The stability of antigorite in subduction zones revisited: the effect of F on antigorite stability and its breakdown reactions at high pressures and high temperatures, with implications for the geochemical cycles of halogens

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Abstract

We present new experimental data on the effect of F on the stability of antigorite and its breakdown products at high pressures (2–6 GPa) and high temperatures (570–850 °C). The experiments show that F does not affect the stability of antigorite, but addition of F to the system affects which minerals are formed when antigorite breaks down. In a F-free system and in a system with intermediate F contents (2 wt% F), antigorite breaks down to olivine and orthopyroxene, but in a F-rich system (5 wt% F), antigorite breaks down to other hydrous and F-bearing mineral assemblages which include chlorite, clinohumite and humite-group minerals (HGM). Since the latter mineral phases are stable at higher pressures and temperatures, and contain more F than antigorite, significant amounts of F and potentially other halogens can be retained in the subducting slab and transported deep into the mantle and possibly even into the Earth’s transition zone.

Keywords Antigorite · Fluorine · Chlorite · Humite minerals · Subduction · Stability

Introduction

Serpentine-group minerals [Mg₃Si₂O₅(OH,F)₄] are common products of hydrothermal alteration of olivines, both in the oceanic crust and the underlying oceanic mantle (e.g., Fumagalli and Klemme 2015). Previous experimental studies show that serpentine-group minerals contain high amounts of H₂O (~ 13 wt%), and are stable in the subducting slab down to depths of about 200 km (Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997; Schmidt and Poli 1998; Poli and Schmidt 2002). This makes them key mineral phases in the geochemical cycle of volatiles as they can transport large quantities of water and other volatiles into the deep mantle (e.g., Ulmer and Trommsdorff 1995; Kendrick et al. 2012, 2013, 2017; Chavrit et al. 2016; Pagé and Hattori 2017; Pagé et al. 2018; Klemme and Stalder 2018; Tiraboschi et al. 2022).

Antigorite is the high-pressure polymorph of serpentine-group minerals. Previous experimental studies identified the break-down reactions that delineate its stability field. This study focuses on two of these reactions:

antigorite → forsterite + enstatite + water (1)

antigorite → forsterite + enstatite + chlorite + water (2)

The position of reaction (1) has been bracketed experimentally over a large pressure range, i.e., 1 to ~ 8 GPa, and from 480 to 700 °C (Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997; Bose and Navrotsky 1998; Bromiley and Pawley 2003). Reaction (2) has been bracketed between 1.6 and 5 GPa, and temperatures from 520 to 650 °C in both natural and experimental samples (Trommsdorff et al. 1998; Bromiley and Pawley 2003). Which of these two reactions will take place depends on parameters such as the Mg/Si of the bulk system, and the availability of volatiles (Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997; Ulmer and Trommsdorff 1999; Bromiley and Pawley 2003; Wu and Koga 2013; Hughes and Pawley 2019; Iacovino et al. 2020).
However, the thermal stability of antigorite is primarily controlled by the presence of trivalent cations (\(\text{Al}^{3+}\) in particular, but also \(\text{Fe}^{3+}\) and \(\text{Cr}^{3+}\)) (Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997; Bromiley and Pawley 2003). Moreover, experimental studies showed convincingly that F increases the thermal stability of other hydrous Mg-rich silicate minerals such as amphibole, clinohumite, and wadsleyite up to ~300 °C (Peterson et al. 1991; Foley 1991; Grützner et al. 2017, 2018). Therefore, the aim of this study was to investigate whether F can also enhance the thermal stability of antigorite and how F may affect its breakdown reactions.

**Experimental strategy**

To study the effect of F on the stability of antigorite and to determine its F storage capacity, we performed experiments with the following three different bulk compositions: (i) a F-free composition; (ii) a composition with intermediate F content (2 wt% F); (iii) a F-rich composition (5 wt% F). Note that only a few natural antigorites have been analyzed for F to date and that these samples contain significantly less than 1 wt% F. (Debret et al. 2014; Páge and Hattori 2017; Páge et al. 2018). It is unclear whether these low F concentrations are due to low bulk F concentrations in the host rocks or whether these low F concentrations are due to a low F storage capacity of antigorite. The experiments with high F contents contribute to the latter as they are designed to saturate antigorite in F and, therefore, determine the maximum F storage potential of antigorite at the P–T conditions of the runs.

We conducted “bracketing experiments” where the starting materials contain both reactants and reaction products, i.e., antigorite, olivine, and orthopyroxene. If an experiment is run inside the antigorite stability field, antigorite grows and the amounts of olivine and orthopyroxene decrease. If an experiment is run outside the antigorite stability field, antigorite is consumed and its modal proportion decreases. Phase identification using SEM, EPMA and XRD techniques show whether the experiment was inside or outside the antigorite stability field.

**Materials and methods**

**Starting materials**

Natural gem-quality antigorite, synthetic forsterite and enstatite were used as starting materials. The antigorite sample was kindly provided by Prof. Kawamoto (pers. comm., 2017) and it was characterized with electron microprobe techniques (EPMA) (Table 1) and X-ray diffraction (XRD) analysis (Supplementary Fig. S1). Forsterite and enstatite were synthesized using analytical-grade SiO₂ and MgO.

### Table 1 Composition of the natural antigorite starting material

| Composition | wt% |
|-------------|-----|
| SiO₂        | 43.94(6) |
| Cr₂O₃       | 0.030(5) |
| Al₂O₃       | 1.22(9) |
| FeO         | 0.87(2) |
| MgO         | 39.9(2) |
| Total       | 86.0(1) |
| H₂O         | 13.9(1) |
| F           | b.dl   |

The starting material antigorite was analyzed with EPMA techniques in two different sessions. Numbers in parentheses represent the 1σ – standard deviation (1σ – SD) of the overall 20 analyses as last significant digits, i.e., 0.07(3) must be read as 0.07 ± 0.03. Water content was determined by subtracting the sum of the major element composition from 100 wt%. Fluorine contents were below detection limit (b.dl.).

### Table 2 Starting materials (wt%)

| Phases  | SFM1-ATG1 | SFM1-ATG2 | SFM1-ATG2F |
|---------|-----------|-----------|------------|
| Forsterite | 24.46 | 19.44 | 18.32 |
| Enstatite | 17.51 | 14.1 | 13.24 |
| Antigorite (c.f. Table 1) | 48.35 | 38.8 | 36.58 |
| Brucite | 9.67 | 25 | 23.54 |
| MgF₂ | – | 3.3 | 8.3 |

SFM1-ATG1 is the starting material with no added F (\(F_{\text{sys}} = 0\)). SFM1-ATG2 is the starting material with 2 wt% F (\(F_{\text{sys}} = 2\)) and SFM1-ATG2F is the starting material with 5 wt% F (\(F_{\text{sys}} = 5\)). Forsterite and enstatite were pre-synthesized (see text). The natural antigorite composition is given in Table 1.

The MgO was fired at 1000 °C for 2 h and kept in a drying cabinet at 110 °C at all times. Forsterite was synthesized in a Linn box furnace at 1450 °C for 6 h. Enstatite was synthesized at 2 GPa and 900 °C in a piston cylinder apparatus for 48 h. Both the forsterite and enstatite starting materials were characterized by XRD (Supplementary Figs. S2 and S3).

The resulting stoichiometric mixture contains antigorite, forsterite, and enstatite (Table 2). Using this mixture (XRD, Supplementary Fig. S4), the following three starting materials were prepared: a F-free, and two F-bearing mixtures with 2 and 5 wt% of F, respectively (Table 2). Brucite and MgF₂ (Alfa Aesar, Germany) were used as sources for H₂O and F. The starting materials were ground and mixed in an agate mortar under acetone, and the resulting homogeneous mixtures were stored in a desiccator. Before each experiment.
the starting materials were dried again in a drying cabinet at 110 °C for 20 min before they were welded into noble metal capsules.

**Experimental techniques**

All experiments were performed in an end-loaded piston cylinder apparatus (Boyd and England 1960) and a 1000-ton Walker-type multi-anvil apparatus (Walker et al. 1990), at the Institut für Mineralogie at the Westfälische Wilhelms-Universität Münster (WWU), Germany. The starting material was loaded into Au capsules which were about 2.5 mm-long and 2 mm in diameter. Oxygen fugacity was unconstrained in all experimental runs. The capsules were welded shut using a commercial Lampert PUK system (Lampert GmbH, Germany).

The piston cylinder high-pressure assemblies consisted of ½” talc-pyrex cylinders, a 6 mm I.D. graphite heater (material FB 254, Schunk, GmbH, Germany), two 6-mm O.D. crushable alumina inserts (TKF Frömgen GmbH, Germany) placed at the top and the bottom of the assembly. The Au capsules were placed inside a 5 mm-long boron nitride cylinder which was placed in the hot-spot of the assembly. Pressures were calibrated using the quartz–coesite transition (Bose and Ganguly 1995) and the MgCr$_2$O$_4$ + SiO$_2$ = MgSiO$_3$ + Cr$_2$O$_3$ reaction (Klemme and O’Neill 1997), and a friction correction of -13% was applied to the nominal pressure. Based on the aforementioned calibrations, pressures are accurate to 0.01 GPa. Temperatures were monitored with a W97Re3–W75Re25 thermocouple and controlled by a Eurotherm controller (Schneider Electric, Germany). The temperature measurements were accurate within ± 10 °C (c.f., Pintér et al. 2021, for similar assemblies). All experiments were run with the hot piston-in technique, where pressure and temperature were manually increased by about 0.1 GPa/100 °C.

The 18/12 multi-anvil assembly (18 mm octahedron edge length/12 mm truncation edge length) consist of a cast ceramic octahedron (Aremco 584 OF) and a straight graphite heater (material FB 254, Schunk GmbH, Germany). Temperatures were monitored using W$_{97}$Re$_3$–W$_{75}$Re$_{25}$ thermocouples (Omega Engineering Inc.). Pressure and temperatures were held constant during the runs using Eurotherm controllers (Schneider Electric, Germany). The temperature measurements were accurate within ± 10 °C (c.f., Pintér et al. 2021, for similar assemblies). All experiments were run with the hot piston-in technique, where pressure and temperature were manually increased by about 0.1 GPa/100 °C.

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Experiments were run at pressures between 2 and 6 GPa and temperatures from 560 to 850 °C. The experimental details and run products are given in Table 3. The run products were examined with XRD and electron microprobe techniques. For the XRD measurements, the Au capsules were carefully opened, and the retrieved samples were ground in an agate mortar under acetone. Samples used for microprobe analysis were mounted in epoxy resin and polished using non-hydrous polishing liquids.

**Analytical methods**

**X-ray diffraction**

X-ray powder diffraction patterns were recorded using a PHILIPS X’PERT PW 9430 diffractometer with Cu-Kα1 radiation and a primary Ge-(111) monochromator of the Johansson Type with rotating samples. The operating conditions were 45 kV and 40 mA, and data were collected at 20 ranging from 5 to 88°. Rietveld refinement was performed using the FULLPROF SUITE 2005 (Rodriguez-Carvajal 2005).

**Scanning electron microscopy and electron microprobe analyses**

Experimental run products were examined initially using a JEOL JSM-6610LV scanning electron microscope (SEM). Major element concentrations of all phases were determined with a 5-spectrometer JEOL JXA 8530F electron microprobe analyzer (EPMA) at the Institut für Mineralogie at the Westfälische Wilhelms-Universität Münster (WWU). The F concentrations of antigorite were determined using a LDE-1 crystal, thus allowing higher count rates, better resolution, and lower detection limits. Pulse Height Analysis (PHA) has been used to eliminate the MgKα peak overlap in the F analysis (Zhang et al. 2016). We used the method described by Flemetakis et al. (2020) to correct for the spectral overlap of the FeLα peak on the FKα peak. The acceleration voltage was 15 kV and the beam current was 15 nA with a 5-μm beam size. Counting times were 20 s on peak and 10 s on the background for major elements and 120 s on peak and 60 s on the background for F. Sandine (Na), diopside (Ca), San Carlos olivine (Mg), hypersthene (Si), rutile (Ti), and fayalite (Fe) were used as reference materials for the major elements and Astimex Fluorite for F. Detection limits (d.l.) for F are in the range of ~ 48–65 μg/gr. Total iron is reported as FeO.

**Results**

**Stability and breakdown of antigorite**

Experiments conducted in a F-free system (Table 3) define the maximum stability of antigorite at 2–2.5 GPa
and ~690 °C (Fig. 1A). These results agree well with published literature values (Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997; Bromiley and Pawley 2003; Maurice et al. 2020), and in this system antigorite breaks down to form olivine, orthopyroxene, and fluid.

Results in the system with 2 wt% F (Fsys = 2 wt%, Table 3) show that the upper thermal stability of antigorite reaches a maximum of ~700 °C at 2 GPa (Fig. 1B), while its stability curve coincides from 2 to 6 GPa and 560 to 700 °C with the stabilities determined in F-free systems (Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997; Bromiley and Pawley 2003; Maurice et al. 2020). In this system antigorite breaks down, and olivine and orthopyroxene are formed as mineral breakdown products.

Similarly, experiments in the system with 5 wt% F (Fsys = 5 wt%, Table 3) reveal that the antigorite stability is identical to that of the other compositions (i.e., F-free system, and Fsys = 2 wt%) at pressures between 2

| Run          | P (GPa) | T (°C) | Time (hh:mm) | Run products | Analytical method |
|--------------|---------|--------|--------------|--------------|-------------------|
| Experiments with SFM1-ATG1 starting material (Fsys = 0) |
| YPC289/SFE1-ATG2 | 2.2     | 620    | 106:01       | atg (+), fo, en | XRD               |
| YPC292/SFE1-ATG2 | 2.5     | 690    | 140:07       | atg (−), fo, en | XRD               |
| GPC662/SFE1-ATG2 | 2.5     | 710    | 142:17       | fo, en             | XRD               |

Experiments with SFM1-ATG2 starting material (Fsys = 2) |
| GPC705/SFE24 | 2.2 | 640 | 120:57 | atg (+), fo, en | EPMA               |
| GPC673/SFE14 | 2.2 | 680 | 95:14  | atg (+), fo, en | XRD               |
| GPC642/SFE2  | 2.2 | 700 | 165:23 | fo, en             | XRD               |
| YPC346/SFE5  | 2.2 | 800 | 111:24 | fo, en             | XRD               |
| GPC607/SFE27 | 2.5 | 650 | 116:24 | atg (+), fo, en, chu | EPMA |
| GPC676/SFE15 | 2.5 | 660 | 93:11  | atg (+), fo, en | XRD               |
| GPC677/SFE16 | 2.5 | 690 | 116:24 | atg (−), fo, en | XRD               |
| GPC662/SFE12 | 2.5 | 710 | 99:27  | fo, en             | XRD               |
| GPC706/SFE28 | 3   | 650 | 134:38 | atg (+), fo, en, chu | EPMA |
| GPC708/SFE26 | 3   | 680 | 116:45 | atg (+), fo, en, chu | EPMA |
| YPC381/SFE10 | 3   | 700 | 136:40 | fo, en             | XRD               |
| GPC646/SFE4  | 3   | 720 | 90:24  | fo, en             | XRD               |
| MA480/SFE30  | 4   | 620 | 142:12 | atg (+), fo (−), en | EPMA               |
| MA484/SFE31  | 4   | 640 | 172:16 | atg (−), fo (−), en | EPMA               |
| MA441/SFE20  | 4.5 | 610 | 107:02 | atg (−), fo, en, chu | EPMA               |
| MA435/SFE17  | 5   | 560 | 68:20  | atg (+), fo, en | XRD               |
| MA466/SFE25  | 5   | 570 | 88:08  | atg (−), fo, en, chu | EPMA               |
| MA493a/SFE32 | 5   | 700 | 213:12 | chu, hu             | EPMA               |

Experiments with SFM1-ATG2F starting material (Fsys = 5) |
| GPC728/SFE1F | 2   | 730 | 210:47 | chn, chl            | EPMA               |
| GPC729/SFE2F | 2   | 850 | 190:43 | fo, en             | EPMA               |
| YPC396/SFE5F | 2.5 | 580 | 67:03  | atg (+), fo (−), en (−) | XRD |
| GPC703/SFE7F | 2.5 | 680 | 100:43 | atg (+), fo (−), en (−) | XRD               |
| GPC730/SFE4F | 3   | 720 | 189:56 | chn, chl            | EPMA               |
| YPC462a/SFE8F | 3   | 760 | 174:30 | chn, chl            | EPMA               |
| MA488/SFE3F  | 4   | 800 | 238:10 | fo, en             | EPMA               |
| MA493b/SFE32F | 5  | 700 | 213:12 | chu, hu, chl        | EPMA               |
| MA489/SFE6F  | 6   | 570 | 169:43 | chn                | EPMA               |

(++ and/or (−) indicate growth or decreasing modal amounts (relative to the starting material) of the phase in the run product.

Mineral abbreviations: atg antigorite, fo forsterite, en enstatite, chu clinohumite, chn chondrodite, chl chlorite, hu humite
Fig. 1 Experimental results of the stability of antigorite and its breakdown reactions in compositions with A no added F ($F_{sys} = 0$ wt%), B 2 wt% F ($F_{sys} = 2$ wt%), and C 5 wt% F ($F_{sys} = 5$ wt%) in the starting materials. Previous results on antigorite stability (all in F-free systems, (A): U&T (1995): Ulmer and Trommsdorff (1995); W&S (1997); Wunder and Schreyer (1997); B&P (2003): Bromiley and Pawley (2003). In (C) the grey curve “FUM (2014)” depicts experimental results on chlorite stability in hydrous peridotite (Fumagalli et al. 2014). The mineralogical composition of the individual run products is given using a pie diagram. Dark parts of the pie indicate stable mineral phases found in run products. Mineral abbreviations: atg antigorite, fo forsterite, en enstatite, chu clinohumite, chn chondrodite, chl chlorite, hu humite, HGM humite group minerals. The extent of the stability fields of chlorite + HGM (stippled curve) is not well known and not the focus of our study but we assume that this stability field is similar to the chlorite stability field (Fumagalli et al. 2014).
and 3 GPa and temperatures between ~570 and 700 °C (Fig. 1C). However, in this system chlorite, clinohumite and/or humite-group-minerals (HGM) are formed upon antigorite breakdown instead of forsterite and enstatite.

Fluorine concentrations of antigorite and other hydrous Mg-silicates

Major element and F concentrations of the experimental run products are reported in Table 4. In the system with 2 wt% F concentrations in antigorite range from ~0.33 to 0.45 wt% (Table 4). Chlorite, when present in the antigorite stability field, contains between 1.6 and 2.2 wt% F.

In the system with 5 wt% F, antigorite breaks down to chlorite (mostly clinochlore) and HGM (predominantly chondrodite). Chlorite contains 0.5–0.8 wt% F and one chlorite showed F content of 2.4 wt% (5 GPa and 700 °C). Fluorine concentrations in HGM range from 6.3 to 7.5 wt% F. Fluorine was absent in forsterite and enstatite in all experiments (Supplementary Table S1).

Table 4 Major element, F and water content (all in wt%) of hydrous phases

| Experiment | SFE24 | SFE27 | SFE28 | SFE26 | SFE30 | SFE4F | SFE8F | SFE1F | SFE32F |
|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Mineral    | atg   | atg   | atg   | atg   | chl   | chl   | chl   | chl   | chl   |
| n          | 83    | 135   | 120   | 98    | 98    | 43    | 39    | 41    | 5     |
| SiO₂       | 44.2(2)| 42.8(1)| 41.95(1)| 41.9(1)| 42.0(1)| 27.8(4)| 28.7(2)| 31.0(3)| 38(1) |
| Cr₂O₃      | 0.034(6)| 0.034(4)| 0.033(6)| 0.033(5)| 0.035(5)| 0.09(2)| 0.07(2)| 0.09(1)| 0.04(2)|
| Al₂O₃      | 1.15(3)| 1.20(2)| 1.26(2)| 1.27(3)| 1.23(3)| 19.1(1)| 19.5(4)| 18.2(4)| 20(4) |
| FeO        | 0.75(1)| 0.73(1)| 0.72(1)| 0.68(1)| 0.78(1)| 0.28(2)| 0.29(1)| 0.29(1)| 0.37(4)|
| MgO        | 39.7(1)| 40.02(6)| 39.80(7)| 40.0(1)| 40.07(7)| 34.8(7)| 34.4(3)| 34.2(3)| 30(1) |
| F          | 0.37(2)| 0.33(1)| 0.347(1)| 0.45(1)| 0.40(2)| 0.5(1)| 0.70(3)| 0.78(3)| 2.4(5) |
| Total      | 86.3(2)| 84.2(1)| 84.4(1)| 84.7(1)| 82.9(7)| 83.7(4)| 84.5(7)| 92(3) |
| H₂O        | 13.7(2)| 15.8(2)| 15.6(2)| 15.3(1)| 17.3(6)| 16.3(4)| 15.5(7)| 7(3) |
| Cations calculated on the basis of 7 oxygens for antigorite and 14 for chlorite |
| Si          | 2.04  | 2.01  | 1.99  | 1.99  | 1.99  | 2.72  | 2.76  | 2.93  | 3.23  |
| Cr          | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.01  | 0.01  | 0.01  | 0.00  |
| Al          | 0.06  | 0.07  | 0.07  | 0.07  | 0.07  | 0.20  | 0.21  | 0.23  | 3.80  |
| Fe          | 0.03  | 0.03  | 0.03  | 0.03  | 0.03  | 0.02  | 0.02  | 0.02  | 0.03  |
| Mg          | 2.74  | 2.80  | 2.82  | 2.83  | 2.83  | 5.07  | 4.93  | 4.82  | 3.80  |
| F           | 0.05  | 0.05  | 0.05  | 0.07  | 0.06  | 0.15  | 0.21  | 0.23  | 0.65  |
| Experiment | SFE6F | SFE4F | SFE32F | SFE27 | SFE28 | SFE26 | SFE20 | SFE25 | SFE32 |
| Mineral    | chn   | chn   | chn   | chn   | chn   | chn   | chn   | chn   | hu    |
| n          | 5     | 3     | 49    | 10    | 7     | 3     | 12    | 12    | 3     |
| SiO₂       | 30.6(9)| 31.7(1)| 32.8(3)| 39.1(4)| 39.5(3)| 39.4(4)| 38.1(8)| 38.7(7)| 37.8(4)| 43.3(1)|
| Cr₂O₃      | 0.02(2)| 0.02(3)| 0.015(4)| 0.02(1)| 0.01(1)| 0.008(9)| 0.03(1)| 0.016(9)| 0.02(1)| 0.04(1)|
| Al₂O₃      | 0.09(2)| 0.01(1)| 0.15(8)| 0.07(3)| 0.15(4)| 0.08(7)| 0.07(2)| 0.11(5)| 0.14(5)| 0.9(3)|
| FeO        | 0.34(2)| 0.37(3)| 0.44(1)| 0.28(4)| 0.32(6)| 0.3(1)| 0.41(7)| 0.49(4)| 0.67(5)| 0.6(1)|
| MgO        | 60.8(3)| 60.0(6)| 58.4(8)| 57.8(3)| 57.0(3)| 57.7(7)| 57.8(4)| 56.0(8)| 57.0(7)| 47.8(2)|
| F          | 7.5(4) | 6.8(2) | 6.3(2) | 2.1(4) | 1.9(3) | 1.6(4) | 2.0(3) | 2.1(3) | 2.2(3) | 1.7(3)|
| Total      | 99.2(5)| 99(1)  | 98.1(4)| 99.5(3)| 98.9(2)| 99.0(7)| 98.4(6)| 97.4(5)| 97.8(5)| 94.5(2)|
| H₂O        | 0.8(5) | 1(1)   | 1.9(4) | 0.5(3) | 1.1(2) | 1.0(7) | 1.6(6) | 2.6(5) | 2.2(5) | 5.5(2)|
| Cations calculated on the basis of 9 oxygens for chondrodite, humite and 12 for clinohumite |
| Si          | 1.56  | 1.60  | 1.70  | 2.74  | 2.78  | 2.78  | 2.70  | 2.76  | 2.68  | 2.87 |
| Cr          | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00 |
| Al          | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  | 0.07 |
| Fe          | 0.01  | 0.02  | 0.02  | 0.02  | 0.02  | 0.02  | 0.02  | 0.03  | 0.04  | 0.03 |
| Mg          | 4.63  | 4.59  | 4.52  | 6.03  | 5.98  | 6.06  | 6.11  | 5.96  | 6.08  | 2.77 |
| F           | 1.21  | 1.10  | 1.04  | 0.47  | 0.42  | 0.36  | 0.45  | 0.47  | 0.49  | 0.36 |

Numbers in parentheses represent the 2—standard deviation (2 – SD) of the analyses as last significant digits, i.e., 0.07(3) must be read as 0.07 ± 0.03. The number of analyses is indicated with ”n”. H₂O was not measured but calculated from the difference of the EPMA total to 100% Mineral abbreviations: atg antigorite, chl chlorite, chn chondrodite, chu clinohumite, hu humite
Discussion

The effect of F on the stability of antigorite and other hydrous minerals at high pressures and high temperatures

The experimental results do not show any effect of F on the thermal stability of antigorite, in any of the investigated F-bearing systems (Fig. 1). Similarly, the limited data from the system with high F-concentrations indicate that the stability field of chlorite is also unaffected by F, when compared to previous experimental results in F-free systems (Staudigel and Schreyer 1977; Fockenberg 1995; Ulmer and Trommsdorff 1999; Fumagalli et al. 2014; Maurice et al. 2020).

However, F increases the thermal stability of clinohumite (300 °C, Grützner et al. 2017), amphibole (100–250 °C, Foley 1991) or phlogopite (Peterson et al. 1991). The increased stability of these minerals was attributed to the replacement of OH⁻ by F⁻ (similar valence but slightly smaller ionic radius ~ 1.40 Å, and 1.33 Å, respectively; Shannon 1976) in their structure, which in amphibole, mica, and HGM leads to extensive solid solutions between F and OH endmembers. Our data indicate that this is not the case for antigorite, which incorporates only about 0.45 wt% of F in its structure (Table 4). Similarly, the limited data from the system with high F-concentrations indicate that the stability field of chlorite is also unaffected by F, when compared to previous experimental results in F-free systems (Staudigel and Schreyer 1977; Fockenberg 1995; Ulmer and Trommsdorff 1999; Fumagalli et al. 2014; Maurice et al. 2020).

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Experimentally determined F concentrations of antigorite and the F-storage capacity of antigorite, compared to that of other hydrous Mg-silicates in subduction zones

Mg-rich hydrous silicate minerals are common and stable at the P-T conditions of a subducting slab at convergent margins. Antigorite is probably the most abundant of these Mg-rich minerals in the upper parts of the slab, whilst chlorite, clinohumite, and other HGM are stable in deeper parts of the subducted slab (Ulmer and Trommsdorff 1995, 1999; Trommsdorff et al. 1998; Bromiley and Pawley 2003; Scambelluri et al. 2004; Fumagalli et al. 2014; Fumagalli and Klemme 2015). All these hydrous Mg-silicates can accommodate variable amounts of F in their structure (Table 4; Duffy and Ringwood 1979; Rice 1980a, b; Bernini et al. 2012; Wu and Koga 2013; Debret et al. 2014; Grützner et al. 2017; Páge and Hattori 2017; Hughes and Pawley 2019).

Data on the F contents of natural antigorite have been reported in only two studies to date. Debret et al. (2014) measured up to 22 µg/g F in antigorite from the Western Alps ophiolites, while Páge and Hattori (2017) reported a maximum of 154 µg/g F in antigorite from the Dominican Republic. The experimental antigorite (in Fsys = 2 wt%) contains between 0.3 and 0.45 wt% F and shows no correlation with P, T, or major element composition. Since the F content remains constant over the investigated P–T range, we propose antigorite to be saturated in F, and 0.40 ± 0.05 wt% F is its maximum storage capacity.

Fluorine concentrations in natural chlorite range from 0.12 to 0.4 wt% (Parry and Jacobs 1975; McPhie et al. 2011), whereas our experimental chlorite (i.e., the clinochloride endmember) contains from 0.5 to 0.8 wt% F. One experimental chlorite contains 2.4 wt% F (Table 4; run SFE32) and this seems to indicate a strong effect of chlorite composition on the F storage potential. Further interpretations are hindered by the lack of experimental data on the solubility of F in chlorite. Although we cannot address these issues further in this study, further experimental studies on the stability of chlorite in complex compositions are needed, as chlorite is one of the key phases that may transport volatiles into the deeper mantle in subduction zones.

Experimental studies showed that clinohumite and HGM incorporate significant amounts of F, for example, clinohumite can incorporate up to 6.2 wt% F, chondrodite up to 9.9 wt% F, and humite up to 8.5 wt% F (Weiss 1997; Stalder and Ulmer 2001; Bernini et al. 2012; Grützner et al. 2017; Wu and Koga 2018; Hughes and Pawley 2019). Our experimental results (Table 4) are in good agreement with these results (Table 4).

Overall, the experiments with chloride and HGM confirm the affinity of hydrous Mg silicates for F and our new data show that antigorite can take up to 0.45 wt% F. These F concentrations can then be qualitatively related to breakdown reactions of antigorite to evaluate the transport mechanisms of F in subduction zones. Additionally, these reactions can be used to understand the process(es) by which F may be released in the overlying mantle wedge and/or transported to the deep mantle.
**Breakdown reactions of antigorite**

**Antigorite → forsterite + enstatite + fluid**

Previous experiments in F-free systems (e.g., Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997; Bromiley and Pawley 2003) showed that antigorite breaks down to form olivine, orthopyroxene, and a hydrous fluid phase (Reaction 1). Our experiments in a F-free (between 2 and 3 GPa) and F-bearing system with 2 wt% F (between 2 and 5 GPa) revealed the same breakdown products. Moreover, in the F-bearing system olivine and orthopyroxene did not contain any F (Supplementary Table S1), and consequently all water and F that is stored in antigorite will be released into the fluid upon antigorite breakdown since F partitions strongly into the fluid (\(D_F\) mineral/fluid for olivine and orthopyroxene is \(< 1\), Bernini et al. 2012). Hence Reaction (1) may be written as follows:

\[
\text{antigorite} \rightarrow \text{forsterite} + \text{enstatite} + F\text{-bearing hydrous fluid,}
\]

\[
\text{Mg}_3(\text{Si, Al})_2\text{O}_5(\text{OH, F})_4 \rightarrow \text{Mg}_2\text{SiO}_4 + \text{Mg(Si, Al)O}_3 + 2(\text{H}_2\text{O}, F)
\]

where F-bearing fluids generated through Reaction (3) may enrich the mantle wedge in F (see section “Recycling of \(H_2O\) and F in subduction zones”).

**Antigorite → chlorite + HGM**

In nature, the formation of chlorite upon antigorite breakdown has been previously documented in chlorite-bearing harzburgites from Cerro del Almirez, Spain (Trommsdorff et al. 1998; Scambelluri et al. 2004). In our experimental runs, the breakdown of antigorite in a F-rich system (\(F_{sys} = 5\) wt%) leads to the formation of chlorite and HGM. Previous studies showed that both the formation of chlorite and HGM is enhanced in systems with elevated Mg contents and high Mg/Si (Wu and Koga 2013; Hughes and Pawley 2019; Iacovino et al. 2020), and/or in systems with F-rich saline fluids (> 1.6 wt% F, Bernini et al. 2012). Thus, the crystallization of chlorite and HGM as breakdown products of antigorite instead of forsterite and enstatite can be attributed to the high Mg and F contents of the system (Fig. 1B, C). Whether this is primarily controlled by Mg or F is unclear. Although it is difficult to assess the exact nature of the reaction due to the complexity of the system, we propose two breakdown reactions that explain our experimental observations. Reaction is valid for pressures < 5 GPa where clinohumite is absent and Reaction 5 is valid for pressures > 5 GPa where clinohumite is stable as follows:

\[
2 \text{antigorite} + 2 \text{forsterite} + \text{enstatite} + 2 \text{brucite} + 2(\text{H}_2\text{O}, F) = \text{chlorite} + \text{humite} + 3 \text{water}
\]

\[
2\text{Mg}_3(\text{Si, Al})_2\text{O}_5(\text{OH, F})_4 + 2 \text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3 + 2 \text{Mg(OH)}_2 + 2(\text{H}_2\text{O}, F)
\]

\[
= \text{Mg}_6(\text{Si, Al})_4\text{O}_{10}(\text{OH, F})_8 + \text{Mg}_7\text{Si}_3\text{O}_{12}(\text{OH, F})_2 + 3 \text{H}_2\text{O}
\]

**Antigorite → chlorite + HGM**

2 antigorite + 3 forsterite + 4 enstatite + 6 brucite + 4(\(H_2O, F\))

\[= \text{chlorite} + \text{humite} + \text{clinohumite} + 8 \text{water}
\]

\[
2\text{Mg}_3(\text{Si, Al})_2\text{O}_5(\text{OH, F})_4 + 3 \text{Mg}_2\text{SiO}_4 + 4 \text{MgSiO}_3 + 4 \text{Mg(OH)}_2 + 4(\text{H}_2\text{O}, F)
\]

\[= \text{Mg}_6(\text{Si, Al})_4\text{O}_{10}(\text{OH, F})_8 + \text{Mg}_7\text{Si}_3\text{O}_{12}(\text{OH, F})_2 + 8 \text{H}_2\text{O}
\]

These reactions describe antigorite breakdown in a F-rich system. Antigorite (saturated in F) reacts with olivine, orthopyroxene, brucite, and a F-bearing hydrous fluid to form chlorite, humite (chondrodite), and a fluid phase at pressures < 5 GPa (Reaction 4). At pressures > 5 GPa, clinohumite occurs as an additional phase (Reaction 5). Whilst \(H_2O\) and significant Mg-contents in the system are necessary to form these phases, the presence of Al (in the antigorite, and in the bulk rock) controls the amount of chlorite formed (Ulmer and Trommsdorff 1999), and F affects both the HGM (Duffy and Ringwood 1979; Rice 1980a, b; Bernini et al. 2012) and potentially also the formation of chlorite (unfortunately no experimental data are available for chlorite).

Since chlorite, humite and clinohumite can incorporate high amounts of F in their structure (Table 4; Duffy and Ringwood 1979; Rice 1980a, b; Bernini et al. 2012; Wu and Koga 2013; Grützner et al. 2017; Hughes and Pawley 2019), Reactions (4) and (5) show that most of the F that resided in antigorite and in the hydrous fluid will partition into chlorite, humite and clinohumite upon antigorite breakdown. The fluid that is generated by the reaction is expected to show low F/\(H_2O\). Therefore, Reactions (4) and (5) provide mechanisms by which F is retained in the minerals of a subducting slab rather than being released into the aqueous liquid, which rises into the mantle wedge above the slab. In summary, our experiments show that in bulk rock compositions with no (F-free) or moderate amounts of F Reaction (3) occurs, and antigorite dehydrates completely to form olivine and orthopyroxene.
However, antigorite breakdown in F-rich systems leads to the formation of F-rich chlorite and HGM (Reactions 4 and 5), which become the prime carriers of F in the mantle due to their larger P–T stability field (Fockenberg 1995; Ulmer and Trommsdorff 1999; Stalder and Ulmer 2001; Pawley 2000; Bromiley and Pawley 2003; Fumagalli et al. 2014; Grützner et al. 2017). In the next paragraph, we will explore the natural scenarios where these reactions may take place and how our experimental results, in conjunction with literature data, may be used to shed new light on water and F recycling processes in subduction zones.

**Recovery of \( H_2O \) and F in subduction zones**

Subducted oceanic plates consist of a 6–7 km-thick layer of variably metamorphosed oceanic crust and underlying serpentinized peridotite (Schmidt and Poli 1998), in which antigorite is the most abundant mineral, (Schmidt and Poli 1998; 2014; Bouilhol et al. 2015). The maximum thermal stability of antigorite is at about 700 °C (e.g., Ulmer and Trommsdorff 1995; Bromiley and Pawley 2003; Maurice et al. 2020; present study) and recent geodynamic thermal models suggest that this temperature is reached in the subducting slab at depths between ~120 and 200 km (e.g., Rüper 2004; Syracuse et al. 2010). Natural antigorites from ophiolites are not saturated in F (Debret et al. 2014; Páge and Hattori 2017).

However, according to our data, antigorite may retain ~0.45 wt% of F, in addition to other halogens (i.e., Cl) as shown in previous studies for high-pressure serpentinites (Scambelluri et al. 2004; Bonifacie et al. 2008; John et al. 2011). Hence, an open system in which F-bearing fluids continuously infiltrate the serpentinite is required to saturate antigorite in F. For example, slab components with similar F contents (i.e., Cl) may be used to shed new light on water and F recycling processes in subduction zones. A potential mechanism that generates such F-rich fluids has been proposed by Tropper and Manning (2007) who investigated the solubility of fluorite (present in subducted sediments and evaporites), in \( H_2O \) and NaCl-bearing fluids. They show that fluorite solubility increases by a factor of 17 between 600 °C and 700 °C (at 0.75–2 GPa) and concluded that fluids generated during devolatilization of fluorite-bearing sediments, can contain between ~0.6 to 4.12 wt% F (Tropper and Manning 2007).

If the percolating fluids attain ~2 wt% F, our experimental results indicate that antigorite will accommodate up to ~0.3 to 0.4 wt% of F, which can then be released upon dehydration into the overlying mantle wedge (Reaction 3). For example, slab components with similar F contents have been calculated for the Kamchatka arc (Portnyagin et al. 2007), partly attributed to the dehydration of serpentinites. Hence, antigorite dehydration over a range of depths (from ~120 km to about 200 km, Schmidt and Poli 2014) can lead to a continuous flux of F-rich fluids into the mantle wedge.

In the event where fluids reach values of ~4 wt% F, antigorite breakdown results in the formation of F-rich chlorite and HGM Reactions (4) and (5), which are stable at higher P and T than antigorite (Fockenberg 1995; Ulmer and Trommsdorff 1999; Pawley 2000; Bromiley and Pawley 2003; Fumagalli et al. 2014; Fumagalli and Klemme 2015) (Stalder and Ulmer 2001; Grützner et al. 2017) and can thus transport F to depths >200 km.

Figure 2 depicts the different scenarios of antigorite breakdown in both F-bearing systems (\( F_{sys} = 2 \) wt%, and \( F_{sys} = 5 \) wt%) for a hot subduction zone P–T path (red dashed line, modeled after slab geotherms of Mexico; Syracuse et al. 2010) and a rather cold subduction zone P–T path (blue dashed line, modeled after slab geotherms of Tonga; Syracuse et al. 2010). Antigorite is the main mineral phase of the serpentinized mantle part of the slab, which is located below ~6 to 7 km of the metamorphosed oceanic crust (Schmidt and Poli 1998; 2014; Bouilhol et al. 2015).

In the system with 2 wt% F, antigorite breaks down to forsterite, enstatite, and a F-bearing fluid (Reaction 3). In a hot slab scenario, antigorite completely dehydrates at about 700 °C and a depth of about 100 km (Fig. 2, point 1), whilst in the Tonga subduction zone (cold slab), it breaks down at 570 °C and 170 km depths. If the slab is undersaturated in terms of F (i.e., a system with low F-concentrations), antigorite breaks in both cases down to anhydrous phases such as olivine and orthopyroxene (Fig. 2), and almost all water and F will be released as a free fluid phase, and this fluid will infiltrate the overlying mantle wedge.

In a system in which antigorites are F-saturated (i.e., a F-rich or a system with high F/H\( _2O \)), our experiments show that antigorite breaks down at the same P–T conditions (Fig. 2, atg-out line), but the mineralogy of the post-antigorite phase assembly changes. In the high F-system, antigorite breaks down to chlorite and HGM at 700 °C and 100 km depths in the Mexico slab (Fig. 2, point 1), and at 570 °C and 170 km depths (Fig. 2, point 2) in the Tonga slab. Reactions (4) and (5) show that much less F-rich fluid is produced in this scenario as both chlorite and HGM incorporate large amounts of F. These phases will retain F in the peridotite layer of the slab, which can further stabilize HGM (Stalder and Ulmer 2001; Grützner et al. 2017).

Hence, dehydration of the serpentinized peridotite layer of
both the hot and the cold slab is not complete and most of the F is retained in chlorite and HGM that can be subducted deeper into the mantle. The chlorite breaks down at ~800 °C and ~125 km depths in the Mexico slab (point 4, Fig. 2) and ~600 °C and ~160 km depths in the Tonga slab (point 3, Fig. 2). In the latter case, some of the water is released at these P – T conditions (i.e., 2 wt%, reaction 3), and to chlorite and HGM in F-rich systems (i.e., 5 wt%, reactions 4 and 5). Point (3) depicts the P–T conditions at which the Moho of the (in a cold subducted slab (e.g., Tonga) will intersect the chlorite-out boundary, and in this scenario HGM will be the prime carriers of F in the slab at depths greater than about 170 km depth. Point (4) displays the P – T conditions F-rich system at which chlorite and HGM break down into anhydrous forsterite and enstatite, thus releasing all the volatiles. The area colored in grey indicates the P – T – depth space in which HGM are the sole F-bearing and water bearing minerals in our system. When chlorite breaks down (chl-out), all F is transferred to HGM, that may transfer F and some water to much greater depths, perhaps even into the transition zone of the mantle (Grützner et al. 2017).

The transport of F into the deeper mantle is depicted in a sketch diagram (Fig. 3), which shows the determined hydrous mineral stabilities of a subducted slab. This scenario agrees well with observations from previous studies that proposed significant fractionation of F from H$_2$O in subduction zones (Straub and Layne 2003). Furthermore, in a pioneering study John et al. (2011) suggested that F resides in the altered harzburgitic lithosphere in the slab and is not significantly released during serpentinization. Instead, they proposed that F remains in the minerals of the subducting slab and that most of the F is recycled back into the mantle. Our study agrees with this line of reasoning and provides a mechanism by which F can be transferred from antigorite to chlorite and HGM, i.e., chondrodite and humite, that are known to accommodate high amounts of F (Evans and Trommsdorff 1983; Lopez Sánchez-Vizcaíno et al. 2005). We also surmise that F-saturated antigorites will be discovered in the near future, especially as improved analytical techniques (e.g., Zhang et al. 2016; Flemetakis et al. 2020) now allow the quantitative analysis of F with the electron microprobe.
Conclusions

- We present the first experiments on antigorite stability in F-bearing systems. The experiments show that F does not significantly affect the thermal stability of antigorite.
- We present the first experimental data on the F storage capacity of antigorite and chlorite.
- In bulk rock compositions where antigorite is not saturated with F, the antigorite breakdown leads to the formation of olivine and orthopyroxene, and all water and F are released into the fluid. However, in rocks in which antigorites are F-saturated, chlorite and humite-group minerals are formed when antigorite breaks down, and in this scenario, F remains in the newly formed mineral phases in the subducting slab.
- Thermal models of subduction zones suggest that chlorite and humite-group minerals, which are formed upon antigorite breakdown, can transport F into the deeper mantle and potentially even into the transition zone.
- Further experimental studies are needed to better understand the role of chlorite in the transport of volatiles in the deep mantle.

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