Experimental hydrogen isotope studies: hydrogen isotope exchange between amphibole and water

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Abstract

Equilibrium hydrogen isotope fractionation factors ($\alpha^e_{min-H_2O}$) were determined experimentally for various amphiboles (tremolite, pargasite, ferroan pargasitic hornblende, actinolite, and arfvedsonite) over the temperature range 350 to 950°C. D–H fractionation in the system tremolite–water is independent of temperature from 350 to 650°C and is described by the expression $1000 \ln \alpha^e_{trem-H_2O} = -21.7 \pm 2$; above 650°C the relationship becomes $1000 \ln \alpha^e_{trem-H_2O} = -31.00(10^6/T^2) + 14.90$. Similarly, D–H fractionation in the system ferroan pargasitic hornblende–water is independent of temperature up to 805°C and is given by the expression $1000 \ln \alpha^e_{hbl-H_2O} = -23.1 \pm 2.5$. Above 850°C the fractionation factor becomes slightly more positive with increasing temperature. At 700°C and 850°C hornblende–water hydrogen isotope fractionation factors are very similar for both the pargasite and ferroan pargasitic hornblende. Estimated D–H fractionation for actinolite–water at 400°C is $1000 \ln \alpha^e_{act-H_2O} \approx -29$, whereas for arfvedsonite–water it is $1000 \ln \alpha^e_{arf-H_2O} \approx -52$. Amphibole–water hydrogen isotope fractionations are not simply related to the composition of the octahedral cation site; the A-site cation (if present) may also influence the fractionation behavior of hydrogen in amphiboles.

The water content of ferroan pargasitic hornblende (in equilibrium with water) decreased from 2.1 wt.% at 350°C to 1.2 wt.% at 950°C, probably because of oxy-hornblende reactions.

Activation energies calculated for hydrogen diffusion in amphiboles fall in the range 16 to 25 kcal/mole. A consequence of the low activation energies is that amphiboles in volcanic rocks may readily quench in their high-temperature hydrogen isotopic compositions, whereas amphiboles in slowly-cooled metamorphic and hydrothermal environments may continue to exchange hydrogen with a coexisting fluid down to temperatures much lower than those of initial amphibole crystallization.

Introduction

Studies of combined hydrogen and oxygen isotope variations in rocks and minerals are widely used to estimate the isotopic compositions and origins of the hydrous fluids associated with a variety of igneous, metamorphic, and hydrothermal processes (see reviews by Taylor, 1974; Sheppard, 1977). The hydrogen isotopic compositions of hydrous minerals are particularly sensitive indicators of the isotopic composition of the last fluid with which they have equilibrated, because most hydrous minerals contain relatively small amounts of hydrogen relative to the interacting fluid, except at very small water-to-rock ratios. In order to calculate the isotopic

composition of a fluid phase which has subsequently been removed from the original mineral–water system, it is necessary to know the isotopic fractionation factors between hydrous minerals and water as a function of temperature and composition.

In this study we report the results of an experimental investigation of hydrogen isotope exchange and fractionation between various amphiboles and water at high pressure and over a range of temperatures representative of hydrothermal and low-grade metamorphic to igneous environments. Amphiboles are a common constituent of a wide range of crustal and some upper mantle rocks. Therefore, the results of this study provide important new data for the determinaton of the stable isotopic compositions and origins of hydrous fluids in a variety of geological environments.

There is already a small amount of published data on the fractionation of hydrogen isotopes between amphiboles and water. Suzuoki and Epstein (1976) measured the D–H fractionation between a "hornblende" and water over the temperature range 400 to 750°C. Their chemical data suggests that the "hornblende" was very low in aluminium, and was probably an actinolite. The equilibrium D–H fractionation for this "hornblende"–water system was found to vary with temperature above 450°C according to the following relationship: $1000 \ln \alpha^{e}_{\text{"hbl"}-\text{H}_2\text{O}} = -23.9(10^6/T^2) + 7.9$. These authors also proposed a general relationship between hydrogen isotope fractionation factors and the octahedral-cation composition of micas and hornblendes such that $1000 \ln \alpha^{e}_{\text{min}-\text{H}_2\text{O}} = -22.4(10^6/T^2) + (2X_{\text{Al}} - 4X_{\text{Mg}} - 68X_{\text{Fe}}) + 28.2$, where X is the mole fraction of the respective cation. This relationship was derived largely from experimental data for micas where OH-group bonding occurs exclusively with octahedrally-coordinated cations. However, preliminary experimental data for the system aluminous hornblende–water by Graham and Sheppard (1978) suggested that hydrogen isotope fractionation in the amphibole–water system was more complex than in the mica–water system and indicated that the Suzuoki–Epstein relationship was not totally applicable to the amphiboles.

In this study we have examined the influence of amphibole composition on hydrogen isotope fractionation factors by direct measurement of equilibrium D–H fractionation for several different amphiboles, including pure tremolite, two hornblendes of differing Fe, Mg, and Al contents, actinolite, and the sodic amphibole arfvedsonite. In addition, we have derived quantitative data on the kinetics of hydrogen isotope exchange between amphibole and water, as well as on the diffusion of hydrogen in amphiboles. This information permits both quantitative assessment of the extent of continued isotope exchange between amphiboles and fluid in cooling igneous, metamorphic, and hydrothermal environments and estimation of "closure" temperatures for the cessation of isotopic exchange.

Starting materials

Minerals. With two exceptions (see below) all amphibole starting materials were mineral separates of >99% purity ground to a mean grain size of 30–60 μm. Powders were not sized, but the fine-grained fraction was removed by repeated elutriation in distilled water. The isotopic and chemical compositions of the various amphiboles used in the study are given in Tables 1 and 2. Tremolite #338 is close to a pure, stoichiometric hydroxy-tremolite. Actinolite #6906 is a typical greenschist-facies actinolite from a tholeiitic metadolerite (*e.g.*, Graham, 1974), and appears to have proportions of Mg and Fe comparable to the "hornblende" used in the experiments of Suzuoki and Epstein (1976; Table 3). The two hornblendes, according to the classification of Leake (1978), are a ferroan pargasitic hornblende #322 (from a garnet amphibolite) and a pargasite #6099 (from an amphibole–plagioclase–clinopyroxene cumulate nodule in a basaltic andesite). The two hornblendes differ in their proportion of Fe and Mg, in Ti contents, and in tetrahedral and octahedral Al contents. The sodic amphibole #516 is an arfvedsonite from a peralkaline granite which has subequal amounts of H₂O and F. Other amphiboles contain only trace amounts of F.

One portion of the tremolite starting material contained a small amount of minute calcite inclusions. Reaction of this calcite with the tremolite during some of the high-temperature experiments produced detectable amounts of diopside (tremolite + calcite → diopside + forsterite + CO₂ + H₂O), enhanced isotope exchange rates, and caused apparent decreases in water content of the tremolite run products. Results of the high-temperature (>400°C) tremolite–water isotope exchange experiments have therefore been omitted from the discussion of water contents and analysis of kinetic data which follows. However, equilibrium fractionation factors calculated from these experiments are not measurably different from those calculated from experiments using a calcite-free tremolite starting material.

Table 1. Isotopic compositions of starting materials

Waters	δD(°/oo)				
	(a)	(b)	(c)	(c)	(e)
I	+51.4	–	–	+65.6	–
II	-2.8	+2.4	–	-1.9	–
III	-51.8	-56.0	-54.7	-47.7	-51.9
IV	-96.0	–	-96.7	–	–
V	-155.9	–	-160.6	-152.6	–
VI	-6.0	–	–	–	–
VII	-120.2	–	–	–	–

Minerals	δD(°/oo)	
tremolite #338	-105.4	
actinolite #6906	-55.6	
hornblende #322	-62.8	(ferroan pargasitic hornblende)
hornblende #6099	-26.8	(pargasite)
arfvedsonite #516	-94.5	

The actinolite #6906 used in the preliminary experiments on the system actinolite–H_2O contains significantly more than the stoichiometric amount of water (Table 2), suggesting the presence of a small amount of a hydrous-mineral contaminant. Small amounts of chlorite intergrowths within actinolite grains were confirmed by XRD analysis. Further work on the actinolite–water system is currently underway with a pure starting material and will be reported elsewhere upon completion.

Waters. Each amphibole starting material was exchanged at various temperatures between 350 and 950° with two or more waters of differing initial hydrogen isotopic composition (Table 1, I–VII). Periodically, mineral powders and aliquots of the various starting waters (Table 1, a–e) were sealed into capsules. Small variations in isotopic composition between successive aliquots of water reflect isotopic fractionation arising from evaporation of standard waters with time. In order to insure internal consistency, each time an individual group of mineral-water runs was prepared, a set of starting waters and experimental run products were then analyzed after each group of the exchange experiments was completed.

Experimental and analytical methods

Experimental and analytical techniques

The experimental techniques and analytical methods are essentially those described by Graham *et al.* (1980). Isotope-exchange runs were made using 5 mm O.D. × 0.5 mm wall thickness × 2.5 cm length Au capsules typically containing 180–250 mg amphibole powder and 8–12 mg water. Runs were made

Table 2.   Chemical analyses of amphibole starting materials and run products

	tremolite #338	actinolite* #6906	arfvedsonite #516	hornblende #6099	hornblende #322	hornblende #322/650	hornblende #322/850
SiO₂	57.71	53.00	49.93	40.63	43.69	44.24	43.51
Al₂O₃	n.d	2.55	0.28	12.35	12.54	11.65	12.25
TiO₂	n.d	0.05	1.48	1.76	0.60	0.55	0.60
FeO(total)	0.14	10.52	34.67	11.16	14.32	14.40	14.19
Fe₂O₃	-	-	10.14	-	2.72	-	4.21
FeO	-	-	25.54	-	11.87	-	10.40
MnO	n.d	0.18	0.64	0.17	0.27	0.27	0.25
MgO	24.09	16.40	0.05	14.10	10.74	11.08	10.83
CaO	13.45	12.87	1.39	11.79	11.13	11.24	11.06
Na₂O	0.02	0.26	8.47	2.50	2.23	2.08	2.24
K₂O	n.d	0.06	1.63	0.47	0.52	0.54	0.51
F	0.03	n.d	1.09	0.07	0.07	0.07	0.07
H₂O	2.18	3.15*	0.90	1.73	2.17	1.78	1.87
	97.61	99.04	101.08	96.70	98.52	97.87	97.77
Number of ions on basis of 24 (O, OH, F)							
Si	8.00	7.71	7.91	6.19	6.50	6.67	6.52
Al^{IV}	-	0.29	0.05	1.81	1.50	1.33	1.48
Al^{VI}	-	0.15	-	0.41	0.69	0.74	0.69
Ti	-	0.01	0.18	0.20	0.07	0.06	0.07
Fe^{3+}	-	-	1.21	-	0.30	-	0.48
Fe^{2+}	0.16	1.28	3.38	1.42	1.48	1.82	1.30
Mn	-	0.02	0.09	0.02	0.03	0.03	0.03
Mg	4.98	3.56	0.27	3.20	2.38	2.49	2.42
Ca	2.00	2.01	0.24	1.93	1.77	1.82	1.78
Na	0.01	0.08	2.60	0.74	0.64	0.61	0.65
K	-	0.01	0.33	0.09	0.10	0.10	0.10
F	0.01	-	0.55	0.03	0.03	0.03	0.03
OH	2.02	*	0.95	1.76	2.15	1.79	1.87

Analyses of grain mounts of starting mineral powders by electron microprobe. H_2O contents determined by radio-frequency induction heating under vacuum, and manometric measurement of hydrogen gas yields. Hornblende analyses #322/650 and #322/850 are run products of 650°C and 850°C hornblende #322–H_2O exchange experiments. FeO and Fe₂O₃ contents of hornblende #322 and #322/850 determined by wet chemical methods (analyst M. J. Saunders). FeO and Fe₂O₃ contents and stoichiometric formula of arfvedsonite #516 calculated assuming that Σ(cations) = 16. A separate H_2O determination on hornblende #322 by a modified Penfield Tube method (analyst M. J. Saunders) gave wt. % H_2O = 2.19. n.d = not detected. *number of ions in actinolite #6906 formula calculated on basis of 23(O) because of high H_2O content resulting from inclusions of chlorite intergrown with actinolite grains (see text).

in Nimonic-105 cold-seal pressure vessels and internally-heated, gas pressure vessels using an argon pressure medium. After quenching, the capsules were pierced under vacuum, the water extracted by heating at ~150°C for one hour, and this water converted to hydrogen for mass spectrometric analysis by passage over uranium metal at 750°C. All hydrogen yields were measured manometrically to check for internal consistency with theoretical values and to monitor variations in the water contents of exchanged amphiboles with temperature. Exchanged mineral powders were examined optically and by XRD analysis to check for absence of mineral alteration. In addition, the two hornblende run products were reanalyzed by electron microprobe and wet chemical techniques (Table 2) to document the exact extents of possible chemical change during the isotope exchange experiments.

The water extracted from the capsules was converted to hydrogen gas by reaction with U at 750°C (Bigeleisen *et al.*, 1952). The D/H ratio of the hydrogen gas was determined on a VG-Micromass 602 B mass spectrometer. Values for the relative concentration of deuterium are given in Tables 1 and 3 in the familiar δ notation relative to the Standard Mean Ocean Water (SMOW) standard as defined by Craig (1961) to a precision of about ±1‰, where

$$\delta D(‰)\text{sample} = \left(\frac{(D/H)\text{sample}}{(D/H)\text{standard}} - 1 \right) \times 10^3.$$

Using this notation, the equilibrium factor α^e is related to δD by the expression

$$\alpha^e_{\text{min–H}_2\text{O}} = \frac{(D/H)\text{mineral}}{(D/H)\text{water}} = \frac{1 + (\delta D\text{mineral}/1000)}{1 + (\delta D\text{water}/1000)}.$$

Analytical precision and interpolation of fractionation factors

The ±1‰ analytical precision for the measurement of both mineral and water D/H ratios means that calculated fractionation factors should be reproducible to ±2‰. Complete isotope exchange at a given temperature is demonstrated either by attainment of the same fractionation in experiments run at the same temperature with starting waters of different isotopic composi-

tion, or by demonstration that the fractionation does not change in experiments run with waters of the same isotopic composition for different lengths of time (where $\alpha_f \neq \alpha_i$). For most experiments, isotope exchange in the amphibole–water system was so slow that equilibrium was not attained, and thus the interpolation method of Northrop and Clayton (1966), as modified by Suzuoki and Epstein (1976), was used to calculate equilibrium fractionation factors (α^e), applying the relationship

$$(\alpha_i - 1) = (\alpha^e - 1) - A(\alpha_f - \alpha_i)$$

to two or more experiments of the same duration run with starting waters of different isotopic composition (where α_i and α_f are the initial and final fractionation factors respectively, and A is a constant related to the extent of isotopic exchange). The value of α^e is obtained from the intercept of $10^3(\alpha^e - 1)$ in plots of $10^3(\alpha_i - 1)$ *vs.* $10^3(\alpha_f - \alpha_i)$; see for example, Figure 1. In this study α^e was calculated algebraically by a least-squares fitting of the isotope exchange data for three or more experiments at a particular temperature run with starting waters of different isotopic composition. Excellent internal consistency of data is usually observed using this partial-exchange interpolation method (see for example Fig. 1, Table 3; also Graham *et al.*, 1980).

Results

The experimentally measured hydrogen isotope fractionations between the various amphiboles and water are given in Table 3, together with the interpolated equilibrium fractionation factors. Exchange rates in the system amphibole–H₂O were sufficiently slow that complete exchange (f ≈ 1.00, Table 3) was attained only in high-temperature experiments for the finest-grained starting material (hornblende, #332) within 3 hours at 950°C and 14 days at 600°C.

Hydrogen exchange between charges and pressure medium

Hydrogen diffusion through capsule walls and D–H exchange between charge and pressure medium during high $P–T$ gas-media experiments may cause significant changes in the bulk δD value of experimental charges. However, the use of thick-walled (0.5 mm) gold capsules minimizes the extent of such changes at temperatures ≤650°C (Graham *et al.*, 1980). In this study results of exchange experiments involving tremolite #338 and hornblende #6099 up to 850°C show no evidence of significant changes in the bulk δD of charges (Table 3). By contrast, mass balance considerations for the system hornblende #332–H₂O indicate significant increases in the bulk δD values for charges in runs at temperatures above 700°C, and a similar effect is more emphatically demonstrated for the runs at 550°C in the system arfvedsonite #516–H₂O. Iron-bearing amphiboles, such as the ferroan pargasitic hornblende #322, are capable of undergoing "oxy-hornblende" reactions during exchange with water at conditions of high P and T which involve the oxidation of Fe^{2+} to Fe^{3+} and liberation of hydrogen, according to the reaction:

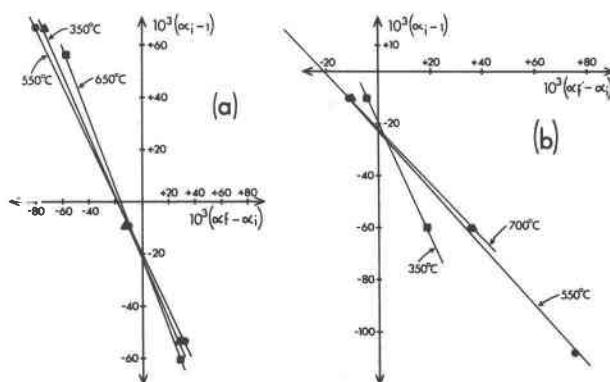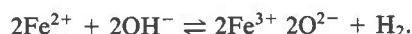$$2Fe^{2+} + 2OH^- \rightleftharpoons 2Fe^{3+} \ 2O^{2-} + H_2.$$

Fig. 1. Interpolation method for determining equilibrium hydrogen isotope fractionation factors (α^e) from partial exchange experiments in the system amphibole–H₂O (after Northrop and Clayton, 1966; Suzuoki and Epstein, 1976). (a) tremolite #338–H₂O; (b) hornblende #322–H₂O. See text and Table 3.

Table 3. Results of hydrogen isotope exchange experiments for the system amphibole–H_2O

Run	T(°C)	P(kbars)	time (sec x 10⁵)	$10^3(\alpha_i-1)$ (starting)	δD (mineral) (after exchange)	δD (water) (after exchange)	$10^3(\alpha_f-\alpha_i)$	$10^3 \ln\alpha_f$	$10^3 \ln\alpha^e$	f	log k_2
Tremolite #338–H₂O											
17	350°C	2	129.009	−53.58(IIIc)+	−88.4	−63.3	+26.80	−27.16⌐		.882	−6.24
25	350°C	2	129.006	−9.63(IVc)	−108.5	−87.4	−13.50	−23.39	−23.47	.993	−
31	350°C	2	129.003	+65.82(Vc)	−132.1	−124.9	−74.00	−8.26⌐		.832	−6.42
20	450°C	2	36.288	−53.58(IIIc)	−82.2	−61.0	+31.00	−22.84⌐		.954	−5.25
27	450°C	2	36.288	−9.62(IVc)	−109.6	−88.6	−13.40	−23.31	−21.36	−	−
33	450°C	2	36.288	+65.82(Vc)	−144.1	−134.4	−77.00	−11.27⌐		.886	−5.67
24	550°C	2	18.144	−53.58(IIIc)	−78.6	−58.0	+31.70	−22.11⌐		.955	−4.93
30	550°C	2	18.180	−9.63(IVc)	−103.9	−84.8	−11.30	−21.09	−20.62	−	−
37	550°C	2	18.195	+65.82(Vc)	−144.0	−131.8	−79.90	−14.15⌐		.927	−5.16
51*	650°C	2	0.4386	−60.50(IIId)	−88.0	−58.6	+29.30	−31.74⌐		.746	−4.17
57*	650°C	2	0.4386	+55.70(Vd)	−138.8	−137.4	−57.40	−1.68⌐	−21.46	.746	−4.17
53*	750°C	3	0.2328	−60.50(IIId)	−78.7	−57.1	+37.60	−23.17⌐		.816	−3.72
56*	750°C	3	0.2328	+55.70(Vd)	−136.1	−134.8	−57.20	−1.55⌐	−14.52	.816	−3.72
76*	800°C	3	0.18360	+16.82(VII)	−110.1	−107.1	−20.23	−3.41⌐		.689	−3.92
78*	800°C	3	0.18360	−56.43(IIIe)	−86.9	−62.5	+30.37	−26.37⌐	−12.54	.692	−3.91
50*	850°C	4	0.1110	−60.50(IIId)	−74.3	−57.3	+42.50	−18.20⌐		.830	−3.36
55*	850°C	4	0.1110	+55.70(Vd)	−134.7	−136.2	−54.00	+1.74 ⌐	−9.37	.831	−3.36
Hornblende #322–H₂O (ferroan pargasitic hornblende)											
129	350°C	4	79.488	−60.20(IIa)	−52.6	−11.4	+18.50	−42.57⌐		.463	−6.97
130	350°C	4	79.488	−11.56(IIIa)	−65.9	−51.1	−4.00	−15.68⌐	−20.41	.465	.6.96
8	400°C	2	67.551	−65.04(IIIc)	−56.0	−19.5	+27.80	−37.94⌐		.688	−6.53
21	400°C	2	67.551	−8.57(IIIc)	−66.3	−48.7	−9.90	−18.67⌐	−23.68	.669	−6.52
93	450°C	4	24.192	−60.20(IIa)	−42.4	−16.0	+33.40	−27.17⌐		.900	−5.43
126	450°C	4	24.192	−11.56(IIIa)	−67.8	−46.8	−10.40	−22.25⌐	−23.38	.904	−5.41
95	550°C	4	12.096	−108.60(Ia)	−4.7	+29.6	+75.30	−33.87⌐		.881	−5.21
127	550°C	4	12.096	−11.56(IIIa)	−67.8	−45.9	−11.40	−23.27	−23.32	.991	−
156	550°C	4	12.096	−60.20(IIa)	−39.4	−15.3	+35.70	−24.81⌐		.962	−4.67
157	700°C	2	12.096	−60.20(IIa)	−20.0	+3.9	+36.40	−24.09⌐	−23.22	1.00	−
158	700°C	2	12.096	−11.56(IIIa)	−52.3	−30.9	−10.50	−22.35⌐	(Ave)	1.00	−
43*	850°C	6	0.1650	−15.84(IIId)	−66.3	−40.5	−11.10	−27.27⌐		1.00	−
46*	850°C	6	0.1650	−61.00(IId)	−33.4	−8.0	+35.40	−25.92⌐	−24.40	1.00	−
48*	850°C	6	0.1650	−61.00(IId)	−29.8	−10.2	+41.19	−20.00⌐	(Ave)	1.00	−
41*	950°C	8	0.1080	−15.84(IIId)	−32.6	−14.4	−2.70	−18.64⌐		1.00	−
42*	950°C	8	0.2196	−15.84(IIId)	−50.6	−30.9	−4.50	−20.54⌐	−18.62	1.00	−
47*	950°C	8	0.1080	−61.00(IId)	−20.6	−4.2	+44.50	−16.69⌐	(Ave)	1.00	−
Hornblende #6099–H₂O (pargasite)											
62*	700°C	4	0.5316	−86.68(Id)	+16.5	+51.0	+53.87	−33.38⌐		.828	−4.04
64*	700°C	4	0.5316	+22.00(IIId)	−51.3	−37.7	−36.12	−14.22⌐	−21.86	.828	−4.05
63*	850°C	6	0.4308	−86.68(Id)	+22.4	+48.6	+61.60	−25.33⌐		.898	−3.69
65*	850°C	6	0.4308	+22.00(IIId)	−44.0	−30.6	−35.82	−13.92⌐	−18.12	.895	−3.70
Actinolite #6906–H₂O											
70	400°C	2	51.029	−49.90(VI)	−54.1	−16.7	+11.81	−38.84⌐		.549	−
72	400°C	2	51.029	−3.90(IIIe)	−68.1	−50.6	−14.47	−18.54⌐	−29.38	.592	−
74	400°C	2	51.029	+73.62(VII)	−88.6	−98.3	−62.63	+10.74⌐		.615	−
Arfvedsonite #516–H₂O											
1	350°C	2	104.940	+1.71(IVa)	−120.1	−89.6	−35.20	−34.08⌐			
2	350°C	2	104.928	+72.80(Va)	−135.5	−136.1	−72.10	+0.70	−51.17		
12	350°C	2	104.928	−40.78(IIIa)	−96.7	−55.0	−3.30	−45.13⌐			
9	450°C	2		−40.78(IIIa)	−73.0	−47.0	+12.90	−28.31⌐			
32	450°C	2	57.189	+78.8 (Vc)	−144.1	−134.4	−90.00	−11.27⌐	−26.13		
4	550°C	2	31.986	+72.80(Va)	−127.4	−94.9	−108.00	−36.57⌐			
19	550°C	2	31.986	−42.05(IIIc)	−50.3	−7.3	−1.20	−44.28⌐	−41.34(?)		
26	550°C	2	31.986	+2.44(IVc)	−71.8	−38.8	−36.70	−34.94⌐			

()⁺ indicates composition of starting water (see Table 1); * indicates experiment conducted in internally-heated gas vessel. α_i = initial (measured) fractionation factor; α_f = final (measured) fractionation factor; α^e = equilibrium fractionation factor. Values of α^e interpolated for experiments in which less than 100% exchange occurred.

f = fractional approach to equilibrium = $\frac{\alpha_f - \alpha_i}{\alpha^e - \alpha_i}$; k_2 = rate constant for second order exchange reaction (see Graham, 1981).

Because of hydrogen-bearing impurities in the argon pressure medium, the bomb walls exert a buffering influence on charges during experiments (Graham et al., 1980). At high temperatures (750–950°C) the imposed oxygen fugacity is between Ni–NiO and Fe_2O_3–Fe_3O_4, but at lower temperatures it is closer to Ni–NiO. This buffering effect provides the driving force for oxy-hornblende reactions which may be demonstrated by the increased Fe^{3+}/Fe^{2+}, decreased H_2O-content, and change in color from green to brownish-green of the Fe-rich hornblende #322 after exchange with water at 850°C (Table 2, column 7), and which must account for the significant change in the bulk δD value of the charges. The change toward more positive δD values is in the same

direction as that observed by Graham *et al.* (1980), who discussed possible diffusion mechanisms in such isotope exchange experiments.

When significant change occurs in the bulk δD value of the amphibole–H_2O charges, it is possible that D–H exchange between charge and pressure medium occurs at a much greater rate than that between amphibole and water. If this situation occurs, and mineral-water isotope exchange is incomplete, one is not justified in using the partial-exchange interpolation method of Northrop and Clayton (1966) to derive equilibrium fractionation factors. Therefore, runs in which significant increases in the bulk δD value of the systems have occurred are not considered in this study unless 100% exchange was documented. In cases of total exchange, the measured final fractionation factor (α^e) is independent (within analytical error) of the increase in δD value of the charge (Table 3).

Water contents of amphiboles at high temperatures

Hydrogen yields from the amphibole run-products of exchange reactions were used to calculate amphibole water contents at various run temperatures. Radio-frequency induction heating under vacuum is considered to produce very accurate and reproducible water analyses of amphiboles (Table 2; see also Boettcher and O'Neil, 1980). Amphibole water contents are plotted against run temperature in Figure 2.

The water content of hornblende #322 decreases progressively with increasing temperature down to 1.2 wt.% at 950°C, although there is considerable scatter in the data. This decrease is explained by the oxy-hornblende reaction outlined above, induced by the increase in oxygen fugacity with increasing temperature resulting from the buffering effect imposed by bomb-walls and

pressure medium, and demonstrated by the high-temperature increase in Fe^{3+}/Fe^{2+} (Table 2). We note that, in general, those experiments which show the greatest increase in δD value of the charge at any temperature contain the hornblendes with the lowest water contents, indicating a relationship between the extent of the oxy-hornblende reaction and the extent of D–H exchange between charge and pressure medium. Infrared studies of our run products, which are currently in progress, may provide new insight on the behavior of the amphibole OH-group as a function of temperature.

The water content of arfvedsonite decreases significantly over the same 550–650°C temperature range; its cause is again attributed to an oxy-hornblende reaction. The arfvedsonite contains a substantial amount of fluorine, but significant F–OH exchange with fluid is unlikely as amphiboles strongly concentrate fluorine relative to coexisting hydrous fluid.

Relationships between fractionation factors (α^e) and temperature

The relationships between the equilibrium hydrogen isotope fractionation factors (Table 3) and temperature (plotted as $10^6/T^2$) for the various amphiboles are plotted in Figure 3. Also shown in Figure 3 are the experimental data for the system "actinolite"–H_2O studied by Suzuoki and Epstein (1976).

Tremolite–H_2O. The fractionation factor is independent of temperature (within analytical error) over the temperature range 350–650°C, and may be represented by the expression

$$1000 \ln \alpha^e_{\text{tremolite–H}_2\text{O}} = -21.7 \pm 2.$$

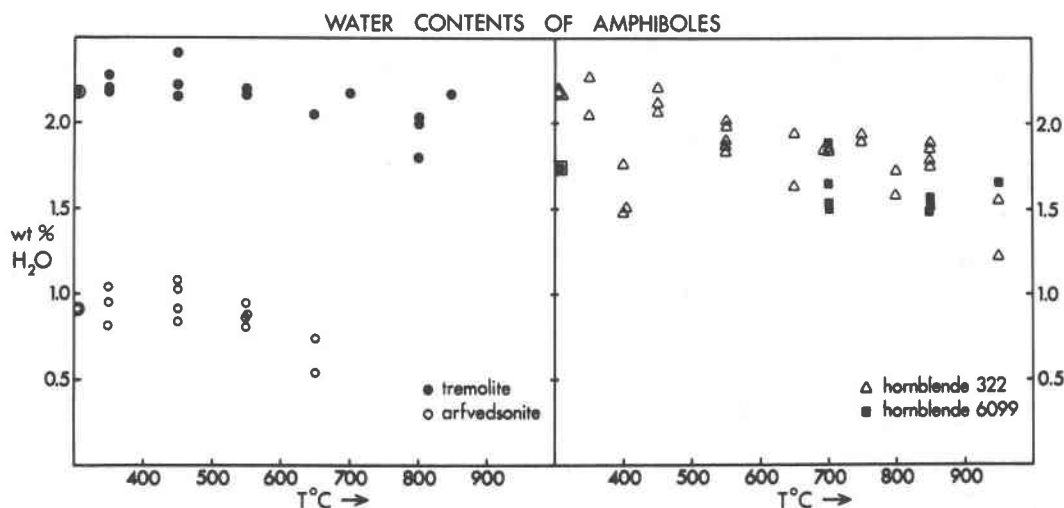Above 650°C, the fractionation changes rapidly with

Fig. 2. Variation of water contents of amphibole run products of amphibole–H_2O exchange experiments (determined by radio-frequency induction heating) with run temperature. Initial water contents of amphibole starting materials are plotted on wt.% axis.

temperature, and fits the linear relationship

$$1000 \ln \alpha^e_{\text{tremolite-H}_2\text{O}} = -31.00(10^6/T^2) + 14.90,$$

where T is absolute temperature (°K).

Hornblende–H$_2$O. Experiments were conducted in the system hornblende–H$_2$O with two different starting compositions to assess the influence of Fe–Mg ratio on fractionation factors, and to provide D–H fractionation data directly applicable to the origin of waters in amphiboles in both igneous and metamorphic environments.

Hydrogen isotope fractionation in the system hornblende–H$_2$O is also independent of temperature over the temperature range of approximately 350–850°C (Fig. 3). For the Fe-rich composition, D–H fractionation between ferroan pargasitic hornblende #322 and water is given by the expression

$$1000 \ln \alpha^e_{\text{hbl-H}_2\text{O}} = -23.1 \pm 2.5.$$

This result confirms and extends the preliminary data of Graham and Sheppard (1978) for the same hornblende starting material. Above 850°C the fractionation becomes slightly more positive with increasing temperature (Fig. 3). At present there is insufficient experimental data to fix the slope of the fractionation curve with confidence in the temperature range 850–1000°C. For lack of data to the contrary, we have assumed that the high-temperature behavior in the system Fe-rich hornblende–H$_2$O is similar to that in the system actinolite–H$_2$O, thus the line through

the two high-temperature data points is given by the relationship

$$1000 \ln \alpha^e_{\text{hbl-H}_2\text{O}} = -31.0(10^6/T^2) + 1.1.$$

Experiments were also conducted to determine the hydrogen isotope fractionation between pargasite #6099 and water at 700°C and 850°C, in order to assess the influence of Fe:Mg ratio on the fractionation factor. The pargasite #6099 has a significantly larger Mg:Fe ratio and Ti-content, but has an otherwise comparable composition to the ferroan pargasitic hornblende #322. At 850°C, exchange was incomplete after 12 hours. Measured fractionation factors are slightly more positive than those for the ferroan hornblende #322, but the difference is small (<5‰) at both temperatures. The small difference in fractionation factors between these two hornblendes is in the same sense as that predicted from the studies of Suzuoki and Epstein (1976), *i.e.*, deuterium is enriched in the more Mg-rich phase.

Actinolite–H$_2$O. Three experiments were conducted to estimate the approximate magnitude of D–H fractionation between actinolite and water at 400°C. These experiments were designed to provide data to permit comparison with the experimental data of Suzuoki and Epstein (1976) on an amphibole of probable "actinolitic" composition, and to aid in assessing the overall influence of composition on mineral–water fractionation factor. A knowledge of the hydrogen isotope fractionation factor between actinolite
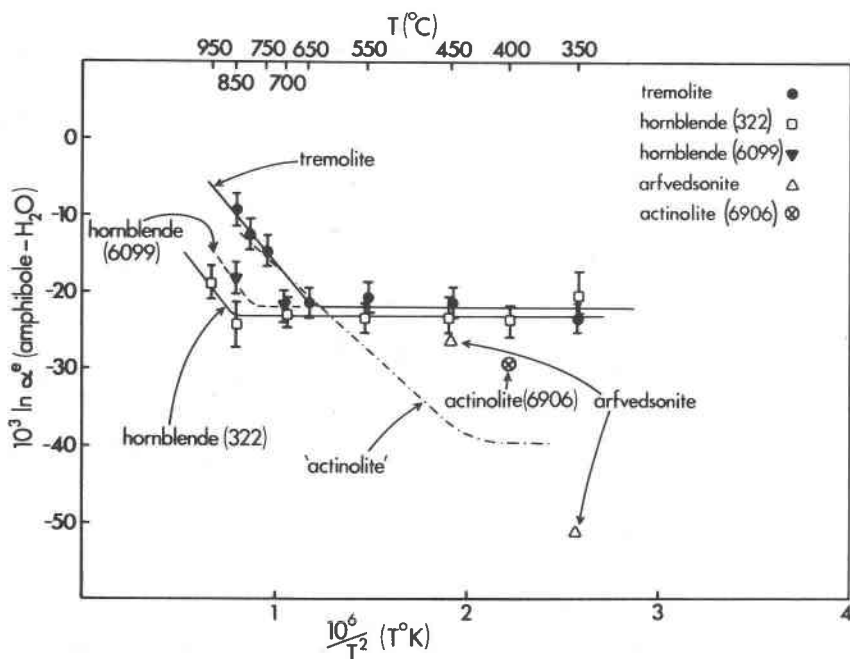

Fig. 3. Experimentally determined relationships between hydrogen isotope fractionation factor (10^3 in α^e amphibole–H$_2$O) and temperature (plotted as $10^6/T^2$) for the system amphibole–H$_2$O. Date for "actinolite"–H$_2$O after Suzuoki and Epstein (1976). Error bars indicate analytical precision.

and water at typical greenschist-facies conditions is essential to interpreting stable isotope studies of hydration and metamorphism of basaltic oceanic crust.

As shown in Figure 3, the experimental data (Table 3) indicate that the equilibrium fractionation factor in the system actinolite #6906–H₂O at 400°C is approximated by the expression

$$1000 \ln \alpha^{\text{e}}_{\text{act–H}_2\text{O}} = -29.$$

However, this result is uncertain because of the minor chlorite contamination of the actinolite. Hydrogen isotope fractionation between chlorite and water was not experimentally studied. The δD value of the natural chlorite coexisting with actinolite #6906 ($\delta D = -55.6\text{‰}$, Table 1) in the parent greenschist-facies metadolerite is -48‰ (Turi et al., 1973). Thus, the equilibrium fractionation factor for pure actinolite is unlikely to be more positive than -29‰ and could likely be slightly more negative. A more detailed study of the systems actinolite–H₂O and chlorite–H₂O is in progress.

Arfvedsonite–H₂O. Fractionation factors in this system are subject to large uncertainty because of the problems of changing bulk δD values of charges encountered in the isotope exchange experiments, possibly even down to temperatures as low as 450°C (Table 3). The fractionation at 350°C is approximately 30‰ more negative than for the calciferous amphiboles at this temperature.

Discussion

The hydrogen isotope fractionation curves for different minerals, even within the same structural group, may be rather complex (Graham et al., 1980) and the amphiboles are no exception (Fig. 3). The simple relationships between the mineral–water fractionation factor and the octahedral cation composition proposed by Suzuoki and Epstein (1976) for the micas do not apply to the amphiboles. The fractionation factors for both tremolite and hornblende are similar and independent of temperature over the low-temperature range, despite their chemical and structural diversity. The two compositionally distinct hornblendes have comparable fractionations at high temperature. Our data for tremolite are significantly different from those of Suzuoki and Epstein (1976) for "actinolite" at temperatures below 650°C, but the fractionation factors for both tremolite and "actinolite" may be represented by a similar curve at temperatures above 650°C. The fractionation factor for D–H exchange between actinolite and water at 400°C measured in our reconnaissance experiments is intermediate between the tremolite–water fractionation factor (this study) and the "actinolite"–water fractionation factor of Suzuoki and Epstein at the same temperature.

Uncertainty regarding the detailed chemistry of the "actinolite" used in the hydrogen isotope exchange experiments of Suzuoki and Epstein (1976) creates difficulty in quantitatively comparing their results with our frac-

tionation curves for tremolite and hornblende. Graham and Sheppard (1978) showed that the predicted fractionation curve for hornblende #322 using Suzuoki and Epstein's (1976) octahedral cation composition model differs radically from the experimentally determined curve (Fig. 3) for this amphibole. The cation sites in the amphiboles most likely to influence behavior of the OH-group are the octahedral (M1, M3) sites and the A site. The importance of the latter interaction was demonstrated by the infrared study of Rowbotham and Farmer (1973) on the O–H stretching frequency in the tremolite–richterite series. These authors observed that substitution of both Na and K into the vacant A site of tremolite caused a change in the stretching frequency of the O–H bond. Thus, the difference between the "actinolite" and tremolite fractionation curves (Fig. 3) may reflect to a large extent their different proportions of Fe and Mg. This difference may be largely compensated in our hornblende samples by their high Na (A) and Al$^{\text{VI}}$ contents. However, our measured actinolite–H₂O fractionation factor at 400°C ($1000 \ln \alpha^{\text{e}}_{\text{act–H}_2\text{O}} = -29$) is significantly more positive than that for the Suzuoki and Epstein (1976) "actinolite" ($1000 \ln \alpha^{\text{e}}_{\text{"act"–H}_2\text{O}} = -39$) at the same temperature, despite the apparently comparable Fe/Mg ratio of the two amphiboles. We note that the "actinolite" apparently lacks octahedral aluminum (see Table 3 of Suzuoki and Epstein, 1976; cf. Table 2, this study), whereas its A-site Na content is undetermined.

Despite these complexities, the similarity of the hydrogen isotope fractionation curves for the chemically-diverse calciferous amphiboles we have studied (Fig. 3), and the insensitivity of isotope fractionation factors over a wide range of temperature, suggests that our fractionation curves may be applied to a potentially wide range of calciferous amphiboles in igneous and metamorphic rocks in stable isotope studies of fluid–rock interactions.

Kinetics of hydrogen isotope exchange

The kinetics of hydrogen isotope exchange between amphiboles and water may be quantified by application of reaction-kinetic theory (Graham, 1981), assuming that exchange reactions may be approximated by second-order kinetics. The relevant equation is

$$f/(1 - f) = K_2 t,$$

where f is the fractional approach to equilibrium, and t is the time of the reaction. Activation energies (Q) for the rate-determining step, the transport of hydrogen in the hydrous mineral, may be derived from the Arrhenius relationship

$$\log K_2 = \log a - Q/2.303 \, RT,$$

where a is a constant. Values of $\log K_2$ for amphibole–water exchange experiments are given in Table 3, and plotted against temperature in Figure 4. Derived activation energies are listed in Table 4. These data are com-
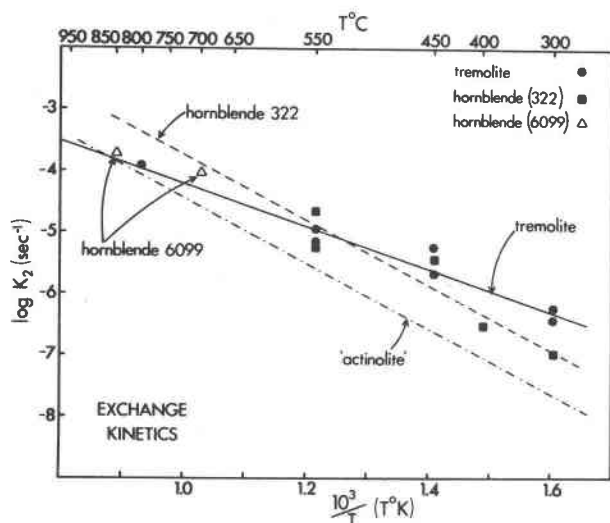
Fig. 4. Arrhenius plot of second order rate constants (log K_2) vs. reciprocal temperature for hydrogen isotope exchange reaction kinetics in the system amphibole–H_2O. Data from this study (Table 3), Suzuoki and Epstein (1976) and Graham (1981). Lines are least-squares fits to data. See text for discussion.

Table 4. Activation energies (Q) for hydrogen isotope exchange in amphiboles derived from the Arrhenius relationship by linear least-squares fitting of calculated second-order rate constants (log K_2)

	Temperature range (°C)	a	b	Q (kcals/ g-atom)	r^2
tremolite #338	350–800	-0.72	-3.49	16.0	0.96
actinolite #6906	400–670	0.91	-5.34	24.4	0.99
hornblende #322	350–550	1.61	-5.34	24.4	0.91

Linear least squares fit of kinetic data (Table 3) to the equation log K_2 = a + b $(\frac{10^3}{T})$, where b = Q/2.303R, and r^2 is the correlation coefficient. Kinetic data for actinolite after Graham (1981), and based on experimental data of Suzuoki and Epstein (1976).

pared with kinetic data for the experiments of Suzuoki and Epstein (1976) for the system "actinolite"–water derived by Graham (1981).

Activation energies for hydrogen transport in hornblende #322 and "actinolite" are comparable (24 kcal/mole H) and slightly larger than the value for tremolite (16 kcal/mole); all these values lie in the range of values (14–31 kcal/mole) derived for hydrogen diffusion in a variety of hydrous minerals (Graham, 1981). Kinetic data for

hornblende #322 show a larger scatter, perhaps reflecting the simultaneous progress to varying degrees of oxy-hornblende reactions during the hydrogen isotope exchange reactions.

Diffusion of hydrogen in amphiboles: closure temperatures

Assumptions and calculations. Closure temperatures for cessation of hydrogen isotope exchange between amphiboles and hydrous fluid or between amphiboles and coexisting hydrous minerals in igneous or metamorphic rocks may be calculated from estimated diffusion parameters for hydrogen diffusion in amphiboles. Methods of calculating hydrogen diffusion coefficients from experimental hydrogen isotope exchange data are described in detail by Graham (1981), and the application of these methods to the amphiboles is briefly outlined here.
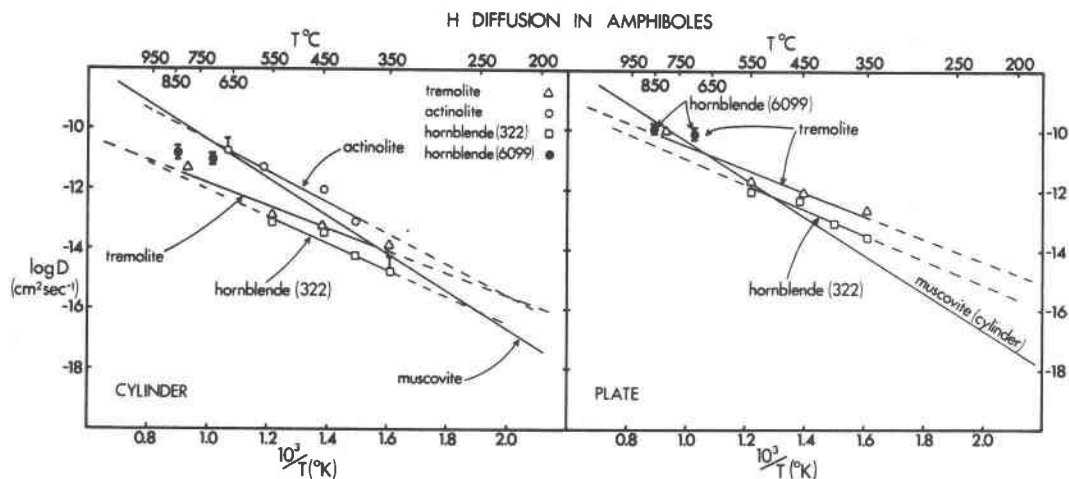

Fig. 5. Arrhenius plot of diffusion coefficients vs. reciprocal temperature for diffusion of hydrogen in amphiboles. Data from this study and after Suzuoki and Epstein (1976). Arrhenius plot for hydrogen diffusion in muscovite (cylinder model) after Graham (1981) shown for comparison. Dashed lines indicate extrapolation beyond experimental range. Error bars indicate uncertainties in calculated diffusion coefficients arising from uncertainties in mineral grain geometry estimates. See text for discussion.

Table 5. Activation energies (Q) for hydrogen diffusion in various amphiboles derived from the Arrhenius relationship by linear least-squares fitting of estimated diffusion coefficients for infinite cylinder and plate models (see text, Fig. 5, Graham (1981)).

	Temperature range (°C)	a	b	Q (kcals/ g-atom)	r²
(a) Cylinder					
tremolite #338*	350–800	-8.05	-3.72	17.0	0.95
actinolite #6906+	400–670	-5.20	-5.16	23.6	0.96
hornblende #322△	350–550	-7.62	-4.39	20.1	0.94
(b) Plate					
tremolite #338*	650–850	-6.75	-3.78	17.3	0.94
hornblende #322△	350–550	-6.80	-4.16	19.0	0.95

Linear least-squares fit of estimated diffusion coefficients where $\log D = a + b(\frac{10^3}{T})$, $b = Q/2.303R$, and r^2 is the correlation coefficient.

* data for tremolite assume prisms of average length 50 μm and average aspect ratio 2.46.

+ data for actinolite derived from experiments of Suzuoki and Epstein (1976), and assume average prism radius of 56 μm (100–200 mesh); 500°C data are excluded (see Graham, 1981).

△ data for hornblende assume prisms of average length 30 μm and average aspect ratio 2.19.

The calculation of diffusivities involves a knowledge of grain geometry. Amphibole starting materials in this study were roughly sized by removal of fine-grained material from crushed mineral powders. Mean prism lengths for the hornblende #322 and tremolite #338 starting powders were in the range 30–50 μm. Mean prism lengths for hornblende #6099 were in the range 50–70 μm. Mean aspect ratios were 2.46, 2.19 and 1.74 for tremolite #338, hornblende #322, and hornblende #6099, respectively. These values are insufficiently large to permit a choice between geometrical models. Uncertainties in grain size lead to uncertainties in calculated diffusion coefficients of less than one order of magnitude for a given choice of geometrical model. The prismatic habit and chain structure of the amphiboles suggest that diffusional anisotropies should be parallel or perpendicular to prism edges, and therefore the infinite plate and cylinder models (Crank, 1975, equations 5.36 and 4.43) were applied to our experimental data. These values are based on quite small extrapolation of our diffusion data. Adopting the cylinder model, for example, a 0.1 mm diameter hornblende prism in a lava would require several days at 950°C for complete hydrogen isotope exchange with hydrous fluid; a 0.5 mm diameter hornblende prism would require several months for complete exchange at this temperature, whereas no detectable exchange would occur in less than several hours. We therefore conclude that amphibole crystals in rapidly quenched lavas will, in the absence of extensive oxidation or alteration, preserve their high-temperature (magmatic) hydrogen isotope composition, and they should therefore preserve useful information on the hydrogen isotope compositions and origins of "magmatic" waters.

Conclusions

(1) The bulk D/H ratio in Fe-rich amphibole-water exchange experiments may increase by a variable amount as a result of hydrogen diffusion through capsule walls, despite the use of thick-walled (0.5 mm) capsules. The effect is probably related to the occurrence of "oxy-hornblende" oxidation of the amphiboles.

(2) Hydrogen isotope fractionation is independent of temperature up to 650°C in the system tremolite–water and 800–850°C in the system hornblende–water. The relationship between hydrogen isotope fractionation factor and octahedral cation composition for OH–mineral–water systems suggested by Suzuoki and Epstein (1976) is not directly applicable to the amphiboles. A-site cations may exert an important influence on the O–H bond in amphiboles.

(3) The temperature-independence of hydrogen isotope fractionations between hornblende and water over a large temperature range means that the hydrogen isotope composition of aqueous fluid in isotopic equilibrium with hornblendes in closed igneous and metamorphic rock systems for temperatures of >350°C may be reliably estimated even when uncertainty exists over the exact closure temperature for cessation of hydrogen isotope exchange.

(4) Low activation energies (16–25 kcal/mole) for hydrogen diffusion in amphiboles are comparable to those for hydrogen diffusion in other hydrous minerals. Closure temperatures for cessation of hydrogen isotope exchange between amphiboles and fluid on slow cooling are far below likely crystallization temperatures of amphiboles in most metamorphic rocks, but rapidly cooled amphiboles in volcanic rocks should readily quench in their high temperature (e.g., 900–1000°C) D/H ratios.

(5) Water contents of Fe-bearing hornblendes in equilibrium with water may decrease significantly with increasing temperature as a result of oxy-hornblende reactions.

Acknowledgments

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