 

300 Apatite in all samples contain high F (2.64-3.75 wt%), but low Cl (<0.06 wt%),

- 301 classifying them as fluorapatites (Table S6; Fig. 5). In addition to CaO and  $P_2O_5$ , most
- 302 samples contain minor amounts of MgO (<0.07 wt%), Na<sub>2</sub>O (<0.09 wt%), K<sub>2</sub>O (<0.15
- 303 wt%), SrO (<0.41 wt%), Ce<sub>2</sub>O<sub>3</sub> (<0.64 wt%), La<sub>2</sub>O<sub>3</sub> (<0.63 wt%), Al<sub>2</sub>O<sub>3</sub> (<0.1 wt%), SO<sub>3</sub>

- 304 (<0.55 wt%), and As<sub>2</sub>O<sub>5</sub> (<0.17 wt%), along with variable FeO (<1.4 wt%) and SiO<sub>2</sub>
  305 (<2.3 wt%).</li>
- 306

**Figure 5**: Volatile contents (atomic proportion) in apatite from lawsonite blueschists of

308 the Tavsanli Zone, northwestern Turkey. Hydroxyl component calculated by difference

309  $(X_{OH} = 1 - X_F - X_{CI})$ . There is overlap with apatites from other HP belts (e.g. Svensen et al.

310 2001, John et al. 2008), however in general the Tavsanli blueschists have higher F.





#### 312 5.3 Halogens

#### 313 5.3.1 Mineral fractions and bulk rock by pyrohydrolysis

- Bulk rock Cl concentrations (8-22 ppm) are two orders of magnitude greater than those
- for Br (0.07-0.24 ppm) and I (0.13-0.52 ppm), with Br/Cl and I/Cl ratios covering a
- and narrow range (0.006-0.019 and 0.011-0.024, respectively; Table S7). Fluorine is the most
- abundant halogen in all bulk samples, with concentrations ranging from 222 to 616 ppm
- and corresponding F/Cl ratios of 25.3 to 74.1.
- 319 Mineral-rich fractions have a larger spread in halogen concentrations, particularly for F
- and Cl. Sodic amphibole-rich fractions show high F (198-608 ppm) compared to the
- heavier halogens (10-40 ppm Cl, 0.16-0.26 ppm Br, and 0.12-1.01 ppm I). Despite the
- 322 wider spread in heavy halogen concentrations, their ratios fall within narrow ranges
- 323 (0.005-0.016 Br/Cl, 0.011-0.025 I/Cl), but F/Cl ratios (7.9-38.4) do not. An even larger
- 324 spread is observed for the halogen concentrations of lawsonite-rich fractions (120-955
- 325 ppm F, 8-56 ppm Cl, 0.14-0.47 ppm Br, and 0.14-1.37 ppm I), but the spread in Br/Cl
- and I/Cl ratios is narrow (0.008-0.021 and 0.018-0.024, respectively) compared to the
- 327 spread in F/Cl ratios (8.8-37.2). The phengite-rich fraction has F/Cl, Br/Cl and I/Cl ratios
- 328 of 34, 0.013 and 0.016, respectively.
- 329 Fluorine and Cl contents of bulk samples are broadly correlated with bulk K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>
- 330 (Fig. S2), providing evidence that phengite and apatite may influence the bulk halogen
- 331 content of these blueschists.
- 332 5.3.2 Hydrous mineral concentrations by SIMS
- Phengite and lawsonite contain higher F (372-572 ppm and 295-861 ppm, respectively)
- than Na-amphibole (84-390 ppm) (**Table 2**). Chlorine concentrations are lower than those

of F for all three minerals and in all samples by an order of magnitude or more, agreeing

336 with the results from bulk pyrohydrolysis extractions in this study. Phengite (21-77 ppm)

and Na-amphibole (18-97 ppm) have similar concentrations, while lawsonite has lower

338 Cl concentrations spanning a narrow range (20-46 ppm). Na-amphibole and lawsonite

339 F/Cl ratios (0.97-21 and 11-36, respectively) cover a range of two orders of magnitude,

- 340 similar to those of the corresponding extracted mineral fractions. Phengite F/Cl ratios
- also cover a range of two orders of magnitude (5-27), slightly lower than the ratio
- 342 reported for the only phengite-rich mineral fraction.
- 343 5.3.3 Apatite concentrations by EMPA

344 Apatite contains higher F concentrations (up to 3.51 wt%; **Table 2**) than Na-amphibole,

lawsonite and phengite, contributing up to 51% of total F in bulk samples. Chlorine

346 concentrations in apatite are also elevated (up to 253 ppm) with respect to the other

347 minerals, but to a lesser extent than F concentrations, as evidenced by apatite's higher

348 F/Cl ratios (114-493).

350 **Table 2:** Halogen concentrations in blueschist facies minerals from the Tavsanli Zone,

351 northwestern Turkey. Na-amphibole, lawsonite and phengite results were determined by

352 SIMS, and apatite by EMPA. Apatite concentrations are an average of 1-3 analyses/grain

353 for 1-4 grains/sample, depending on grain size and abundance.

	H <sub>2</sub> 0	F	Cl	F/Cl
	wt%	ppm	ppm	
Phengite		••	••	
TUR14A	5.75	503	77	6.54
TUR30	5.77	572	21	26.9
TUR33	6.07	372	69	5.35
Average	5.87	482	56	12.9
Na-amphibole				
TUR12	2.15	218	46	4.79
TUR14A	2.17	335	97	3.47
TUR30	2.02	390	18	21.4
TUR32	2.09	256	46	5.60
TUR33	2.19	84	87	0.967
Average	2.12	257	59	7.25
Lawsonite				
TUR23	10.5	334	20	16.9
TUR30	10.1	383	33	11.8
TUR31	10.7	861	24	35.9
TUR32	10.4	295	27	10.8
TUR33	10.0	538	46	11.6
Average	10.3	482	30	17.4
Apatite				
TUR12		30600	nd	nd
TUR14A		30590	130	235
TUR23		32790	163	201
TUR30		29560	60	493
TUR31		35070	108	325
TUR32		31800	113	281
TUR33		28770	253	114
Average		31310	138	275
nd - not detected	1			

#### 355 5.3.3 Mineral partitioning

356 The distribution of halogens among Na-amphibole, phengite and lawsonite is varied 357 across samples. In TUR30, F distributes evenly between amphibole and lawsonite (distribution coefficient,  $D_{Amp-Lws}^{F}=1.0$ ), and Cl concentrates in lawsonite ( $D_{Amp-Lws}^{Cl}=1.0$ ) 358 Lws=0.56). However, in TUR32 and TUR33, F partitions into lawsonite (D<sup>F</sup><sub>Amp-Lws</sub>=0.16-359 0.87) and Cl into amphibole (D<sup>Cl</sup><sub>Amp-Lws</sub>=1.67-1.87). Phengite/lawsonite distribution 360 coefficients reveal F preferentially partitions into phengite ( $D_{Ph-Lws}^{F}=1.5$ ) and Cl into 361 lawsonite (D<sup>Cl</sup><sub>Ph-Lws</sub>=0.65) for sample TUR30, but the reverse is observed (D<sup>F</sup><sub>Ph-Lws</sub>=0.69, 362 D<sup>Cl</sup><sub>Ph-Lws</sub>=1.5) for TUR33. The phengite/amphibole distribution coefficients for Cl cover 363 364 a small range around  $\sim 1$  (0.79-1.2, avg. 0.92), indicating equal partitioning in both minerals, whereas F preferentially concentrates in phengite (D<sup>F</sup><sub>Ph-Amp</sub>1.5-4.4, avg. 2.5) for 365 366 all samples. 367 Fluorine concentrations in apatite are two to three orders of magnitude greater than in the 368 hydrous minerals (**Table 2**). The partitioning of F between apatite and Na-amphibole is varied across all samples ( $D^{F}_{Ap-Amp}=76-343$ ), more so than the distribution between 369 apatite and lawsonite ( $D_{Ap-Lws}^{F}=41-108$ ) or phengite ( $D_{Ap-Ph}^{F}=52-77$ ). The distribution of 370 Cl between apatite and Na-amphibole ( $D^{F}_{Ap-Amp}=1.3-3.3$ ), lawsonite ( $D^{F}_{Ap-Lws}=1.8-8.2$ ), 371 and phengite ( $D^{F}_{Ap-Ph}=1.7-3.6$ ) is similar for all three mineral pairings. 372 373

#### 374 **6. Discussion**

#### 375 6.1 Halogen concentrations in blueschists

376 Bulk rock halogen abundances were calculated based on the measured halogen 377 concentrations of Na-amphibole, lawsonite, phengite and apatite along with their modal 378 abundances in each sample. Calculated F and Cl values in bulk rock are generally in good 379 agreement with the measured bulk rock concentrations (Table S8). This verifies that 380 there are no other major halogen-rich phases in the blueschist samples. 381 6.1.1 Halogen uptake 382 Since the Taysanli zone blueschists are characterized by prograde mineral assemblages 383 with very little retrogression (Table 1), halogens in these samples represent those deep in 384 the subduction zone, as opposed to acquired during retrogression at shallow depths. 385 The presence of hydrous minerals and high Na in our samples are consistent with seafloor 386 alteration prior to subduction, which should enrich Cl in basaltic rocks. However, the Cl 387 content of these blueschists is much lower than that of the altered oceanic crust (e.g. 334 388 ppm; Sano et al. 2008), indicating that Cl may have been expelled before or during 389 blueschist metamorphism.

390 Very few studies have been carried out on the abundance of Br and I in oceanic crust.

391 Since amphibole is considered to be the major host of halogens in altered mafic rocks, the

392 halogen concentrations of secondary amphibole from oceanic metagabbros (Kendrick et

al. 2015) are used to approximate altered oceanic crust. The Br content of the

394 metagabbros (0.46-1.98 ppm) is comparable to the range of Br in unaltered MORB (0.26-

395 3.12 ppm; Kendrick et al. 2012), and up to an order of magnitude higher than Br

396 concentrations in the Tavsanli Zone blueschists. This may suggest that like Cl, Br is lost

397 from the slab during subduction, however, elevated Br/Cl ratios with respect to unaltered

and altered MORB (Fig. 7) may indicate preferential retention of Br in the down-goingslab relative to Cl.

400 This study shows elevated abundances of I and F in bulk rock and mineral-rich fractions

401 compared to the values in unaltered MORB (avg. 0.046 ppm I, Kendrick et al. 2012; avg.

402 147 ppm F, Le Roux et al. 2006) and altered oceanic crust (avg. 0.023 ppm I, Kendrick et

403 al. 2015; avg. 216 ppm F, Straub & Layne 2003). Seawater concentrations of F and I are

404 too low to explain this enrichment. A plausible source of F and I are sediments on the sea

405 floor or near subduction zones (e.g. John et al. 2011). High F values are reported in

406 pelagic clays (up to 1300 ppm; Li 1982) and organic-rich sediments, in particular, contain

407 high concentrations of I (e.g. Muramatsu et al. 2007). Following fluid circulation through

408 overlying sediments near subduction zones, it is likely that the oceanic crust becomes

409 enriched in F and I on the sea floor prior to subduction, or along bending-related

410 extensional faults at the outer rise. In addition, a large supply of I-rich shallow water

411 sediments would have been available given the close proximity of continents to this

412 particular subduction zone.

#### 413 6.1.2 Halogen fractionation

414 A positive correlation between Cl, Br and I in mineral fractions suggests an overall

similar behaviour in subduction zones (Figs. 6a, b). Conversely, F concentrations do not

416 correlate well with the heavier halogens (Fig. 6c). This difference in behaviour of

417 halogens is attributed to the enhanced reactivity of F due to its smaller size and higher

418 electronegativity. Of the four halogens, the ionic radius (1.33 Å) of F is most similar to

419 that of OH<sup>-</sup> (1.35 Å), making it most compatible for substitution in hydrous minerals. An

- 420 additional mechanism for the incorporation of F into silicate minerals is the coupled
- 421 substitution of  $Al^{3+}$  and  $F^{-}$  with  $Si^{4+}$  and  $O^{2-}$  (1.21 Å), as previously suggested to explain
- 422 F uptake in pyroxenes (Mosenfelder & Rossman 2013). The elevated I/Cl, Br/Cl and F/Cl
- 423 ratios of our samples relative to altered oceanic crust (Fig. 7), suggest either I, Br and F
- 424 are enriched in the crust prior to subduction, or these halogens are preferentially retained
- 425 relative to Cl during subduction-related metamorphism.

- 427 **Figure 6**: Halogen content of bulk samples and mineral separates for lawsonite
- 428 blueschists of the Tavsanli Zone, northwestern Turkey. Chlorine is plotted against (a) I,
- 429 (b) Br and (c) F. There is a positive correlation between Cl, Br and I, but not F.



431	Figure 7: Compilation of halogen ratios in unaltered and altered oceanic crust,
432	sedimentary marine reservoirs and Tavsanli Zone blueschist bulk rocks. (a) Given the
433	scarcity of bulk rock data for Br and I in altered oceanic crust, Br/Cl and I/Cl of
434	secondary amphiboles in oceanic metagabbros (Kendrick et al. 2015) are used as a proxy
435	for altered oceanic crust. The low Br/Cl ratios of the altered oceanic crust relative to
436	unaltered MORB and seawater (Li 1982) suggest Cl is preferentially incorporated into
437	amphibole over Br during hydrothermal alteration. Br/Cl and I/Cl ranges for MORB
438	(Kendrick et al. 2012) overlap with the lower range of pore fluids of marine sediments
439	(Muramatsu et al. 2007). Pore fluid data extends to higher values, overlapping with
440	incoming plate sediments (John et al. 2011), and the Tavsanli zone blueschists analyzed
441	in this study. (b) The F/Cl range for altered oceanic crust (Magenheim et al. 1995) is
442	lower than that of unaltered MORB (Le Roux et al. 2006), but significantly elevated
443	relative to seawater (Li 1982). F/Cl values of the Tavsanli blueschists are higher than
444	MORB values, and overlap with the upper range of incoming plate sediments.



#### 447 6.2.1 Chlorine

448 Chlorine preferentially partitions into phengite and Na-amphibole, with average 449 concentrations for each mineral in all samples of 59 ppm for Na-amphibole, 56 ppm for 450 phengite and 27 ppm for lawsonite (Table 2). The low Cl content of lawsonite may be 451 related to structural differences among the three minerals. Micas and amphiboles have appreciably more M<sup>2+</sup> cations in their octahedral sites than lawsonite, which minimizes 452 453 distortion of their hydroxyl sites and allows for greater substitution of Cl<sup>-</sup> in the OH<sup>-</sup> site 454 (Volfinger et al. 1985). Furthermore, hydrogen bonding may also affect halogen uptake. 455 Amphibole and phengitic muscovite have weak hydrogen bonding (Catlow & Wright 456 1999; Gatta et al. 2011), but lawsonite contains multiple hydrogen bonds (Libowitzky & 457 Rossman 1996). Therefore, hydroxyl substitution may be less energetically favourable in 458 lawsonite given the additional energy requirements to overcome these bonds.

#### 459 *6.2.2 Fluorine*

460 In situ measurements reveal F preferentially concentrates in phengite (avg. 482 ppm) and

lawsonite (avg. 482 ppm) over Na-amphibole (257 ppm). Fluorine may be more readily

- retained by phengite and lawsonite due an increase in the electrostatic attraction between
- 463 F and interlayer  $K^+$  in phengite and A-site  $Ca^{2+}$  in lawsonite. When F<sup>-</sup> substitutes for OH<sup>-</sup>,
- the reduced distance between the halogen and interlayer/cavity cations allows for a
- greater attraction between them. The Na-amphiboles, on the other hand, have vacancy in
- the A-site, and thus may not as readily retain F. Our results are in agreement with data

467 from other eclogites showing higher F in phengite over co-existing amphiboles (e.g.468 Svensen et al. 2001).

#### 469 6.2.3 Bromine and Iodine

470Partitioning of Br and I between co-existing minerals is evaluated from pyrohydrolysis471extractions of amphibole- and lawsonite-rich fractions. Bromine concentrations appear472uniform between both mineral phases in all samples, except for TUR33 in which the473lawsonite concentrate has two times more Br. Iodine seems to preferentially partition into474lawsonite, as observed by elevated concentrations in the lawsonite-rich fractions of TUR47530, 32 and 33. In addition to substitution for OH<sup>-</sup> groups, large cavities containing H<sub>2</sub>O476and Ca<sup>+</sup> in lawsonite's structure may accommodate I ions.

477

#### 478 *6.3 Halogens in apatite*

479 Apatite preferentially incorporates F from fluids (Spear & Pyle 2002), and the small F ion 480 can easily fit in the columnar anion site, coplanar with the M2 cations. In contrast, Cl and 481 OH ions are too large, and are displaced above or below the cation plane. With increasing 482 pressure, the incorporation of small F is favoured. Since F is an essential component of 483 fluorapatites, it is preferentially concentrated in apatite over other minerals, such as 484 amphibole, lawsonite and phengite. The halogen abundance of apatite in our samples is 485 similar to metamorphic apatite from Norwegian eclogites (Svensen et al. 2001). 486 Measured F contents in phengite in our samples are similar, but those in Na-amphibole 487 and lawsonite are higher than those in blueschist facies metagabbros reported by Debret

- 488 et al (2016). Furthermore, their estimated bulk F contents based on concentrations in
- these minerals and their modal abundances are much lower than our measured values.

The difference may be related to apatite since it is the major mineral phase hosting F in
our samples, but is not considered in their calculations as their samples may contain low
P.

- 493
- 494 6.4 Implications for halogen recycling

495 Low Cl concentrations recorded for all hydrous minerals in these samples imply that Cl is

496 expelled at much shallower depths in the subduction zone. This is in good agreement

497 with previous estimates that as much as 75% of the subducted Cl in rocks and pore fluids

498 may be released from the accretionary prism at slab depth <15 km (Jarrard 2003).

499 Metamorphism before or during the blueschist facies may also contribute to Cl loss from

500 the subducting slab before 80 km depth. This proposed interpretation is supported by the

501 broad correlation between bulk rock Cl and As concentrations (0.5-2.2 ppm) (Fig. S3).

502 Since As is lost early from subducting slabs (< 35 km depth; Hattori et al. 2005), the

503 evidence supports Cl loss in addition to other fluid-mobile elements during shallow

subduction. Similarly low concentrations of Cl have been reported for bulk rock

505 blueschists (60-300 ppm) and eclogites (30-60 ppm) from the island of Syros, Greece

506 (Marschall et al. 2009).

507 In contrast, elevated F concentrations in these blueschists suggest F is retained during

subduction to at least 80 km depth. A positive correlation between F and Be in our bulk

509 rocks (Fig. S3) supports this interpretation, since Be exhibits conservative behaviour

510 during subduction-related dehydration reactions (Marschall et al. 2007).

511 Na-amphibole decomposition at < 90 km depth (associated with the blueschist-eclogite

transition) has been proposed to contribute to partial melting for arc magmatism (Peacock

513 1993). However, the F/Cl ratios for Na-amphibole in these blueschists are higher than 514 those reported for volcanic arc outputs and back-arc basin basalts (Fig. 8), suggesting 515 amphibole dehydration may not be the dominant source for these halogen signatures. 516 Given the relatively shallow depth of dehydration, Na-amphibole is likely not relevant for 517 the transfer of halogens to the deeper mantle. However, F in the amphibole structure may 518 widen its stability to higher pressures and temperatures, allowing F-rich Na-amphibole to 519 remain stable under eclogite facies conditions (Holloway & Ford 1975), and carry F to 520 greater depths.

521 The high F contents of lawsonite and phengite in this study are of particular interest given

the wide stability of these minerals in cool subduction zones. Lawsonite is stable to 80-90

523 kbar, and phengite to 100 kbar, at 900°C (Schmidt & Poli 1998). Once they decompose,

524 the resulting fluids would have high F/Cl ratios. It is interesting to note that these ratios

are comparable to melt formed at deep levels, including ocean island basalts (e.g. Hauri

526 2002, Kendrick et al. 2015), and kimberlites (e.g. Paul et al. 1976) (Fig. 8), suggesting

527 the importance of these minerals for the transfer of F to the deep mantle.

528 Despite not contributing to the water budget of subducting slabs, apatite is likely an

529 important repository of halogens during HP metamorphism, transporting F (and some Cl)

beyond subarc depths. Upon apatite breakdown at ~200 km, halogens in apatite may be

released to the overlying mantle, or possibly incorporated into stable hydrous silicates

such as phengite and lawsonite (Konzett & Frost 2009).

522

533 Chlorite (12 wt% H<sub>2</sub>O) is present in variable abundance in all samples, and the texture

and occurrence suggest it is a prograde product. Chlorite stability is primarily

temperature dependent, and in cold subduction zones it may remain stable to 40+ kbar

(~100+ km; Mookherjee & Mainprice 2014). Although we did not determine halogen
contents in chlorite due to its intergrowth with other minerals, the bulk rock data for
chlorite-rich TUR31 (582 ppm F, 8 ppm Cl) suggest chlorite likely contains F and Cl
concentrations similar to the other hydrous minerals, and there is little partitioning of F
and Cl between chlorite and other minerals.

541 Low Cl and high F content in the Tavsanli Zone blueschists support previously proposed 542 interpretation based on the halogen content of arc magmas that Cl is effectively liberated 543 during subduction at shallow depths, whereas F is largely retained in the down-going slab 544 beyond arc front depths (Straub & Layne 2003). Liberation of Cl during early subduction 545 is also documented by expulsion of saline fluids from accretionary prisms (e.g. Godon et 546 al. 2004). High I/Cl ratios of bulk samples and mineral separates suggest I may be 547 fractionated from Cl during subduction, and like F, incorporated into hydrous minerals. 548 Bromine may also be fractionated from Cl based on slightly elevated Br/Cl ratios, but to a 549 much lesser extent than F or I. Chlorine, and most Br, is likely released before or during 550 blueschist metamorphism, whereas F is retained in phengite, lawsonite and apatite at 551 blueschist depth. When apatite eventually breaks down at ~200 km, F may be 552 redistributed to phengite and lawsonite, whereas minor Cl in apatite is most likely 553 released to the overlying mantle wedge. Finally, at ~280-300 km in cold subduction 554 zones, lawsonite and phengite decompose, releasing F to the deeper upper mantle.

555

556

557 Figure 8: Box-and-whisker plot displaying the F/Cl ratios of apatite, Na-amphibole, 558 lawsonite and phengite from the Tavsanli Zone blueschists, northwestern Turkey. For 559 comparison, F/Cl ratios for various magmas have been added. High F/Cl ratios of 560 lawsonite and phengite suggest these minerals may provide a means for transporting F to 561 the deep upper mantle, supplying magmas of deeper origin such as ocean island basalts 562 (e.g. Hawaiian melt inclusions, Hauri 2002; Samoa glasses, Kendrick et al. 2015) and 563 kimberlites (e.g. bulk rock from Greenland, South Africa and India, Paul et al. 1976). 564 Volcanic arc data are from Lesser Antilles melt inclusions (Heath et al. 1998), Central 565 American Arc pyroclastic rocks (John et al. 2011), and Izu Arc glasses and fallout tephra 566 (Straub & Layne 2003). Back-arc basalt data are bulk rock data from the Lau Basin 567 (Bezos et al. 2009).



## 569 **7. Conclusions**

570

571 concentrations, suggesting F is preferentially retained, whereas Cl is lost at shallow 572 depths (< 80 km) in subduction zones. A positive correlation between Cl, Br and I 573 contents of the pyrohydrolysis extracts suggests Br and I may behave similarly to Cl in 574 subduction zones, although high I/Cl and slightly high Br/Cl ratios relative to MORB 575 indicate some fractionation of I and Br from Cl during subduction and blueschist facies 576 metamorphism. 577 Chlorine partitioning among the four analysed minerals follows apatite>phengite≈Na-578 amphibole >lawsonite, and F partitioning follows apatite >>phengite ≈lawsonite >Na-579 amphibole. The halogens preferentially reside in apatite because they are accommodated 580 in the M2 site. The eventual decomposition of apatite at ~200 km may lead to a 581 redistribution of F into lawsonite and phengite. The accommodation of F in lawsonite and 582 phengite suggests F may be transported by these minerals to a depth of 280-300 km in 583 cold subduction zones, and may contribute to the high F content observed in deep mantle 584 magmas, such as ocean island basalts and kimberlites. 585

Hydrous blueschist minerals of the Tavsanli Zone contain high F and low Cl

### 586 Appendix A.

587 Pyrohydrolysis method for halogen extraction

588 A 0.5 g weight of finely ground sample was combined in a silica boat with an equal

weight of reagent grade  $V_2O_5$  (Elemental Microanalysis Ltd) previously heated to  $325^{\circ}C$ 

590 for 24 hours. A wet oxygen gas flow of 0.8 Lmin<sup>-1</sup> was created using an Erlenmeyer flask

591 of water on low heat connected to a tank of UHP oxygen gas. The main silica tube was

592 housed in a Lindberg Blue M tube furnace set at an initial temperature of 500°C. A glass 593 rod was used to insert a silica wool plug into the main tube and position it just beyond the 594 wall of the furnace. The purpose of plug was to prevent solid material from entering the 595 trap and clogging the frit. The sample was slowly introduced to the main tube and 596 positioned directly in the middle of the furnace. Once the system was reconnected, the 597 furnace temperature was increased to 1100°C for 15 minutes. The temperature on the 598 output end of the main tube beyond the furnace was maintained at 120°C+ with heating 599 tape to prevent condensation. The evolved gas was passed through a frit inside the trap to 600 maximize surface area contact with the 7 mL of 25 mM NaOH trap solution (prepared 601 from extra pure N<sub>2</sub>-flushed NaOH pellets from Acros Organics). The collection vessel 602 was submerged in an ice bath during collection to promote condensation of the halogens 603 in solution. After 15 minutes the furnace temperature was reduced to 500°C before 604 expelling the sample and quartz wool from the main tube. The system was purged with 605 oxygen for 10-15 minutes, fresh quartz wool and the next sample were inserted, and a 606 clean collection vessel was connected to the trap. All glassware was cleaned with 607 deionized water after every two to three runs (i.e. duplicates or triplicates of one sample). 608 Collected solutions were diluted 5x for ICP-MS analysis, and 1% HNO<sub>3</sub> was added to 609 stabilize anions in solution. Dilution was not necessary for IC analysis.

610

#### 611 Appendix B

- 612 Supplementary material
- 613 Supplementary material related to this article can be found online.

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Outcrop in	Samula ID	Mineralogy				
Figure 1	Sample ID	Major	Minor			
1	TUR12	Lws, Na-Amp, Chl, Jd, Ttn	Qz, Ap, Ep			
1	TUR14	Lws, Na-Amp, Ph, Chl	Qz, Ttn, Rt, Ap			
2	<b>TUR23</b>	Lws, Chl, Ph, Ttn	Na-Amp, Ap, Py			
	TUR30	Lws, Na-Amp, Ph, Qz, Chl	Ap, Ttn, Rt			
2	TUR31	Lws, Chl, Ph, Qz	Ap, Ttn, Ab			
3	TUR32	Lws, Na-Amp, Qz, Ab	Chl, Ttn, Ap			
	TUR33	Lws, Na-Amp, Ph, Ap, Ttn	Fe-oxides, Chl			

 Table 1: Summary of sample mineralogy of Tavsanli Zone blueschists in northwest Turkey.

 Outgrop in

	H <sub>2</sub> 0	F	Cl	F/Cl
	wt%	ppm	ppm	
Phengite				
TUR14A	5.75	503	77	6.54
TUR30	5.77	572	21	26.9
TUR33	6.07	372	69	5.35
Average	5.87	482	56	12.9
Na-amphibole				
TUR12	2.15	218	46	4.79
TUR14A	2.17	335	97	3.47
TUR30	2.02	390	18	21.4
TUR32	2.09	256	46	5.60
TUR33	2.19	84	87	0.967
Average	2.12	257	59	7.25
Lawsonite				
TUR23	10.5	334	20	16.9
TUR30	10.1	383	33	11.8
TUR31	10.7	861	24	35.9
TUR32	10.4	295	27	10.8
TUR33	10.0	538	46	11.6
Average	10.3	482	30	17.4
Apatite				
TUR12		30600	nd	nd
TUR14A		30590	130	235
TUR23		32790	163	201
TUR30		29560	60	493
TUR31		35070	108	325
TUR32		31800	113	281
TUR33		28770	253	114
Average		31310	138	275
nd - not detected				

**Table 2:** Halogen concentrations in blueschist facies minerals from the Tavsanli Zone, nor Turkey. Na-amphibole, lawsonite and phengite results were determined by SIMS, and apatite

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