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FLUORINE–HYDROXYL SUBSTITUTION IN TREMOLITE

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ABSTRACT

Experiments at 1 to 2 kbar total pressure, 600–850°C aimed at exchanging fluorine and hydroxyl ions in tremolite under controlled conditions of HF and H_2O fugacities have only been partially successful. The fluorine buffer technique of Munoz and Eugster was used in the gas system O–H–F with the solid assemblages anorthite + fluorite + sillimanite + quartz (higher HF/H_2O) and wollastonite + fluorite + quartz (lower HF/H_2O). Melting of the first buffer at a temperature greater than 700°C at 2 kbar limits its utility.

Fluorine–hydroxyl exchange is much slower in tremolite compared to reported rates for biotites. The slow rate of exchange may be due to the structural differences between sheet and chain silicates, lack of *A*–site occupancy in this amphibole, and grain size effects. Tremolite also extracts less fluorine from a coexisting vapor than does phlogopite.

A breakdown loop involving the production of talc marks the lower thermal stability of intermediate F/OH tremolite. This loop was found at 700°C, 1 kbar for intermediate (F,OH) tremolite, and could exist at a higher temperature for pure fluortremolite.

INTRODUCTION

In recent years, members of the rock–forming amphibole group have been studied anew by crystallographic methods with the goal of understanding relationships between their chemistry and structure (*e.g.*, Papike, Ross, and Clark, 1969; Mitchell, Bloss, and Gibbs, 1971), and by experimental methods with the aim of understanding the relationship between chemistry and stability, (*e.g.*, Greenwood, 1963; Ernst, 1966; Gilbert, 1966; Forbes, 1971). Some of the prior experimental work has also been directed towards investigating effects on structure of substituting various cations for one another (Colville, Ernst, and Gilbert, 1966; Huebner and Papike, 1970). However, amphibole structure and stability is also known to depend strongly on anionic substitutions, principally between F and OH in the O_3 position of the structure (Fig. 1). Previously, F end members of some standard amphibole compositions have been synthesized (*e.g.*, Comeforo and Kohn, 1954; Huebner and Papike, 1970), and a large program on the synthesis of fluorinated amphiboles was undertaken by the U.S. Bureau of Mines in the 1950's (summarized in Shell, Come-

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foro, and Eitel, 1958). Russian workers have long been active in this field (*e.g.*, Fedoseev *et al.*, 1970). However, few syntheses of amphiboles containing both F and OH in the O_3 position have been reported. Techniques in which fugacities of volatile contituents can be buffered to definite values at elevated pressure are now available (Eugster and Skippen, 1967). Control of fluorine–water fugacity ratios has specifically been attempted by Munoz and Eugster (1969) for phlogopite and by Munoz (1971) for annite. We have attempted fluorine–hydroxyl substitution in amphiboles (1) in order to get some idea of F/OH exchange ability in chain silicates, (2) to determine F/OH fractionation between the vapor and solid phase, and (3) as a first step in looking at the stability relations of F/OH–bearing amphiboles. Furthermore, experimental determination of fluorine distribution among solid and fluid phases in crystallizing environments may aid geothermometric studies which are based on the fractionation of fluorine into different natural minerals (Stormer, Carmichael, and Hemming, 1970).

Tremolite, $\square Ca_2Mg_5Si_8O_{22}(OH,F)_2$ was chosen for the exchange experiments for several reasons. It has a relatively simple chemistry with no *A*–site occupancy. Both the pure OH and pure F end members had been synthesized previously (Boyd, 1959; Comeforo and Kohn,

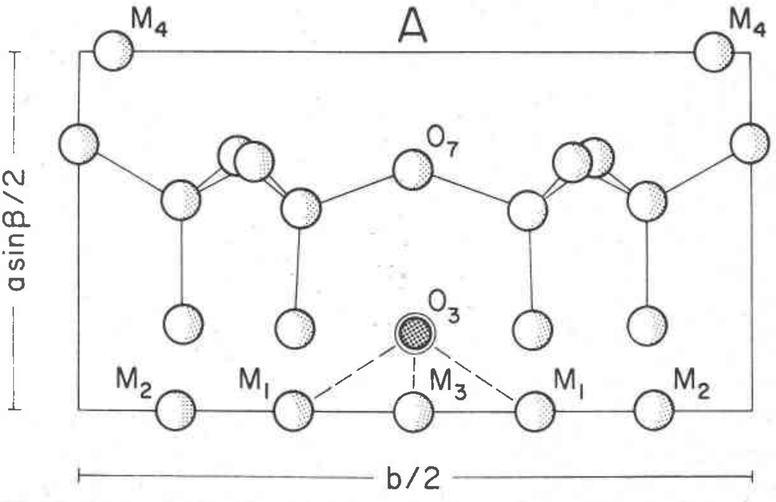

FIG. 1. Schematic drawing of 1/4 of the tremolite unit cell. The O_3 anion position is shown as a double circle representing a radius of 1.34Å when occupied by OH^- and of 1.30Å when occupied by F^-. The coordination/bonding to the three metal ions M_1, M_3, M_1 is depicted by dashed lines. Capital "A" indicates the vacant *A*–site in tremolite which lies on the line joining the M_4 positions.

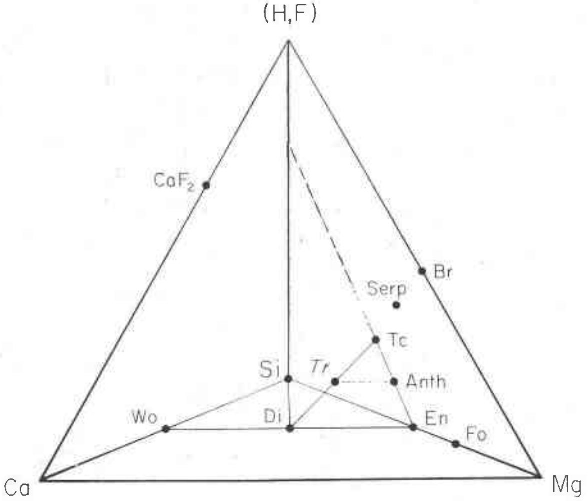

FIG. 2. Phase tetrahedron of the OH–F tremolite system. For the OH system each corner is the oxide except the top which is OH. For the F system, replace OH by F and plot CaF_2 as if Ca corner is oxygen–free. The only quaternary phase is tremolite which appears on the join between diopside and talc. The plane defined by wollastonite, enstatite, and tremolite cuts the Si–(H,F) side of the tetrahedron as indicated by the sloping dashed line. Possible solid solution is shown by a dashed line connecting tremolite and anthophyllite. Abbreviations: Wo = wollastonite; Di = diopside; En = enstatite; F = forsterite; Tr = tremolite; An = anthophyllite; Tc = talc; Serp = serpentine; Br = brucite.

1954) which insured that starting materials for the exchange experiments could be obtained. It was also of importance that the OH–tremolite structure was well known (Papike, Ross, and Clark, 1969) and that the F–tremolite structure was being determined concurrently by M. Cameron (1971). Of direct geological significance was the fact that tremolites from some metamorphosed carbonate rocks are F–bearing and it was hoped that interpretation of HF and H_2O fugacities in those natural environments would be aided.

EXPERIMENTAL PROCEDURES

Apparatus

Experiments were performed in conventional hydrothermal apparatus using 1-1/4″ O.D., horizontally–mounted, cold–seal pressure vessels of Stellite (Haynes alloy #25) or Rene 41 alloy. Temperature sensing was accomplished with unsheathed chromel–alumel thermocouples inserted in the wall of the vessels in conjunction with a Leeds and Northrup type K-4 potentiometer. Temperatures were continuously monitored with an Esterline Angus multipoint recorder. Temperatures reported here are uncorrected. Subsequent calibration by K. L.

Cameron against the melting points of NaCl (800.5°C) and CsCl (646°C) yielded corresponding temperatures of 808°C and 649°C respectively. Total fluid pressures were read on 16-inch Bourdon-tube, Heise gauges with ranges to 4, 5, or 7.7. kilobars.

Starting materials

Two mix compositions for the end members (OH)-tremolite and F-tremolite were prepared with the following compounds: $CaCO_3$ (Fisher Lot 750542) dried 5 hours at 460°C; CaF_2 (Fisher Lot 754200) dried at about 400°C; MgO (Material Research Corporation, Job No. 30635) dried at *ca.* 1000°C for 24 hours; SiO_2 glass (Corning silica glass code 7940) crushed, sieved (120–130 mesh), boiled in HCl, and dried.

Buffer methods

Two kinds of buffers were chosen to establish different HF/H_2O fugacity ratios. The AFSQ-buffer, which gives the higher HF/H_2O values, is based on the reaction:

$$\text{anorthite} + 2HF \leftrightarrows \text{fluorite} + \text{sillimanite} + \text{quartz} + H_2O$$

The WFQ-buffer reaction is:

$$\text{wollastonite} + 2HF \leftrightarrows \text{fluorite} + \text{quartz} + H_2O$$

Materials for the AFSQ-buffer were synthetic anorthite and sillimanite, CaF_2 (Fisher Lot 754200), and natural quartz. These were combined in proportions to produce a balanced reaction, except, by mistake, only one half the amount of sillimanite needed was used. Synthesis of anorthite was carried out at 815°C at 2 kbar water pressure (168 hours) and that of sillimanite attempted at 800°C at 1 kbar water pressure (340 hours). X-ray powder diffraction patterns of the anorthite charge showed traces of wollastonite and metastable corundum; for sillimanite, some quartz and metastable cristobalite. The X-ray pattern of the aluminum silicate did not exclude the possibility of mullite synthesis. The fact that the run seemed to carry an excess of SiO_2 could indicate that some mullite may have been synthesized. Quartz for both buffers was taken from a clear 2 inch quartz crystal ground in agate with acetone and boiled for 2 hours in 30 percent HCl. The aluminum for anorthite and sillimanite syntheses was Al-oxide hydrated (Type RH of United Mineral and Chemical Corp.; purity 99.99 wt.%; weight loss on drying, 31.61%). Difficulties arose with the AFSQ-buffers at temperatures above 700°C because of melting. Where melt appears and a solid phase is lost, HF/H_2O fugacity ratios are not explicit. The WFQ-buffer was mixed using synthetic wollastonite (made at 790°C, 2 kbar water pressure, 164 hours) with CaF_2 and SiO_2 sources as listed above.

Arrangement of capsules for the solid fluorine buffer assemblages is similar to that described by Munoz and Eugster (1969). The sample is housed in an unsealed gold tube which is then sealed in a platinum capsule (0.120″ O.D.) with 4 mg H_2O and the fluorine buffer assemblage. These, in turn, were sealed in gold capsules (0.210″ O.D. 1-1/2″ long) containing a Ni–NiO buffer and 20 mg. distilled H_2O.

Cell Parameter Determinations

Cell parameters of synthesized end member tremolites and tremolites subjected to the exchange experiments were determined using a Norelco X-ray powder diffractometer equipped with a graphite crystal monochrometer and using copper radiation. The internal standard employed was a synthetic spinel-powder ($MgAl_2O_4$: $a = 8.083$ Å, determined by J. V. Smith and G. V. Gibbs) that yielded the following reflections calculated in 2θ, $CuK\alpha$: (111) 19.016°; (220) 31.298°; (311) 36.878°; and in 2θ, $CuK\alpha_1$; (400) 44.810°; (511) 59.358; (440) 65.236°; (620) 74.122°; (553) 77.342°. These eight peaks taken from a mixed tremolite–plus spinel pattern gave fairly smooth correction curves. Indexing of the amphibole peaks was done by comparison with the peaks listed in Borg and Smith (1969, p. 362). Strip chart patterns ran for 6 scans, three up and three down scale at a scan rate of 1/4° 2θ/min and a chart rate of 1 in/min. Reflections were measured to 0.05 inch for every scan. Averages of these values were corrected by the internal standard curve. All amphibole peaks below $2\theta = 38°$ were determined for $K\alpha$, all peaks above for $K\alpha_1$. Peaks were measured at a level of 2/3 of the peak height. The number of tremolite peaks measured ranged between 25 and 35, chosen in each case according to the sharpness of the peak. Calculations of the lattice parameters were accomplished by two different computer programs: the program coded by Burnham (1962), which weights the high angle peaks more than the low, and the program designed by Evans, Appleman, and Handwerker (1963) run using unit weights throughout. The resulting refinements, based on the different weighting schemes, were usually, but not always, nearly the same. The data are reported in Tables 1, 3, and 4 using the Burnham program. Refinements were completed in three cycles using 0.01 Å cut off between observed and calculated *d*–values on the first cycle and 0.005Å thereafter.

SYNTHESIS OF THE PURE END MEMBERS

OH–tremolite synthesis is not easy to achieve (see Boyd, 1959). Only one data set for the unit cell of a synthetic OH–tremolite was previously known (Colville, Ernst, and Gilbert, 1966) (see our Table 1). Production of OH–tremolite was accomplished by sealing an oxide mixture in gold capsules with distilled H_2O and (1) running for 360 hours at 650°C, 1 kbar, then grinding and rerunning under the same conditions for 1506 hours; or (2) running for 362 hours at 775°C, 4 kbar, grinding and rerunning for an additional 618 hours under the same conditions. The 1 kbar runs were slightly less well crystallized compared to the 4 kbar runs. Also, traces of talc were noted on the X–ray powder diffraction scans of the 1 kbar runs. Abundance of the amphibole in these synthesis runs was estimated to be 85–95 percent of the charge. F–tremolite was synthesized in a platinum–wound quenching furnace under 1 atm external pressure and temperatures ranging between 1090° and 1155°C. The stoichiometric starting mixture was sealed in 0.120″ O.D. platinum capsules of 1 to 1-1/4 inch length. Only 1/10 to 1/5 of the capsule was filled with oxide mixture and the balance collapsed so that some volume would be available for a gaseous fluorine phase. Individual experiments lasted 20 hours to 1 week. Longer runs seem to yield larger crystals but the percentage of amphibole could not be improved. No mixture was converted to 100 percent fluor–tremolite, however tremolite was always the main phase at an estimated 80–90 percent of the assemblage. Besides tremolite, clinopyroxene, fluorite, and tridymite or cristobalite were found microscopically and by X-ray powder diffraction. These phases are possibly the high temperature breakdown products (*cf.*, Fig. 2). On the basis

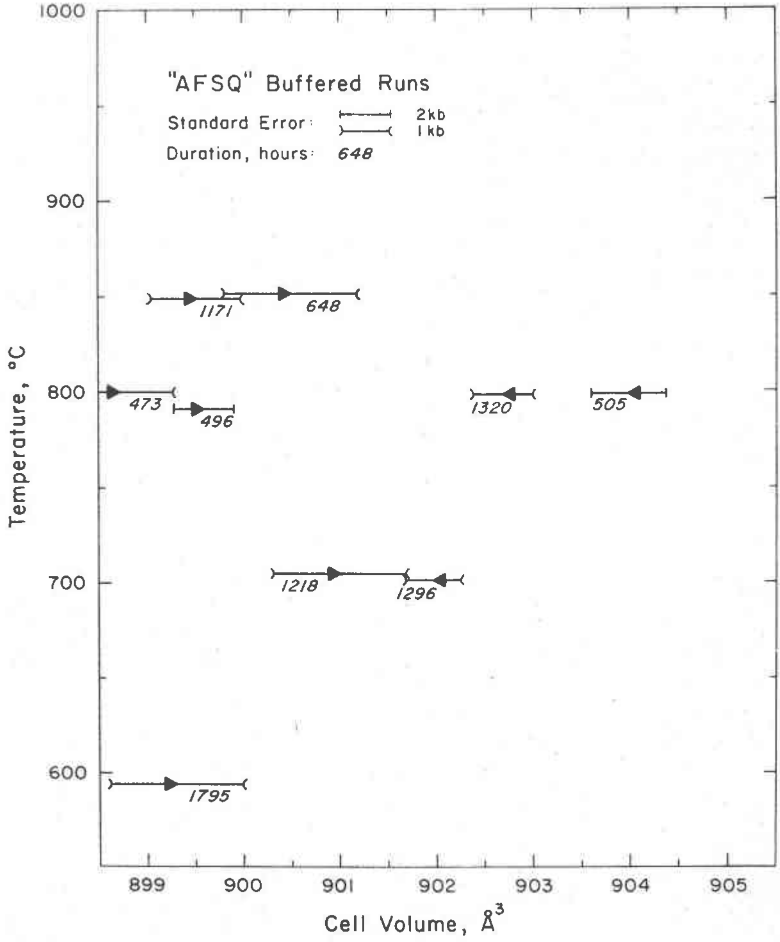

FIG 3. Plot of temperature versus cell volume of exchanged tremolites. Only the runs at 700°C and below have HF fugacity controlled by the anorthite + fluorite + sillimanite + quartz (*AFSQ*) buffer. Above 700°C the "buffer" assemblage partially melts. Arrows show direction from which the cell volume was approached. Length of bar represents the standard error computed by the Burnham least-squares refinement program.

of 38 synthesis runs, it appears that the upper thermal stability of F–tremolite lies between 1155° and 1165°C. This is in contrast to prior reports that imply F–tremolite may be stable to 1200°C or greater (Comeforo and Kohn, 1954) or that F–tremolite melts incongruently to forsterite + liquid on breakdown (report of Van Valkenburg and Pike noted in Comeforo and Kohn, 1954). However, it should be emphasized that the breakdown assemblage reported here is a metastable one because only one diopside–like, but Mg–rich, pyroxene phase is present whereas both an orthopyroxene and a clinopyroxene should be present (Boyd and Schairer, 1964).

A previously crystallized F–tremolite run at 690°C for one week showed no sign of decomposition. Either F–tremolite was still in its stability field or the breakdown reaction rate on the low temperature side is extremely slow. Results discussed later in this paper may indicate that the lower thermal stability should be at a higher temperature than 700°C.

Two F–tremolites and two OH–tremolites chosen for determination of the cell dimensions are listed in Table 1. Data are also listed for a selected single crystal of a F–tremolite grown with the same equipment reported in Cameron (1971). Evaluation of the F/OH value of exchanged intermediate tremolites was based on a linear extrapolation between averages of the cell volumes of these end members (Table 2). The significant changes in the lattice parameters occur in the *a* and *b* crystallographic directions. The ionic radius of three–coordinated F is 1.30Å (Shannon and Prewitt, 1969), and of three–coordinated OH is 1.34Å (Ribbe and Gibbs, 1971). The difference between their diameters is then 0.08Å which is about twice the observed changes in *a* and *b* (Table 2).

The amphiboles obtained in the synthesis of the pure end members are assumed to be on composition. With the bulk chemistry employed here, solid solution is possible only with anthophyllite component, $\square Mg_7Si_8O_{22}(OH,F)_2$. This orthoamphibole has a cell volume of 1756$Å^3$ for the synthetic OH end member (Greenwood, 1963). Comparison of the cell volume of OH–tremolite (905.6$Å^3$) and of 1/2 that of OH–anthophyllite (878$Å^3$) indicates that solutions containing anthophyllite component should tend toward lower volumes. As the volumes for several different syntheses of ours compare well with those reported by other workers for both end members (Table 1), and as the proportions of breakdown phases remain nearly constant whether or not an amphibole is present, we conclude that our tremolites are nearly stoichiometric. The chemical analyses of natural tremolites listed in Table 5 also show no evidence of solution toward anthophyllite.

Table 1. Conditions of Synthesis and Lattice Parameters of End Member Tremolites

Starting Mixture	T, °C	P, bars	duration, hours	a, Å	b, Å	c, Å	β	Vol, Å^3
(OH)-Trem	650	1010	1866	9.8275(28)[1]	18.0594(64)	5.2763(26)	104°42'(2')	905.8(4)
(OH)-Trem	775	4060	980	9.8217(24)	18.0548(52)	5.2771(18)	104°38'(1')	905.4(4)
(OH)-Trem[2]				9.833(5)	18.054(9)	5.268(4)	104°31'(5')	905.3(1.0)
F-Trem	1142	1 atm	29	9.7831(25)	18.0161(41)	5.2675(25)	104°31'(2')	898.8(5)
F-Trem	1132	1 atm	71	9.7766(36)	18.0126(56)	5.2645(17)	104°30'(2')	897.5(6)
F-Trem[3]	1150	1 atm	168	9.787(3)	18.004(2)	5.263(2)	104°26'	898.1(5)
F-Trem[4]				9.781(5)	18.007(4)	5.267(6)	104°31'(5')	898.0
F-Trem[5]				9.7808(12)	18.0102(22)	5.2679(8)	104°31'(1')	898.4(2)

1) One estimated standard deviation indicated in parentheses refers to the last digits.
2) Colville, Ernst and Gilbert, 1966, Table 2. Original sample from Boyd, 1959.
3) Single crystal measurement by Cameron (1971) using a Picker four-circle diffractometer.
4) Comeforo and Kohn, 1954. Table 5.
5) Spacing data of Comeforo and Kohn, 1954, Table 3, run through the least squares refinement program of Burnham using CuKα wave lengths up to 38° two theta and CuKα_1 wave lengths above 38°.

EXCHANGE EXPERIMENTS

General Statement

Experiments aimed at achieving F–OH exchange equilibrium in tremolite were attempted using the previously synthesized pure end members. The effect of the buffers in establishing various F–OH in tremolites was monitored by determining the change of their lattice parameters, principally the cell volume. A summary of the experiments is provided in Figures 3 and 4. They indicate that a change in the cell volumes can be achieved to a certain extent, but that equilibrium was difficult to obtain. Lack of equilibrium in most runs

Table 2. Averages of the (OH,F)-tremolite end members

	Lattice parameters of (OH)-tremolite [2 powder measurements]	Lattice parameters of F-tremolite [2 powder measurements]	Difference in lattice parameters
a, Å	9.8246	9.7799	0.0447
b, Å	18.0571	18.0144	0.0427
c, Å	5.2767	5.2660	0.0107
β, degree	104°40'	104°30'	10'
a sin β, Å	9.5045	9.4684	0.0361
Vol., Å^3	905.6	898.2	7.4

Table 3: Lattice Parameters of AFSQ-buffered runs

Starting Material	T, °C	P, bars	duration, hours	a, Å	b, Å	c, Å	β	Vol., Å^3
(OH)-Trem.	799(1)	1975	505	9.8172(33)	18.0451(39)	5.2744(19)	104°39'(2')	904.0(4)
(OH)-Trem.	799(1)	995	1320	9.8156(16)	18.0297(22)	5.2722(13)	104°39'(1')	902.7(3)
(OH)-Trem.	702(1)	1020	1296	9.8130(20)	18.0253(30)	5.2709(10)	104°39'(1')	902.0(3)
F-Trem.	849(6)	1005	1171	9.7935(24)	18.0144(35)	5.2677(13)	104°34'(1')	899.5(4)
F-Trem.	851(3)	975	648	9.7962(27)	18.0312(46)	5.2676(32)	104°35'(3')	900.5(7)
F-Trem.	791(2)	1990	496	9.7874(17)	18.0211(29)	5.2682(17)	104°30'(1')	899.6(3)
F-Trem.	800°(1)	988	473	9.7940(38)	18.0018(52)	5.2672(26)	104°35'(2')	898.7(6)
F-Trem.	705(5)	1025	1218	9.7557(64)	18.0114(66)	5.2957(38)	104°28'(3')	901.0(7)
F-Trem.	594(1)	990	1795	9.7814(42)	18.0083(99)	5.2723(26)	104°28'(2')	899.3(7)

stands in contrast to the fairly rapid exchange in phlogopite documented by Munoz and Eugster (1969, Fig. 5). Explanation for the difficulty is probably to be found in factors such as grain size, or in bonding and/or crystal structure differences between chain and sheet silicates.

The largest grains of synthetic F-tremolite were commonly 100 to 150 μm in long dimension (Cameron, 1971, used a synthetic crystal 800 μm long) while the largest synthetic OH-tremolite grains were only 10 to 15 μm. Because prior experience had shown that F-phlogopite of grain size of 100 μm exchange extremely slowly (Munoz, personal communication), it was felt at first that this might be an

Table 4: Lattice Parameters of WFQ-buffered Runs.

Starting Materials	T, °C	P, bars	duration, hours	a, Å	b, Å	c, Å	β	Vol., Å^3
(OH)-Trem.	846(1)	1550	242	9.8077(30)	18.0318(43)	5.2723(17)	104°39'(2')	902.1(5)
(OH)-Trem.	799(1)	1990	862	9.8313(21)	18.0298(27)	5.2713(16)	104°42'(1')	903.8(4)
(OH)-Trem.	797(4)	1980	452	9.8191(16)	18.0408(32)	5.2707(10)	104°41'(1')	903.2(3)
F-Trem.	846(1)	1550	242	9.7868(46)	18.0127(55)	5.2693(23)	104°32'(2')	899.2(7)
F-Trem.	799(1)	1970	452	9.7958(43)	18.0294(60)	5.2726(25)	104°37'(3')	901.1(7)
F-Trem.	800(1)	1990	859	9.7934(11)	18.0198(34)	5.2696(18)	104°29'(1')	900.4(3)
F-Trem.	700(1)	1970	737	9.7852(13)	18.0144(26)	5.2647(14)	104°30'(1')	898.5(3)
F-Trem.	614(1)	2000	2130	9.7963(17)	18.0273(26)	5.2669(12)	104°34'(1')	900.3(3)

explanation for the lack of agreement between OH– and F– originated runs. However, inspection of Figures 3 and 4 shows there is no certain or obvious improvement in exchange rate from the OH side and also that duration of run did not systematically lead to larger exchanges. A combination of the effects of variable grain size and diffusion path in the structure could work together to lead to the unsystematic results.

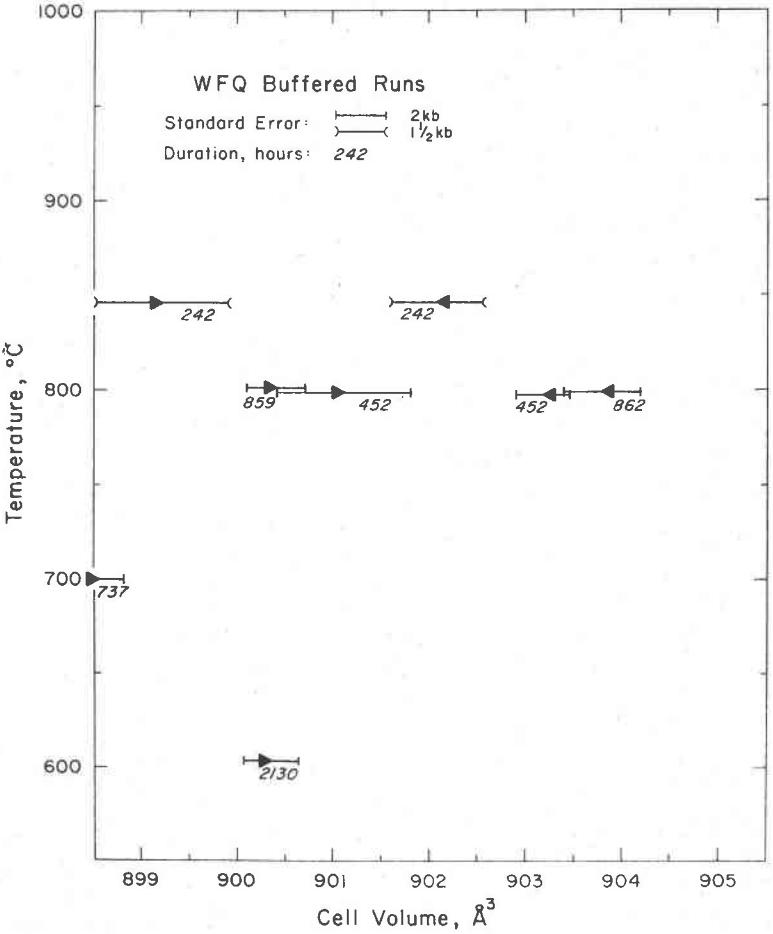

FIG. 4. Plot of temperature versus cell volume of exchanged tremolites. HF fugacity controlled by the buffer assemblage wollastonite + fluorite + quartz (*WFQ*). Arrows show direction from which the cell volume was approached. Length of bar represents the standard error computed by the Burnham least-squares refinement program.

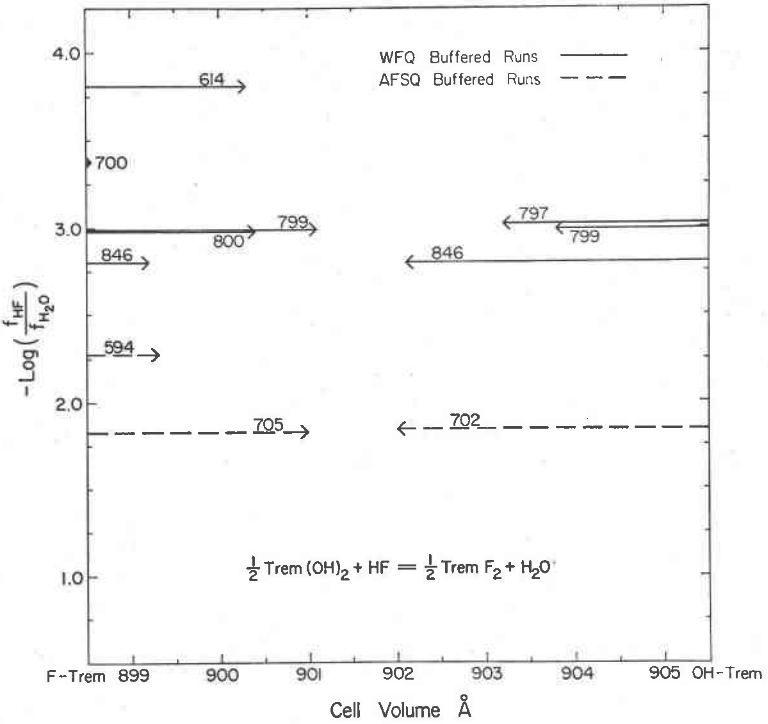

FIG. 5. Plot of the equilibrium constant, $-\log K = -\log (f_{HF}/f_{H_2O})$ against cell volume for the truly buffered runs. Values for the fugacities were taken from Munoz and Eugster (1969). Run temperatures in °C are indicated.

It is interesting that the one set of runs showing equilibration also showed nucleation and growth of talc (Fig. 3). This growth of talc necessitates recrystallization and adjustment of F/OH in the amphiboles in a breakdown loop limiting their stability on the low temperature side. Such an alteration in the phase relations would probably facilitate F/OH exchange in the tremolite.

The AFSQ–buffered runs

As partial melting of the buffer material was observed in the temperature region above 700°C, the HF/H_2O fugacity ratio has the calculated values given by Munoz and Eugster (1969, Table 3) only in the runs with temperatures at 700°C and below. The 700°C runs of 1296 hours from the hydroxyl side and of 1218 hours from the fluorine side meet and point to an equilibrium of a tremolite solid solution with an approximate cell volume of 901.5Å^3 which corresponds

Table 5. Chemical Analyses of Natural Tremolites with known Lattice Parameters

Analysis No.	1	2	3
SiO_2	56.76	58.90	57.66
TiO_2	0.08	0.02	0.01
Al_2O_3	1.84	0.56	1.51
Fe_2O_3	0.21[1]	....	0.23
FeO	....	0.22	0.33
MgO	24.15	24.74	24.34
CaO	12.55	13.00	13.79
Na_2O	1.62	0.40	0.12
K_2O	0.64	0.10	0.02
MnO	0.05	0.42	0.01
P_2O_5	0.15	....	....
H_2O+	0.86	1.19	2.22
H_2O^-	0.01	....	0.04
F	1.51	0.30	0.00
B_2O_3	0.23	....	....
CO_2	<0.03	0.10	....
	100.66	99.95	100.28
O≡F(+Cl)	0.64	0.13	....
	100.02	99.82	100.28

[1] Total iron

Analysis No. 1: Tremolite single crystal several inches long from a metamorphosed dolomite at Richville, New York (Adirondack Mtns.). The sample contains tiny impurities of phlogopite. Original analysis from U.S. Geological Survey. CaO value was too low and the value reported here was redetermined by D.A. Hewitt with the Acton electron microprobe at Yale University. A fluorine analysis was rerun at the Chemistry Department, V.P.I. & S.U. and gave 1.46% F.

Analysis No. 2: Lavender-colored tremolite from Arnold pit, Fowler, New York (St. Lawrence County, Gouverneur Mining district). Ross, Smith and Ashton (1968) collected the sample, labeled G-21, and partially described its chemistry and x-ray properties. A wet-chemical analysis by J.J. Fahey is presented in Ross, Papike and Shaw (1969) Table 3, and the unit cell parameters are listed in Papike, Ross and Clark (1969) Table 1.

Analysis No. 3: Tremolite, locality unknown, from Zussman, (1959) Analyst: R.A. Howie.

Table 6. Lattice Parameters of Natural Tremolites from Table 4

	a,Å	b,Å	c,Å	β	Vol, Å^3
No 1	9.8550(17)[1]	18.0250(33)	5.2686(15)	104° 46'(1')	905.0(4)
No 1a[2]	9.8532(15)	18.0280(21)	5.2674(12)	104° 45'(1')	904.8(2)
No 2	9.818(5)	18.047(8)	5.275(3)	104° 39'(3')	904.2(6)
No 3	9.840	18.052	5.275	104° 42'	906.2

[1] The estimated standard deviation indicated in parentheses refers to the last digits.

[2] Tremolite No. 1 used as starting material in a WFQ-buffered run lasting 862 hours at 800°C and 1990 bars.

to a tremolite with $(OH)_{45}F_{55}$. The 600°C run ought to have an equilibrium position to the OH side of the 700°C reversal if the phlogopite exchange work can be used as a guide (Munoz and Eugster, 1969, Fig. 5a). Failure to achieve such a position indicates that the exchange proceeds exceedingly slowly.

The 800° and 850° temperature runs are in the range where the buffer assemblage contains melt and the HF/H_2O fugacity ratio may vary, but between some fixed limits. No systematic behavior of these runs is evident. However, F–OH exchange has clearly occurred.

The WFQ—buffered runs

As melting of the *WFQ* buffer does not occur up to 900°C under 2 kilobars total pressure, tremolites in these experiments should have been controlled by a fixed HF/H_2O fugacity ratio (Fig. 4). None of these experiments yielded definite equilibrium values for F/OH. However, a medial line sloping downward to the right should exist between the arrows representing the directions of exchange. In the best defined range, from 800°C to 850°C, this line might be plotted in the region between the cell volumes 902.1 and 903.2 $[(OH)_{39}F_{61}–(OH)_{53}F_{47}]$. The experiments at 850°C were run together in separate charge capsules but inside one buffer capsule so that all external conditions were the same. Even at this temperature, equilibration will apparently take an appreciable amount of time.

One natural tremolite, chosen because it has the highest fluorine content known (Table 5, No. 1), was investigated by measuring its lattice parameters before and after an exchange experiment (Table 6, No. 1 and 1a). The cell volume of the initial crystal is relatively large compared to pure OH–tremolite. Probably the partial occupation of the *A* site and the partial substitution of Al for Si are the reasons for these properties. No significant change of the lattice parameters could be obtained in an *WFQ* buffered run at 800°C and 1900 bars (862 hours). Either the reaction was sluggish and dependent on the grain size or the initial F/(OH) ratio corresponds to the HF/H_2O fugacity values present in the experiment.

Comparison of Buffered Runs

By writing the reaction $1/2[\text{trem } F_2] + H_2O = 1/2[\text{trem } (OH)_2] + HF$, so that $-\log K = -\log (f_{HF}/f_{H_2O})$, and using the values of the fugacities from Munoz and Eugster (1969) for the applicable runs, comparison can be made more easily of the results obtained from the two sets of truly buffered runs (Fig. 5). Assuming behavior consistent with the trends found for phlogopites by Munoz and Eugster (1969), subparallel lines sloping downward to the left should exist which would separate isothermal sets of tremolite buffered runs with *AFSQ* runs showing more fluorine enrichment. The slopes cannot be defined, however, because of the lack of closure.

INTERPRETATION OF THE RESULTS

Interpretation of these experiments must be seen in the light of results reported prior to this study. Munoz and Eugster (1969, p. 953) carried out 12 runs, for 3 of those using *WFQ*/NiNiO and for one using *AFSQ*/NiNiO buffers. The higher HF fugacity of the *AFSQ*–buffer provided a phlogopite of the composition $F_{95}(OH)_5$ at 700°C, 2 kbars within 68 days. For the OH-phlogopite, this means an immense exchange of 95 percent of the OH. Their *WFQ* runs, as is to be expected, show smaller exchange:

775°C	2 kbar	10 days	$F_{75}(OH)_{25}$
700	2	54	$F_{71}(OH)_{29}$
550	2	108	$F_{60}(OH)_{40}$

Compared with the tremolite experiments, phlogopite extracts more fluorine from the vapor under comparable conditions and at an apparently faster rate. The solid solutions of $F_{95}(OH)_5$ in phlogopite [*AFSQ*, 700°C, 2 kbars] and of $F_{67}(OH)_{33}$ in annite [*AFSQ*, 700°C, 2 kbars] (Munoz, 1971) correspond to $F_{55}(OH)_{45}$ in tremolite [*AFSQ*, 700°C, 1 kbar]. For the *WFQ*–controlled runs, experiments of Munoz and Eugster (1969) yielded a phlogopite with the composition $F_{75}(OH)_{25}$ [*WFQ*, 775°C, 2 kilobars], while one with annite (Munoz, 1971) yielded $F_{24}(OH)_{76}$ [*WFQ*, 700°C, 2 kbars]. The tremolites of this study have a composition between $F_{61}(OH)_{39}$ and $F_{47}(OH)_{53}$ at elevated temperature [*WFQ*, >800°C, 2 kbars]. If the behavior of annite compared to phlogopite is representative of the behavior of the iron analogue of tremolite compared to tremolite, a strikingly low value for fluorine would occur in ferrotremolite. The explanation of this must lie in bonding effects between Fe and F and limitations imposed by the geometry of the structures. Cameron (1971) has found that Fe avoids bonds with F in synthetic, Fe–Mg, fluororichterites, being concentrated in M_2 (Fig. 1).

The low temperature *AFSQ*–buffered runs (600°C and 700°C under 1 kibobar water pressure) are complicated by the appearance of talc and thus the partition of fluorine between coexisting tremolite and talc. A considerable amount of talc nucleated and grew from a charge originally containing pure F–tremolite in a run at 594°C and 1 kilobar. The calculated cell dimensions based on the monoclinic cell are $a = 5.306(8)$Å, $b = 9.151(5)$Å, $c = 19.00(1)$Å, $\beta = 99°30\ (10)'$, $V = 910(2)$Å^3. Most of the reflections were very weak and difficult to measure. The cell parameters are obviously too large for even pure OH–talc (Ross *et al.*, 1968, Table 5). All cell volumes previously reported show smaller unit cells; the largest one of those was given by Stemple and Brindley (1960) for talc from Manchuria with 904.94Å^3. The runs at 705°C from the F–side and at 702°C from the (OH)–side grew much smaller amounts of talc, barely discernible on powder diffraction patterns. It might seem that the talc which grew in these runs would show higher F/OH than the coexisting tremolites. However, the cell volume is not consistent with that interpretation. Van Valkenburg (1955, p. 216) conducted experiments from 400° and 800°C at 1.1 to 1.4 kbars that synthesized talcs with a F/OH up to 1:1. These appear to be the most F–rich talcs ever synthesized. Natural talcs have been reported which have a F/OH of about 1/10 (Ross *et al.*, 1968). Experiments aimed at synthesizing a pure fluoro-talc from a stoichiometric oxide mixture in 1 atm runs at 1150°, 1000°, and 705°C and in a 1 kbar run at 713°C (45 hours) were unsuccessful.

The *AFSQ* runs in which talc grew indicate that the lower thermal stability of F–tremolite has been exceeded. Because talc grew from previously crystallized charges which were dominantly tremolite, talc must be a more stable phase under these conditions.

FLUORINE IN NATURAL AMPHIBOLES

Leake's (1968) collection of 1217 chemical analyses of calciferous and subcalciferous amphiboles contains 396 analyses with determined fluorine. About 15 percent of them show a fluorine content of >1.0 wt percent. The theoretical value for pure fluoro-tremolite is 4.65 wt percent F, (H_2O in pure OH–tremolite is 2.22 wt %). Interestingly, more F–amphiboles have been reported in metamorphic rocks than in magmatic ones. Magmatic rocks with especially high amounts of fluorine in their amphiboles are foyaites, syenites, and some granites. The highest F contents in metamorphic rocks are found in marbles and calc silicate rocks. Only a few F–rich calcic amphiboles with a vacant or nearly vacant *A*–site have been reported. Most of the calcic amphiboles reported are more complex hornblendes (pargasites–hastingsites). The most fluorine–rich natural tremolite known to us is the Richville sample supplied by D. A. Hewitt. This sample has about 1/3 of the O_3 positions filled with fluorine (Table 5). The Richville area is in that part of the northwest Adirondack Mountains, New York, extensively discussed by Engel and Engel (1958, 1960, 1962). The metamorphic grade corresponds to that of the upper amphibolite facies with the

Richville area in the sillimanite zone. Wones and Eugster (1965) have estimated that f_{H_2O} is only of the order of 1–10 bars whereas f_{CO_2} is of the order of 435 to 10,000 bars in this region. For interlayered marbles and gneisses this is perhaps to be expected. Now if we assume that the Richville tremolite did equilibrate with the fluid phase in the previously described experiment,

$$\log \frac{f_{HF}}{f_{H_2O}} = -2.96,$$

using fugacity data from Munoz and Eugster (1969). Thus, if the estimates of f_{H_2O} of Wones and Eugster (1965) can be applied, then f_{HF} during crystallization of the tremolite should be in the range 0.01 to 0.001 bars. The value estimated here is probably low for many other natural environments due to the large amount of CO_2 in the fluid in this case.

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