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Imprint of meteoric water on the stable isotope compositions of igneous and secondary minerals, Kap Edvard Holm Complex, East Greenland

Abstract Hydrogen and oxygen isotope analyses have been made of hydrous minerals in gabbros and basaltic xenoliths from the Eocene Kap Edvard Holm intrusive complex of East Greenland. The analyzed samples are of three types: (1) primary igneous hornblendes and phlogopites that crystallized from partial melts of hydrothermally altered basaltic xenoliths, (2) primary igneous hornblendes that formed during late–magmatic recrystallization of layered gabbroic cumulates, and (3) secondary actinolite, epidote and chlorite that formed during subsolidus alteration of both xenoliths and gabbros. Secondary actinolite has a $\delta^{18}O$ value of $-5.8\%_{oo}$ and a δD value of $-158\%_{oo}$. These low values reflect subsolidus alteration by low–$\delta^{18}O$, low–δD hydrothermal fluids of meteoric origin. The δD value is lower than the -146 to $-112\%_{oo}$ values previously reported for amphiboles from other early Tertiary meteoric–hydrothermal systems in East Greenland and Scotland, indicating that the meteoric waters at Kap Edvard Holm were isotopically lighter than typical early Tertiary meteoric waters in the North Atlantic region. This probably reflects local climatic variations caused by formation of a major topographic dome at about the time of plutonism and hydrothermal activity. The calculated isotopic composition of the meteoric water is $\delta D = -110 \pm 10\%_{oo}$, $\delta^{18}O \approx -15\%_{oo}$. Igneous hornblendes and phlogopites from pegmatitic pods in hornfelsed basaltic xenoliths have $\delta^{18}O$ values between -6.0 and $-3.8\%_{oo}$ and δD values between -155 and $-140\%_{oo}$. These are both much lower than typical values of fresh basalts. The oxygen isotope fractionations between pegmatitic hornblendes and surrounding hornfelsic minerals are close to equilibrium fractionations for magmatic temperatures, indicating that the pegmatites crystallized from low–$\delta^{18}O$ partial melts of xenoliths that had been hydrothermally altered and depleted in ^{18}O prior to stoping. The pegmatitic minerals may have crystallized with low primary δD values inherited from the altered country rocks, but these values were probably overprinted extensively by subsolidus isotopic exchange with low–δD meteoric–hydrothermal fluids. This exchange was facilitated by rapid self–diffusion of hydrogen through the crystal structures. Primary igneous hornblendes from the plutonic rocks have $\delta^{18}O$ values between $+2.0$ and $+3.2\%_{oo}$ and δD values between -166 and $-146\%_{oo}$. The ^{18}O fractionations between hornblendes and coexisting augites are close to equilibrium fractionations for magmatic temperatures, indicating that the hornblendes crystallized directly from the magma and subsequently underwent little or no oxygen exchange. The hornblendes may have crystallized with low primary δD values, due to contamination of the magma with altered xenolithic material, but the final δD values were probably controlled largely by subsolidus isotopic exchange. This inference is based partly on the observation that coexisting plagioclase has been extensively depleted in ^{18}O via a mineral–fluid exchange reaction that is much slower than the hydrogen exchange reaction in hornblende. It is concluded that all hydrous minerals in the study area, whether igneous or secondary, have δD values that reflect extensive subsolidus isotopic equilibration with meteoric–hydrothermal fluids.

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Introduction

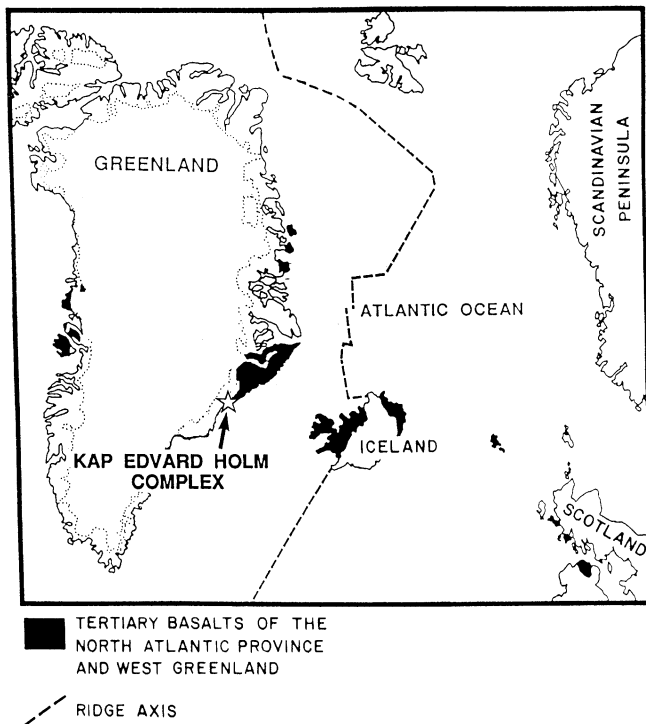The Early Tertiary lavas and plutons exposed in Scotland, Ireland, and eastern Greenland are among the

Fig. 1 Map of the North Atlantic Tertiary Igneous Province

This paper presents hydrogen and oxygen isotope analyses of hydrous minerals from mafic rocks of the Kap Edvard Holm intrusive complex, an Eocene plutonic center on the east coast of Greenland. These data suggest that, during subsolidus alteration, igneous and secondary amphiboles exchanged hydrogen with low–δD hydrothermal fluids of meteoric origin. These fluids were derived from Eocene meteoric waters that were isotopically lighter than any Early Tertiary meteoric waters previously inferred for the region.

Geologic setting

The Kap Edvard Holm Complex is located 15 km southwest of the Skaergaard intrusion in the Kangerdlugssuaq area of East Greenland (Fig. 2). It consists mainly of layered gabbros, intruded locally by mafic dikes and syenitic plutons (Deer and Abbott 1965; Elsdon 1969, 1972; Abbott and Deer 1972; Deer et al. 1984; Bernstein et al. 1992). The gabbros are hosted by Precambrian gneisses to the north and west and by Paleocene basaltic lavas to the south and east. The basalts overlie the gneisses stratigraphically, and the present exposure pattern reflects southeastward tilting of the area following emplacement of the gabbro complex (Elsdon 1969; Abbott and Deer 1972).

The study area comprises a group of cliffs consisting mainly of layered olivine gabbro, located near the western margin of the complex. These cliffs are referred to collectively as "Stand and Deliver Nunatak" (Fig. 3). Igneous hornblende from this locality has yielded $^{40}Ar/^{39}Ar$ ages ranging from 49 to 50 Ma (Nevle et al., 1994). The layered gabbro at Stand and Deliver Nunatak contains abundant xenoliths of hornfelsed metabasalt, and hosts numerous discordant bodies of massive gabbro and peridotite. These rocks contain hydrous minerals of both igneous and secondary origin.

Xenoliths

Xenoliths constitute roughly 10% of outcrop in the study area and occur as flat–lying slabs up to 5 m thick and > 100 m long. They
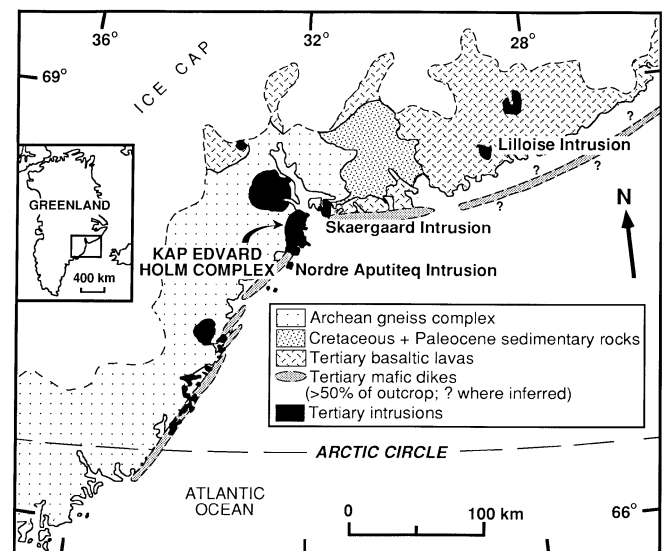
oldest rocks of the North Atlantic Tertiary Igneous Province (Fig. 1). Most igneous activity in these areas took place between 64 and 50 million years ago, during an episode of voluminous basaltic magmatism that began shortly before the onset of rifting in the modern North Atlantic ocean basin (Soper et al. 1976; Nielsen et al. 1981; Bott 1987; Mussett et al. 1988; Noble et al. 1988). Basaltic magmatism was followed by comparatively minor silicic plutonism, which continued until approximately 30 Ma in eastern Greenland (Gleadow and Brooks 1979; Noble et al. 1988).

Most of these Tertiary rocks have been altered by low–$\delta^{18}O$, low–δD hydrothermal fluids of meteoric origin. This subsolidus alteration produced secondary minerals with anomalously low values of $\delta^{18}O$ and δD, and commonly left relict igneous minerals depleted in ^{18}O (Taylor and Forester 1971, 1979; Forester and Taylor 1976, 1977; Sheppard et al. 1977; Farver and Giletti 1989; Rose 1989; Fehlhaber and Bird 1991; Nevle et al. 1994; Manning and Bird 1995). Hydrogen and oxygen isotope compositions of secondary minerals in the altered rocks have been used to calculate the isotopic compositions of paleo–hydrothermal fluids, and of the meteoric waters from which these fluids were derived. Resulting estimates of Eocene meteoric water compositions in the North Atlantic region have ranged from $\delta D \approx -85\%_0$ and $\delta^{18}O \approx -12\%_0$ in Scotland (Forester and Taylor 1977) to $\delta D \approx -100\%_0$ and $\delta^{18}O \approx -14\%_0$ in eastern Greenland (Taylor and Forester 1979).

Fig. 2 The central east coast of Greenland, showing the Kap Edvard Holm Complex and other intrusions referred to in the text
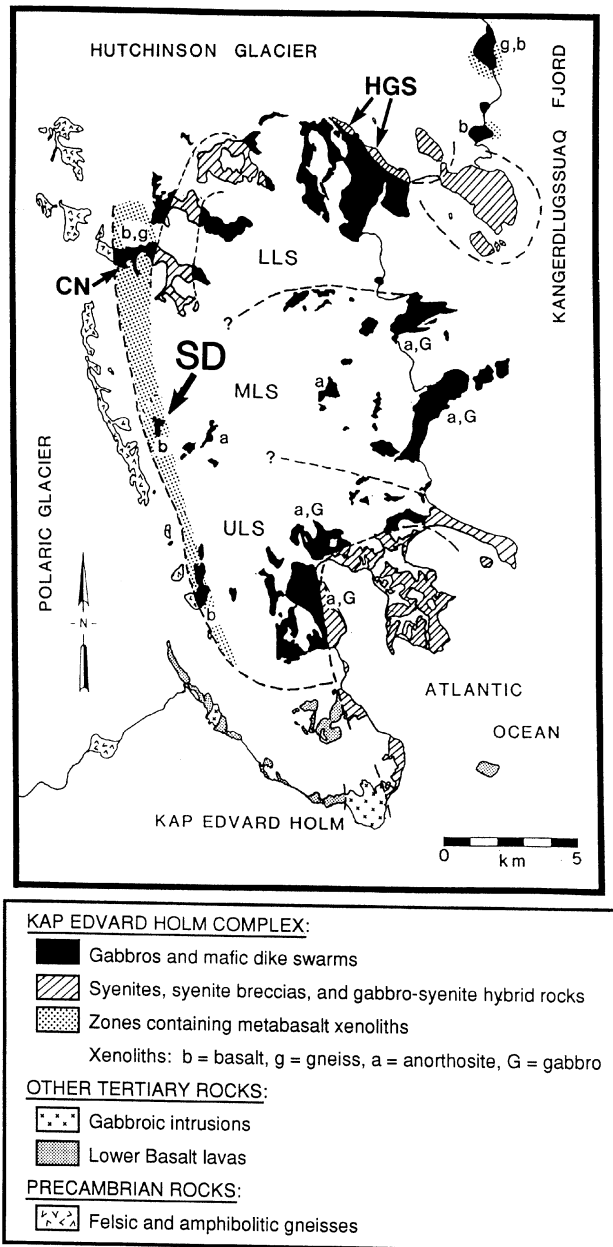
Fig. 3 Map of the Kap Edvard Holm Complex, showing the locations of Stand and Deliver Nunatak (*SD*), Contact Nunatak (*CN*), and the Hutchinson Glacier syenites (*HGS*). The layered gabbros are divided into Lower, Middle and Upper Layered Series (*LLS*, *MLS* and *ULS*; after Abbott and Deer 1972)

consist of metabasaltic country rock that has been hornfelsed to assemblages of augite + plagioclase + magnetite ± olivine ± orthopyroxene ± ilmenite. Two–pyroxene thermometry gives recrystallization temperatures of roughly $1050°$ C (Brandriss 1993). Most xenoliths have been strongly depleted in incompatible elements due to partial melting (Brandriss 1993), and some enclose small pods of pegmatite that crystallized from the partial melts. These pods contain centimeter to decimeter–sized crystals of magnesiohornblende and phlogopite (Fig. 4A).

The xenoliths are fragments of Tertiary basaltic lava from a volcanic unit known as the Lower Basalts (the Lower Basalts have been

studied by Nielsen et al. 1981; Holm 1988; Gill et al. 1988; Manning and Bird 1991, 1995; Manning et al. 1993; and Fram 1994). Throughout the region, the Lower Basalts have been altered to secondary mineral assemblages under conditions ranging from the zeolite facies in regionally metamorphosed rocks to the sanidinite facies in contact metamorphic aureoles (Bird et al. 1988a; Manning et al. 1993; Manning and Bird 1995). Alteration occurred in the presence of isotopically light meteoric–hydrothermal fluids which depleted the metabasalts in ^{18}O and deuterium (Taylor and Forester 1979; Manning and Bird 1995): whole–rock analyses have yielded $\delta^{18}O$ values as low as $-2.3‰$ (Taylor and Forester 1979) and δD values as low as $-136‰$ (Brandriss 1993). The xenoliths contain hornfelsic plagioclase and augite with $\delta^{18}O$ values as low as $-5.2‰$ and $-5.5‰$ respectively, reflecting their derivation from this hydrothermally altered and ^{18}O–depleted protolith (Brandriss et al. 1992; Brandriss 1993). The water contained in hydrous secondary minerals in the metabasalts probably facilitated partial melting in the xenoliths (Brandriss 1993).

Postcumulus bodies

Late–magmatic recrystallization locally resulted in the replacement of layered gabbroic cumulates by discordant bodies of feldspathic peridotite and magnetite–rich gabbro. This occurred in response to localized influxes of H_2O, which caused destabilization of the primary cumulus assemblage (Brandriss 1993). The replacement bodies are spatially associated with metabasaltic xenoliths, indicating that some of the water was probably supplied by devolatilization or dehydration–melting of xenoliths within the cumulus pile. The postcumulus peridotites and gabbros typically contain several per cent primary igneous magnesiohornblende as intergranular or poikilitic crystals (Figs. 4B,C).

Some of the postcumulus rocks contain small dikes of hornblende–andesine pegmatite, which appear to have crystallized from late–magmatic segregations of evolved intercumulus liquid. These dikes contain blades of igneous magnesiohornblende up to a centimeter thick and a few centimeters long (Fig. 4D).

Secondary alteration

All rocks in the study area contain secondary hydrous minerals. The most common secondary assemblage consists of actinolite, chlorite, talc, magnetite, and orthoamphibole. This is similar to the *actinolitic hornblende + chlorite + talc* alteration type previously described in the Kap Edvard Holm Complex by Bird et al. (1988b). Maximum temperatures of formation for this assemblage are inferred to have been $500–600°$ C (Bird et al. 1988b). A less common assemblage, occurring mainly in the most altered gabbros, consists of epidote, albite, actinolite, chlorite, sericite, and titanite, sometimes with minor hedenbergite or hornblende. This is equivalent to the *calcic amphibole + epidote + albite* assemblage of Bird et al. (1988b), for which they inferred metamorphic temperatures of $380–500°$ C. The pegmatites and magnetite–rich gabbros are generally the most altered rocks, containing up to 80% and 50% secondary minerals respectively (Figs. 4C,D). Other rock types typically contain 1–10% secondary minerals.

Macroscopic hydrothermal veins filled with secondary minerals are present in many outcrops. Most veins contain *actinolitic hornblende + chlorite + talc* assemblages, but a few contain *calcic amphibole + epidote + albite* assemblages (Fig. 4E).

Analytical methods

Hydrogen and oxygen isotope analyses of mineral separates were performed at the University of Michigan. Oxygen was extracted by
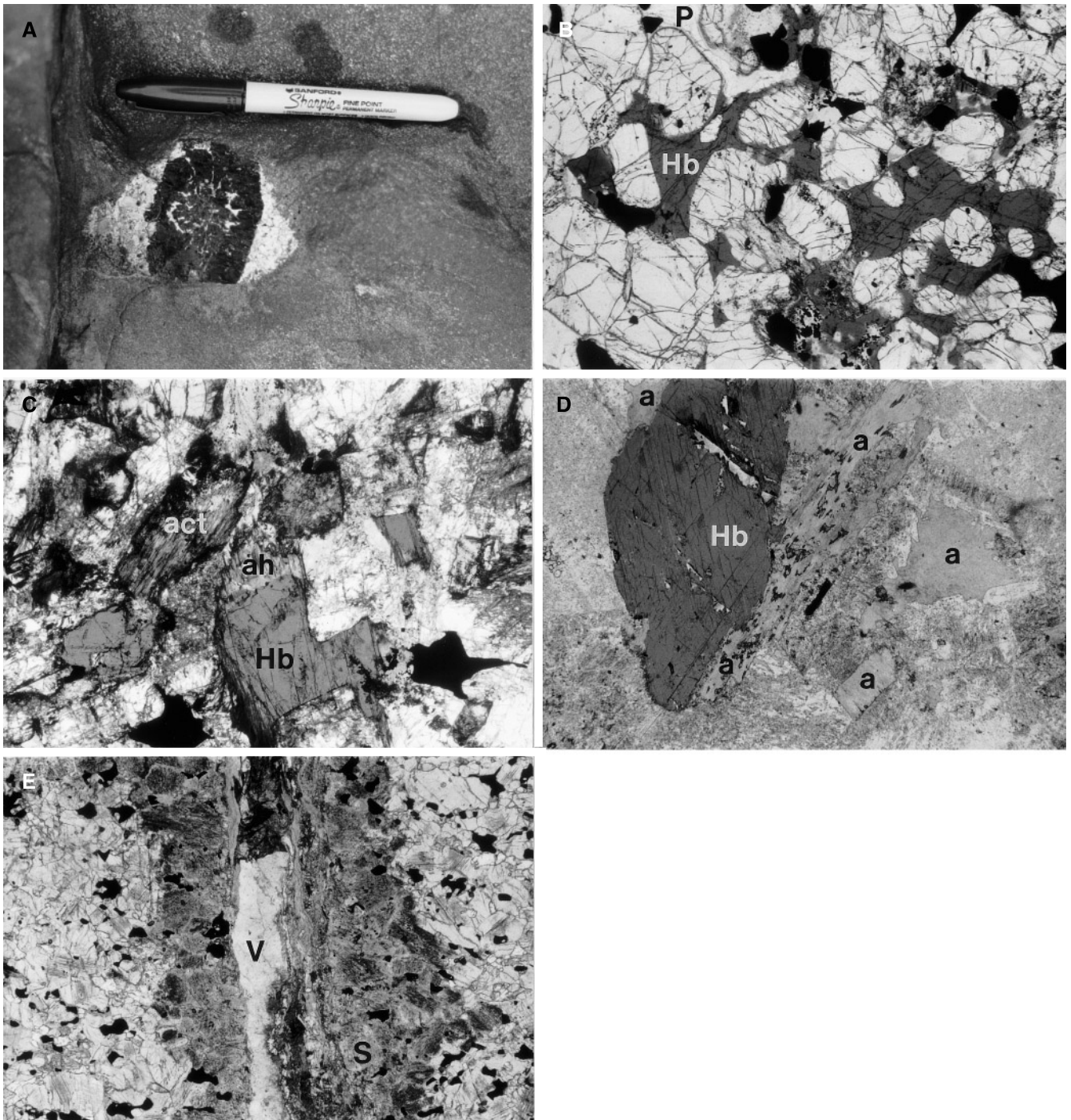
Fig. 4A–E Hydrous minerals in the various rock types. **A** Pegmatitic pod in hornfelsed metabasalt xenolith. The xenolith takes up the full field of view; the pod contains a single crystal of hornblende (*black*) flanked by patches of medium–grained plagioclase (*white*). The dark spots above the pen are raindrops. **B** Postcumulus peridotite (sample KEH406B). Equant olivine crystals are enclosed in poikilitic hornblende (*Hb*) and plagioclase (*P*). Field of view 6 mm wide. **C** Postcumulus massive gabbro (sample KEH414). Intergranular hornblende (*Hb*) is partially replaced by secondary actinolitic hornblende (*ah*) and fibrous actinolite (*act*) intergrown with secondary chlorite. Field of view 6 mm wide. **D** Pegmatitic dike (sample KEH402A) containing a hornblende megacryst (*Hb*) surrounded by secondary actinolite (*a*) and sericitized plagioclase (most of the area). Field of view 6 mm wide. **E** Hydrothermal vein cutting hornfelsed metabasalt xenolith (sample KEH259E). The vein center (*V*) consists mainly of actinolite, actinolitic hornblende and epidote, while the selvedge (*S*) contains abundant actinolite, epidote and chlorite. Field of view 6 mm wide

reaction with BrF_5, using a method similar to that of Clayton and Mayeda (1963). The reproducibility of oxygen analyses was typically better than $\pm 0.2\%$. Hydrogen isotope analyses were done by the Zn reduction method of Vennemann and O'Neil (1993), and included determination of water by mass spectrometer voltage calibration. Hydrogen analyses were typically reproducible to within $\pm 2\%$, although a few anomalous values were obtained during multiple analyses of some samples. The chemical compositions of amphiboles and micas were determined by wavelength–dispersive electron microprobe analysis of polished thin sections at Stanford University. Results of isotope analyses are presented in Table 1, and mineral compositions are presented in Table 2.

Results

All of the hydrous minerals, whether igneous or secondary, have δD and $\delta^{18}O$ values that are substantially lower than those of mantle–derived basaltic magmas. As earlier studies have shown for other igneous rocks in the region, these low values reflect the isotopic signature of meteoric water (e.g. Sheppard et al. 1977; Taylor and Forester 1979). The secondary minerals from Stand and Deliver Nunatak typically have δD values between -163 and -138% and $\delta^{18}O$ values between -5.8 and -5.5%. For comparison, typical mantle values are roughly -80% and $+5$ to $+7\%$ respectively (Kyser 1986). Igneous minerals from the metabasaltic xenoliths are isotopically similar to the secondary minerals, with δD values of -155 to -139% and $\delta^{18}O$ values of -6.0 to -3.8%. Igneous hornblendes from the postcumulus plutonic rocks have similar δD values (-166 to -146%) but somewhat higher $\delta^{18}O$ values ($+2.0$ to $+3.2\%$). Even the highest values, however, are substantially lower than those of "normal" basaltic magmas. The isotopic signature of meteoric water is thus clearly discernible in all hydrous minerals from the study area. The nature and timing of interactions between magmas, rocks and meteoric waters can be elucidated through analysis of the data presented below.

Secondary minerals

Most of the secondary minerals are finely intergrown and difficult to separate. In one case, however, it was possible to extract pure secondary actinolite from an altered pegmatitic dike (sample KEH402A). This actinolite had a $\delta^{18}O$ value of -5.5% and a δD value of -158%, clearly reflecting alteration by isotopically light hydrothermal fluids of meteoric origin (e.g. Taylor 1974, 1977; Criss and Taylor 1986). Primary igneous hornblende from the same rock had $\delta^{18}O = +3.0\%$, a value more typical of igneous minerals.

The δD of the secondary actinolite can be used to calculate the δD of the hydrothermal fluid with which it equilibrated. The low $\delta^{18}O$ value of the actinolite indicates that the amount of fluid was sufficient to alter the oxygen isotope composition of the rock substantially. This implies that the amount of hydrogen in the fluid must have been far greater than the amount in the rock, because rocks are rich in oxygen but poor in hydrogen. The δD of the fluid therefore could not have been modified greatly by water–rock interaction, and as a result, the original δD of the meteoric water can be calculated from the measured δD of the actinolite with which it equilibrated. Assuming equilibration temperatures between 380 and 600° C, and taking into account the effects of amphibole composition (Table 2), the amphibole–water fractionation equation of Suzuoki and Epstein (1976) yields a δD value of $-110 \pm 10\%$ for the meteoric water. The corresponding $\delta^{18}O$ of this meteoric water would have been approximately -15% (Craig 1961).

These results are corroborated by analyses of two samples of finely intergrown actinolite and chlorite. These samples (both from the same rock, but with different proportions of the two minerals) contained 3.4 and 7.3 wt% H_2O with δD values of -153 and -138%, respectively. The $\delta^{18}O$ of the second sample was -5.5%. The low values are once again diagnostic of meteoric–hydrothermal alteration. The δD values for the two minerals can be crudely estimated from mass balance calculations by assuming that the chlorite contained ~ 11 wt% H_2O and the actinolite contained ~ 2 wt% H_2O. This yields values of $\delta D_{actinolite} \approx -170\%$ and $\delta D_{chlorite} \approx -135\%$, roughly consistent with the value obtained for the sample of pure actinolite.

The isotopic composition of another sample is somewhat anomalous. This sample (KEH259E) is a mm–wide hydrothermal vein containing actinolite, chlorite, epidote, and minor actinolitic hornblende (Fig. 4E). Petrographically, it is notably dissimilar to most veins in the study area, which are very thin ($\ll 1$ mm) and contain no epidote. A sample of nearly pure epidote from the vein selvedge yielded $\delta D = -75\%$, and a mixture of epidote and actinolite from within the vein yielded $\delta D = -109\%$. The relative proportions of minerals in the mixture can be calculated from x-ray $K\alpha$ peak heights determined by powder diffractometry, using the absorption–diffraction method applied to a binary mixture (Snyder and Bish 1989, Eq. 22). This yields a rough estimate of ~ 25 wt% epidote and ~ 75 wt% actinolite. Mass balance calculations (based on these proportions and on the measured δD of the pure epidote) give an approximate δD value of -120% for the actinolite. This relatively high value could be due to localized alteration by a fluid that was isotopically heavier than that inferred from the other samples, possibly indicating a separate and isotopically distinct alteration event. It must be emphasized, however, that this is a rare type of vein, containing a secondary assemblage that is mineralogically distinct from the dominant type of alteration in the area.

Table 1 Isotope analyses of hydrous minerals from Stand and Deliver Nunatak[a]

Secondary minerals

Sample	Mineral	Rock type	δD	$\delta^{18}O$[b]	wt% H_2O[c]
KEH259E	Actinolite + epidote	Hydrothermal vein	− 109		2.00
	Epidote	Hydrothermal vein	− 75		1.60
KEH402A	Actinolite	Pegmatitic dike	− 161	− 5.8 (4)	1.99
	Actinolite	Pegmatitic dike	− 158		2.05
	Actinolite	Pegmatitic dike	− 158		2.04
	Actinolite	Pegmatitic dike	− 163		1.97
	Actinolite	Pegmatitic dike	− 150		2.01
KEH414	Actinolite + chlorite	Postcumulus gabbro	− 138	− 5.5 (1)	7.30
	Actinolite + chlorite	Postcumulus gabbro	− 153		3.39

Igneous minerals in plutonic rocks

Sample	Mineral	Rock type	δD	$\delta^{18}O$[b]	wt% H_2O[c]
KEH303I	Magnesiohornblende	Pegmatitic dike	− 150	2.0 (2)	0.90
KEH402A	Magnesiohornblende	Pegmatitic dike	− 152	3.0 (2)	1.02
	Magnesiohornblende	Pegmatitic dike	− 146		1.02
	Magnesiohornblende	Pegmatitic dike	− 148		1.06
	Magnesiohornblende	Pegmatitic dike	− 160		1.05
KEH289	Magnesiohornblende	Postcumulus peridotite	− 146		1.62
KEH303C	Magnesiohornblende	Postcumulus peridotite	− 166	2.3 (3)	1.40
KEH406B	Magnesiohornblende	Postcumulus peridotite	− 161	3.2 (3)	1.51
KEH407	Magnesiohornblende	Layered gabbro, replaced	− 160	3.0 (2)	1.46
	Magnesiohornblende	partially by peridotite	− 158		1.45
KEH414	Magnesiohornblende	Postcumulus gabbro	− 159	2.9 (2)	1.18

Igneous minerals in pegmatitic pods enclosed in xenoliths

Sample	Mineral	Rock type	δD	$\delta^{18}O$[b]	wt% H_2O[c]
KEH259A	Magnesiohornblende	Pegmatitic pod in xenolith	− 152	− 6.0 (2)	1.16
KEH263	Magnesiohornblende	Pegmatitic pod in xenolith	− 154		1.04
KEH274E	Magnesiohornblende	Pegmatitic pod in xenolith	− 149		0.84
KEH274F	Magnesiohornblende	Pegmatitic pod in xenolith	− 155	− 4.4 (2)	0.65
	Magnesiohornblende	Pegmatitic pod in xenolith	− 155		0.64
	Magnesiohornblende	Pegmatitic pod in xenolith	− 155		0.72
KEH290	Phlogopite	Pegmatitic pod in xenolith	− 142		1.50
	Phlogopite	Pegmatitic pod in xenolith	− 139		2.34
KEH302	Magnesiohornblende	Pegmatitic pod in xenolith	− 149	− 3.8 (2)	0.52
	Magnesiohornblende	Pegmatitic pod in xenolith	− 149		0.51
	Phlogopite	Pegmatitic pod in xenolith	− 150		1.13
	Phlogopite	Pegmatitic pod in xenolith	− 147		1.17

[a] All values for isotope analyses are reported in per mil relative to SMOW
[b] Average of multiple analylses; the number of analyses is given in parentheses. Reproducibility was typically better than ± 0.2 per mil
[c] H_2O contents determined by mass spectrometer voltage calibration (Vennemann and O'Neil 1993)

Igneous minerals in pegmatitic pods enclosed in xenoliths

Centimeter to decimeter–sized crystals of hornblende and phlogopite were separated from pegmatitic pods enclosed in mafic xenoliths. Hornblende megacrysts yielded $\delta^{18}O$ values of − 6.0, − 4.4, and − 3.8‰. The unequivocally igneous textures of the pegmatitic horn-blendes suggest that these low $\delta^{18}O$ values reflect crystallization from low–$\delta^{18}O$ melts of the host xenoliths. This interpretation is supported by isotopic data for the enclosing hornfels: the hornfels a few centimeters away from one pegmatitic body (sample KEH274F, $\delta^{18}O_{hornblende} = − 4.4‰$) contains pyroxene with $\delta^{18}O = − 4.3‰$ and plagioclase with $\delta^{18}O = − 3.8‰$, yielding isotopic fractionations between hornblende,

Table 2 Representative electron microprobe analyses of hydrous minerals (*HV* hydrothermal vein cutting metabasalt xenolith, *PD* pegmatitic dike, *PER* postcumulus peridotite body, *MG* postcumulus magnetite-rich gabbro body, *XENO* pegmatitic pod enclosed in metabasalt xenolith)

Mineral	Secondary amphibole					Igneous hornblende				
Rock type	HV[a]	PD[a]	MG[a]	MG[a]	MG[a]	PER	PER[a]	PER[a]	PER[a]	MG[a]
Sample[b]	259E	402A	414	414	414	289	303C	406B	407	414
SiO_2	54.05	51.86	53.87	39.83	44.15	42.93	42.62	43.69	42.61	40.78
TiO_2	0.09	0.08	0.23	0.16	0.36	4.00	3.70	4.09	4.05	3.90
Al_2O_3	0.94	0.49	1.42	11.45	10.27	10.78	10.30	10.11	10.61	10.05
Cr_2O_3	0.00	0.00	0.12	0.00	0.00	0.05	0.09	0.16	0.08	0.02
FeO^c	17.28	20.51	10.67	22.26	17.61	10.54	10.07	10.65	11.70	10.95
MnO	0.31	0.28	0.15	0.39	0.33	0.17	0.07	0.13	0.20	0.09
MgO	13.39	11.36	18.40	8.54	12.33	14.13	16.03	15.60	14.80	15.73
CaO	12.54	12.03	12.71	12.15	12.24	11.58	11.45	11.30	11.56	11.91
Na_2O	0.11	0.14	0.23	1.90	1.83	2.43	2.71	2.48	2.18	2.20
K_2O	0.03	0.05	0.02	0.17	0.09	1.12	1.04	0.92	1.00	1.28
Cl	0.00	0.00	0.03	0.65	0.26	0.03	0.04	0.03	0.04	0.06
F[d]	0.00	0.00	0.06	0.00	0.41	0.12	1.09	0.58	0.52	1.30
Sum	98.74	96.80	97.91	97.50	99.88	97.88	99.21	99.74	99.35	98.27
$X(Fe)^e$	0.42	0.49	0.21	0.60	0.45	0.29	0.22	0.24	0.26	0.21

Mineral	Igneous hornblende					Igneous phlogopite				
Rock type	XENO	XENO	XENO	XENO	XENO	XENO	XENO	XENO[a]	XENO	XENO
Sample[b]	259A	263	274E	274F	274F[f]	302	3031	402A	290	302
SiO_2	43.71	44.54	42.52	43.02	43.03	42.62	43.77	40.71	38.70	38.84
TiO_2	2.79	3.11	3.72	3.78	3.82	3.81	3.52	3.80	5.79	6.03
Al_2O_3	9.88	10.01	10.37	10.70	10.76	10.46	9.90	9.88	12.95	13.15
Cr_2O_3	0.15	0.07	0.06	0.11		0.03	0.00	0.06	0.08	0.11
FeO^c	8.64	8.81	9.13	8.38	8.52	8.72	10.40	11.79	11.25	9.82
MnO	0.18	0.13	0.13	0.07]	0.10]	0.11	0.19	0.18	0.11	0.00
MgO	16.28	16.08	15.57	16.11	16.31	16.17	14.73	15.25	17.07	17.43
CaO	11.72	11.24	11.72	11.54	11.77	11.78	11.14	11.37	0.02	0.05
Na_2O	2.33	2.11	2.53	2.46	2.41	2.25	2.89	2.46	0.37	0.50
K_2O	0.75	0.56	1.10	0.82	0.94	1.47	0.71	1.01	9.15	9.02
Cl	0.00	0.08	0.00	0.00		0.00	0.00	0.04	0.05	0.01
F[d]	0.63	0.65	1.01	0.70		1.24	1.22	1.35	1.03	1.73
Sum	97.06	97.39	97.86	97.69	97.66	98.66	98.47	97.90	96.57	96.69
$X(Fe)$	0.22	0.23	0.23	0.21	0.21	0.21	0.28	0.23	0.24	0.21

[a] Analyses collected at the University of California, Davis. All other analyses were collected at Stanford University. A complete tabulation of data, and details of analytical methods, are presented by Brandriss (1993)

[b] All sample numbers have the prefix "KEH"

[c] All Fe as FeO

[d] Fluorine concentrations must be regarded as approximations due to poor reproducibility (for individual samples, F concentrations determined on the University of California, Davis microprobe were roughly twice as high as those determined on the Stanford University microprobe)

[e] X(Fe) is the mole fraction of Fe in the octahedral sites. In the amphiboles, it is assumed that all five octahedral sites are occupied only by Mg, Fe, and Ti, and that all Mg and Ti reside in octahedral sites

[f] XRF analysis of fused disk, with all Fe reported as FeO. The actual FeO content of this sample was determined by wet chemistry using a slightly modified version of the technique of Wilson (1955); analysis in triplicate gave a value of $7.37 \pm 0.06\%$ FeO

pyroxene and plagioclase that are almost identical to the predicted equilibrium values for temperatures of 900–1000° C (Bottinga and Javoy 1975; Matthews et al. 1983). This supports the inference that the pegmatites and hornfelses formed at high temperature from the same reservoir of ^{18}O–depleted country–rock material, implying that the ^{18}O depletion occurred *prior* to stoping. Petrographic analysis of the hornfelses strongly supports this interpretation. The hornfelses are the least altered rocks in the study area, yet contain pyroxenes with $\delta^{18}O$ values as low as $-5.5\%_{oo}$ (Brandriss et al. 1992; Brandriss 1993). Pyroxene is strongly resistant to subsolidus ^{18}O exchange (e.g. Criss and Taylor 1986), so the low–$\delta^{18}O$ values must have been inherited from the country rock protolith. This is consistent with studies of the country rocks, which have shown

that hydrothermal alteration produced abundant low–δD and low–$\delta^{18}O$ secondary minerals in meta-basalts throughout the region (e.g. Taylor and Forester 1979; Manning and Bird 1995).

The δD values of the pegmatitic hornblendes and phlogopites range from −155 to −141‰, clearly reflecting the isotopic signature of meteoric water. The pegmatitic minerals crystallized from melts of hydrothermally altered, low–δD country rocks, so it is likely that they formed with low primary δD values. The measured values, however, are not necessarily the primary values. Hydrogen self–diffuses rapidly through these minerals (Cole et al. 1983; Graham et al. 1984), so the low δD values that were ultimately preserved could reflect a subsolidus hydrothermal overprint.

Igneous minerals in plutonic rocks

Igneous hornblendes from the plutonic rocks have $\delta^{18}O$ values ranging from +2.0 to +3.2‰. These are much higher than the values for secondary minerals, and are only a few per mil lower than "normal" values for mantle–derived igneous rocks. The slight shift from normal igneous values is probably attributable either to contamination of the parent magmas by low–$\delta^{18}O$ xenolithic material, or to high–temperature subsolidus exchange of oxygen between isotopically "normal" igneous hornblende and low–$\delta^{18}O$ meteoric–hydrothermal fluids (Brandriss, 1993). Analyses of coexisting hornblende and augite yield $\delta^{18}O_{augite-hornblende}$ fractionations of +0.6 to −0.2‰, which are similar to equilibrium fractionations for temperatures of 500–1000°C ($\approx$ 0 to 0.5‰; Bottinga and Javoy 1975). This could potentially be consistent with either of the hypotheses mentioned above.

The δD values of the igneous hornblendes range from −166 to −146‰. These are similar to the values of the secondary actinolites, but much lower than the values of mantle–derived basaltic magmas, indicating that most of the hydrogen must be of meteoric origin. This can potentially be explained by contamination of the magma with hydrothermally altered low–δD material (such as the basaltic xenoliths), by subsolidus exchange of hydrogen with meteoric–hydrothermal fluids, or by some combination of these processes.

Discussion

Origin of low δD values of hydrous minerals

The low δD values of secondary minerals from Stand and Deliver Nunatak are clearly attributable to subsolidus alteration by low–δD hydrothermal fluids of meteoric origin. The low δD values of igneous minerals, however, can potentially be explained in at least two ways: some may have crystallized directly from low–δD magmas, whereas others may have exchanged hydrogen with low–δD hydrothermal fluids.

Direct evidence for subsolidus hydrogen exchange is not readily identifiable in the igneous minerals. However, evidence for subsolidus *oxygen* exchange is clearly discernible in other igneous minerals from the same rocks. Brandriss (1993) showed that *all* of the hornblende–bearing peridotites and gabbros contain clear, fresh–looking plagioclase that has exchanged oxygen with low–$\delta^{18}O$ meteoric–hydrothermal fluids, producing $\delta^{18}O_{plagioclase}$ values as low as −5.4‰. These values reflect subsolidus ^{18}O depletions of as much as 9.5‰ (Fig. 5). If the intergranular hornblende in these rocks exchanged hydrogen with the fluid as readily as the plagioclase exchanged oxygen, then the *final* δD values of the hornblendes must have been controlled largely by subsolidus isotopic equilibration.

Rates of isotopic exchange between fluids and minerals are strongly dependent on exchange mechanisms (e.g. Cole and Ohmoto 1986). In feldspars, oxygen exchange is relatively rapid if it occurs by in situ dissolution and reprecipitation of mineral grains (O'Neil and Taylor 1967) but is orders of magnitude slower if it occurs by self–diffusion of oxygen through the crystal structure (Giletti et al. 1978; Giletti 1985). For the plagioclase analyzed in this study, several factors suggest that self–diffusion, rather than dissolution–reprecipitation, was the dominant mechanism of oxygen isotope exchange. The plagioclase is clear and fresh–looking in mineral separates and in thin sections, and many grains contain complex forms of primary compositional zoning that could not plausibly have survived secondary dissolution and reprecipitation (Fig. 6). In addition, at the high alteration temperatures inferred from secondary mineral assemblages, self–diffusion rates are sufficiently rapid that extensive oxygen exchange could easily have occurred during the lifetime of a large hydrothermal system (Giletti et al. 1978). It is therefore concluded that self–diffusion was the dominant mechanism of oxygen exchange in igneous plagioclase.

By comparing the self–diffusion coefficients for oxygen and hydrogen, we can determine the extent to which oxygen exchange in plagioclase would have been accompanied by hydrogen exchange in hornblende. Experiments have shown that the self–diffusion coefficient for hydrogen in hornblende is two to three orders of magnitude greater than the self–diffusion coefficient for oxygen in plagioclase (Giletti et al. 1978; Graham et al. 1984). This implies that the hornblende would have exchanged hydrogen much faster than the plagioclase exchanged oxygen. Therefore, given the evidence for extensive oxygen isotope exchange in plagioclase, the coexisting intergranular hornblendes could *not* have retained much of their original hydrogen. Instead, their final hydrogen isotope compositions were probably
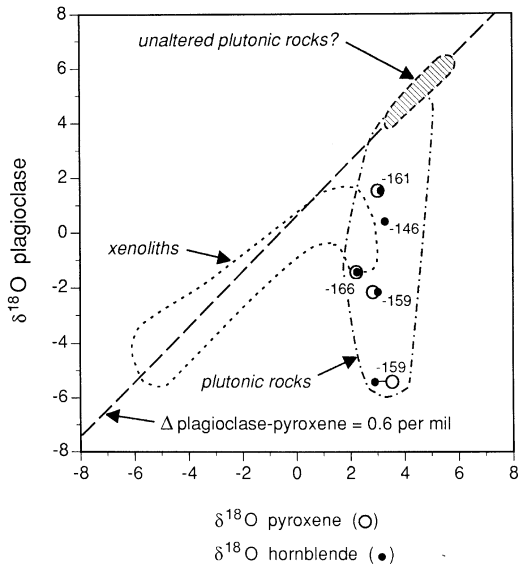
Fig. 5 $\delta^{18}O$ of plagioclase plotted against $\delta^{18}O$ of coexisting pyroxene and hornblende, for samples from Stand and Deliver Nunatak. Symbols are shown only for those rocks (all plutonic) in which igneous hornblende was analyzed; the number beside each symbol is the δD value of the hornblende. *Overlapping symbols*, and *symbols joined by a thin line*, represent pairs of analyses from a single rock sample. The fields for xenoliths and plutonic rocks are for plagioclase–pyroxene pairs, and are taken from Brandriss (1993). The plagioclase–pyroxene fractionation line represents equilibrium at ∼ 950°C (Matthews et al. 1983). The vertical distance that an analysis falls below this line represents the minimum amount of subsolidus ^{18}O depletion in the plagioclase (e.g. Gregory et al. 1989). The "*unaltered plutonic rocks?*" *field* includes typical values for fresh basalts from around the world (Taylor 1974), but has been extended toward lower $\delta^{18}O$ values to account for possible contamination of the magma with low–^{18}O xenolithic material

Fig. 6 Examples of complex igneous zoning in plagioclase, sample KEH407. Plagioclase and pyroxene in this rock have $\delta^{18}O$ values of − 2.6 and + 2.8‰, respectively. Assuming an initial plagioclase–pyroxene oxygen isotope fractionation of 0.5‰ in the crystallizing magma (Matthews et al. 1983), the measured values indicate subsolidus depletions of at least 5.9‰ in the plagioclase despite its fresh appearance and the widespread preservation of primary compositional zoning. Each field of view 3 mm wide

controlled largely by subsolidus isotopic equilibration with meteoric–hydrothermal fluids.

The time required for hydrogen isotope exchange in hornblende can be estimated from experimentally determined diffusion coefficients, using the analytical expressions derived by Crank (1975). For the purposes of calculation, the minerals are assumed to have been enclosed in fluid. This is consistent with the observation that mineral grains in these rocks are commonly surrounded by grain–boundary microfractures lined with hydrous secondary minerals (Brandriss et al. 1992). It is also assumed that the amount of hydrogen in the fluid was much greater than the amount in the hornblende, so that the fluid can be treated as an infinite reservoir of hydrogen of constant isotopic composition. Sample calculations have been performed for a grain size of 0.4 mm, which is about the size of hornblende–filled intergranular spaces in the peridotites and gabbros.

The calculated timescales required for measurable isotopic exchange are short compared to the lifetime of a large hydrothermal system (Fig. 7). The model hornblende exchanges 25% of its hydrogen within weeks at
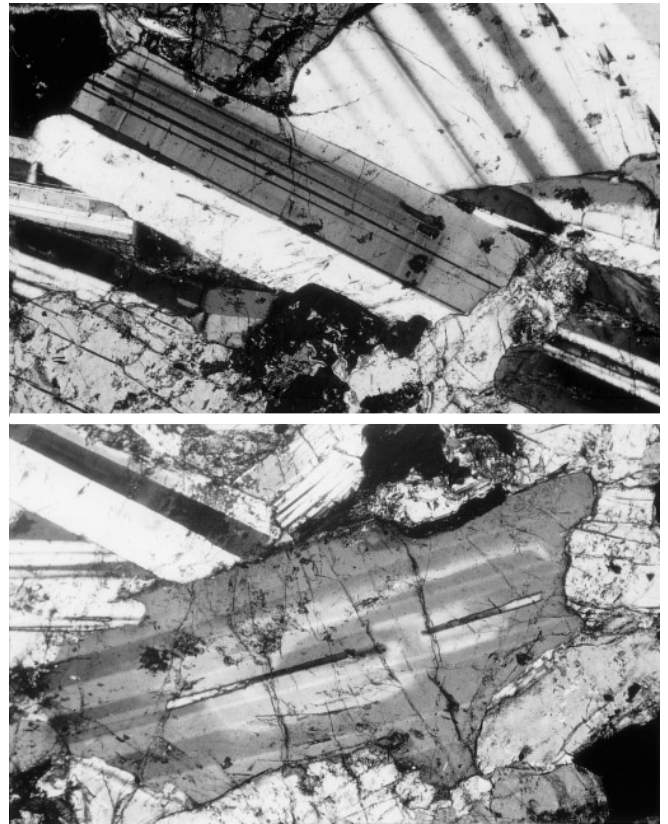
800°C, and within a few years at 500°C. Nearly complete exchange occurs within several years at 800°C, a reasonable temperature for the early post–magmatic stages of meteoric–hydrothermal circulation (Bird et al., 1988b). These results are consistent with the inference that primary intergranular hornblende could not have retained its original hydrogen during the alteration event. In contrast, the relatively high $\delta^{18}O$ values for hornblende indicate that it *was* resistant to *oxygen* exchange, presumably because oxygen self–diffusion is several orders of magnitude slower than hydrogen self–diffusion in amphiboles (Graham et al. 1984; Farver and Giletti 1985).

Compared to the intergranular hornblende, the pegmatitic hornblende and phlogopite could have been more resistant to hydrogen exchange due to their much larger grain sizes. This might explain some of the variations in measured δD values. The pegmatitic crystals tend to have slightly higher δD values than the intergranular crystals, despite being otherwise similar in composition (Table 2; Fig. 8). If the magma had
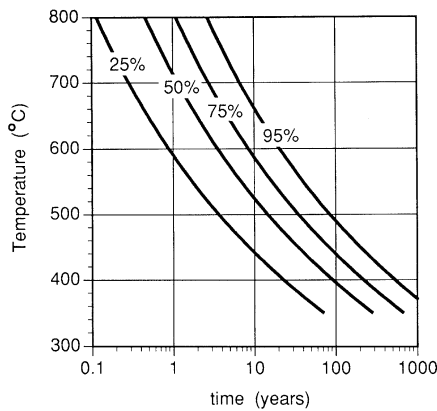
Fig. 7 Time required to achieve various amounts of hydrogen isotope exchange between hornblende and water. The labels on the curves refer to the fraction of hydrogen exchanged in a 0.4 mm grain of hornblende, assuming all diffusion occurs parallel to the c–axis (i.e. the hornblende grain is modeled as an infinite plate 0.4 mm thick). Curves are calculated from Figure 4.6 of Crank (1975), using the self–diffusion coefficients of Graham et al. (1984) and assuming that the water is an infinite reservoir of hydrogen. Experimentally measured diffusion coefficients (D) were extrapolated to 800° C by assuming a linear relationship between log D and $1/T$.

a higher δD value than later hydrothermal fluids, then greater retention of magmatic hydrogen in the pegmatitic crystals might account for some of the measured isotopic variation. Such a grain size effect could have been partially offset, however, by the presence of permeable microfractures within mineral grains (Fig. 9). Also, some of the isotopic variability might simply reflect localized variations in fluid composition or final isotopic equilibration temperature.

Despite such uncertainties, the low δD values indicate that *most* hydrogen in *all* of the igneous minerals was derived ultimately from the regional meteoric water. Partial melting of altered metabasalt, or assimilation of altered crust, could have produced low–δD magmas from which low–δD minerals crystallized. Subsolidus isotopic exchange with meteoric–hydrothermal fluids was probably ubiquitous, and would likewise have produced low (though not necessarily identical) δD values. It is possible that some igneous minerals crystallized with low primary δD values, and changed isotopic composition only slightly during subsolidus isotopic re–equilibration.

δD values in other parts of the Kap Edvard Holm Complex

Hydrogen and oxygen isotope compositions of secondary minerals in other parts of the Kap Edvard Holm complex have been measured by Fehlhaber and Bird (1991), Brandriss (1993), and Nevle et al. (1994). These studies have shown that the complex was affected by more than one major hydrothermal event.
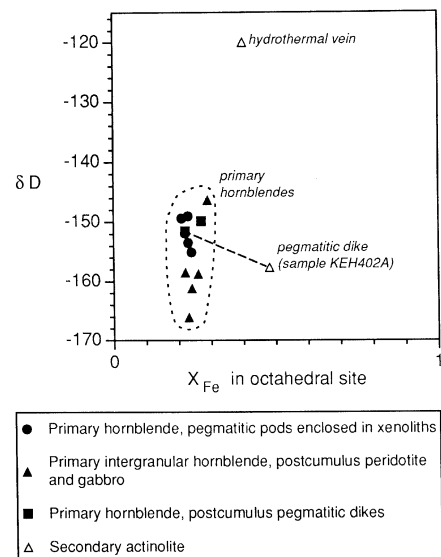

Fig. 8 Values of δD plotted against the mole fraction of octahedral sites occupied by iron (both Fe^{+2} and Fe^{+3}) for amphibole samples from Stand and Deliver Nunatak. The *dashed line* joins secondary actinolite and primary hornblende that were separated from a single hand sample. The δD value for the vein–filling actinolite was calculated from analyses of actinolite–epidote mixtures (see text). Values of X_{Fe} were calculated from the averages of multiple electron microprobe analyses (representative analyses are presented in Table 2). No attempt was made to estimate the proportions of Fe^{+2} and Fe^{+3}
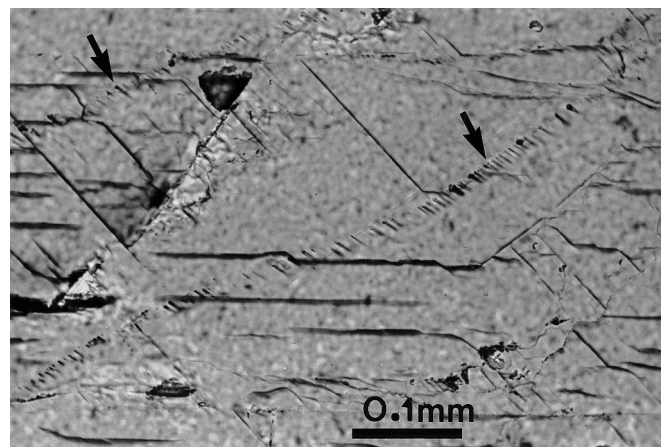

Fig. 9 Trains of tubular fluid inclusions (*arrows*) in a single crystal of hornblende, revealing the locations of healed microfractures (pegmatitic dike, sample KEH402A; see also Fig. 4D)

Near the northeastern margin of the complex, the gabbros were thoroughly recrystallized during a contact metamorphic event caused by emplacement of the Hutchinson Glacier syenite intrusions (Fig. 3). Within a few hundred meters of the contacts the gabbros contain secondary hornblendes with δD values between -125 and $-123\%_0$ (Nevle et al. 1994). These

hornblendes have Ar–Ar ages of 42 Ma (Nevle et al. 1994). and are therefore younger than the ~ 50 Ma hornblendes of Stand and Deliver Nunatak. The δD values in the syenite aureoles thus reflect alteration by meteoric waters that were younger and isotopically heavier than those which left their signatures at Stand and Deliver Nunatak. This younger hydrothermal system may also account for the δD value of $-131\%_0$ reported by Fehlhaber and Bird (1991) for an actinolite in altered gabbro several kilometers from the syenite contact.

Several samples have also been analyzed from Contact Nunatak, located near the northwestern corner of the complex (Fig. 3; Brandriss 1993). A sample of actinolite lining a vug in gabbro had a δD value of $-143\%_0$ and a $\delta^{18}O$ value of $+4.0\%_0$. Phlogopite in a pegmatitic pod from a xenolith in a nearby outcrop had a δD value of $-128\%_0$. These δD values are higher than those of similar minerals at Stand and Deliver Nunatak, and might record the effects of a younger meteoric–hydrothermal system associated with emplacement of syenites a few hundred meters east of the sample locality (Fig. 3). These syenites intruded and brecciated the layered gabbros over an exposed area of tens of square kilometers (Abbott and Deer 1972).

In summary, most hydrous minerals from the northern parts of the Kap Edvard Holm Complex have δD values that are higher than those of minerals at Stand and Deliver Nunatak. Many of these higher δD values, and perhaps all of them, can be attributed to alteration of the gabbros by meteoric–hydrothermal systems associated with younger syenitic intrusions. It is possible that the similarly high δD values of minerals from the epidote–actinolite vein at Stand and Deliver Nunatak (sample KEH259E) might reflect very localized alteration along a vein system associated with these younger hydrothermal events.

Early Tertiary meteoric water compositions

Rocks from Stand and Deliver Nunatak interacted with Eocene meteoric waters that were isotopically lighter than any early Tertiary meteoric waters previously inferred for the North Atlantic Tertiary Igneous Province. The hydrothermal system was supplied with meteoric water that had a δD value of $-110 \pm 10\%$; δD values of -100 to $-85\%_0$ have been calculated for meteoric waters in early Tertiary hydrothermal systems associated with the Skaergaard and Lilloise intrusions in eastern Greenland, and the Skye intrusive center in northwestern Scotland (Forester and Taylor 1977; Sheppard et al. 1977; Taylor and Forester 1979). In all of these studies, the δD values of meteoric waters were calculated from the hydrogen isotope compositions of secondary minerals in altered rocks. When the δD values of minerals are compared directly (Fig. 10), the differences between Stand and Deliver Nunatak and
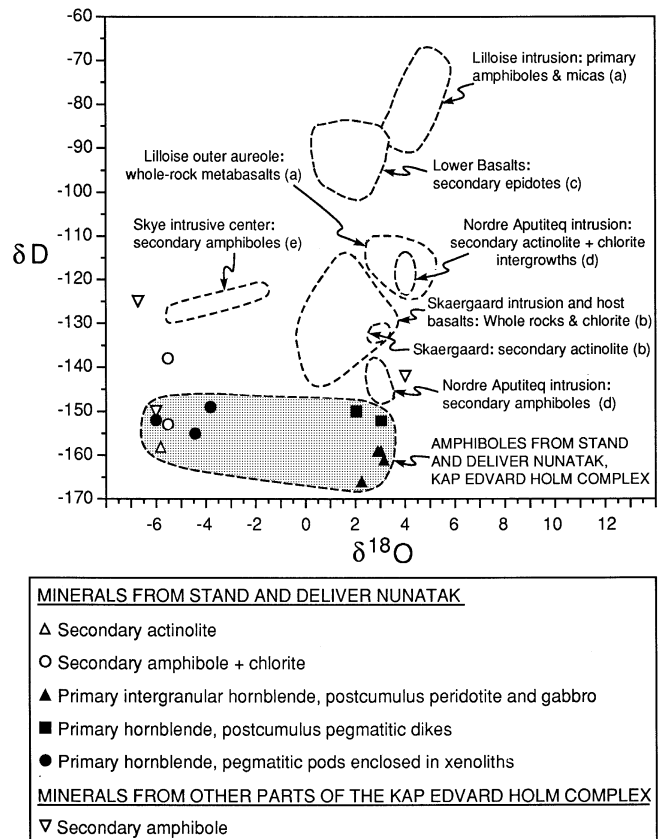

Fig. 10 Hydrogen and oxygen isotope compositions of rocks and minerals from early Tertiary lavas and intrusions in East Greenland and Scotland. Data for Stand and Deliver Nunatak are from this study. Data for other samples from the Kap Edvard Holm Complex are from Fehlhaber and Bird (1991), Brandriss (1993), and Nevle et al. (1994). Sources of other data are: (a) Sheppard et al. 1977, (b) Taylor and Forester 1979, (c) D.K. Bird, unpublished data, (d) Rose 1989, (e) Forester and Taylor (1977)

the other intrusions (up to $60\%_0$ for amphibole) are seen to be even greater than the differences in calculated meteoric water compositions. Thus, if the same assumptions are used to calculate isotopic fractionations between minerals and water in all of the different intrusions, then the contrast between calculated meteoric water compositions is even greater than that inferred from published estimates.

The anomalously low δD values of the Eocene meteoric waters at Stand and Deliver Nunatak might be related to the development of a regional topographic anomaly at around the time that the gabbros were emplaced and the hydrothermal system was active. Brooks (1979) and Gleadow and Brooks (1979) postulated that the Kangerdlugssuaq area was uplifted about 50 million years ago, forming a structural dome several hundred kilometers in diameter with a maximum uplift of about 6.5 km at the center. Their postulated age for the doming event is similar to the $^{40}Ar/^{39}Ar$ ages of 49–50 Ma measured for low–δD hornblendes from Stand and Deliver Nunatak (Nevle et al. 1994). The

Kap Edvard Holm complex is located on the flank of the postulated dome, with a cumulative uplift of about three or four kilometers projected for Stand and Deliver Nunatak (Brooks 1979, 1985). The isotopic compositions of meteoric waters are known to vary dramatically with altitude, with δD values typically decreasing by about 1.5–4.0‰ per 100 m increase in elevation (Dansgaard 1964; Yurtsever and Gat 1981). If the recharge area of the hydrothermal system were uplifted by several kilometers, then the elevation change could easily account for the low δD values of meteoric–hydrothermal waters at Stand and Deliver Nunatak (Nevle et al. 1994). Isotopic variations in this exhumed pluton thus appear to provide information on localized climatic variations during the early Tertiary tectonic evolution of the North Atlantic ocean basin.

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