

Oxygen isotope evidence for short-lived high-temperature fluid flow in the lower oceanic crust at fast-spreading ridges

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Abstract

Millimeter-scale amphibole veins in the lower oceanic crust record fracture-controlled fluid flow at high-temperatures but the importance of this fluid flow for the thermal and chemical evolution of the lower oceanic crust is unclear. In the section of lower oceanic crust recovered at Hess Deep from ODP Hole 894G, which formed at the fast-spreading East Pacific Rise, these veins are randomly distributed with an average spacing of ~1 m. We unravel the history of fluid flow through one of these veins by combining *in situ* O-isotope analyses of wall-rock plagioclase with major element analyses, geothermometry and diffusion modeling. Thermometry indicates vein sealing by amphibole at ~720 °C over a narrow temperature interval (± 20 °C). *In situ* O-isotope analyses by ion microprobe, with a precision of <0.5‰, reveal zoning of O-isotopes in plagioclase adjacent to the vein. The zoning profiles can be reproduced using a diffusion model if the duration of O-isotope exchange was ≤ 100 yr. A similar interval of fluid–rock exchange is suggested by modeling potassium depletion in plagioclase adjacent to the vein. If representative of fracture controlled fluid flow in the lower oceanic crust the limited duration of fluid flow, and its occurrence over a narrow temperature interval, suggest that high-temperature fluid flow in this porosity network does not transport significant heat.

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1. Introduction

Hydrothermal circulation at mid-ocean ridges profoundly modifies the composition of both the oceanic

crust and seawater, plays a critical role in controlling the magmatic and tectonic processes involved in crustal accretion, and is responsible for the formation of metal-sulphide deposits. Most studies of hydrothermal circulation at mid-ocean ridges have focused on the upper crust (lavas and dikes) while the lower (plutonic) crust has received less attention. However, the larger mass of the lower crust (approximately double), and the intimate linkages between processes operating in different portions of the crust, suggest that fluid flow in the lower crust needs to be understood.

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Hydrothermal circulation in the lower crust at fast-spreading ridges has started to be more closely scrutinized in recent years. This is largely because geophysical data suggests that the lower crust is, at least in some places, cooler in the near-axis region than is predicted by thermal models that do not include hydrothermal circulation in the lower crust (Dunn et al., 2000; Crawford and Webb, 2002). If true, this requires some form of hydrothermal cooling. The only area of the modern oceans where the hydrothermal alteration of lower crust formed at a fast-spreading ridge has been studied is at Hess Deep (Gillis et al., 1993; Gillis, 1995; Agrinier et al., 1995; Manning and MacLeod, 1996; Manning et al., 1996a; Lecuyer and Gruau, 1996; Fruh-Green et al., 1996; Weston, 1998; Coogan et al., 2002a). These studies are complemented by studies from the Oman ophiolite (Gregory and Taylor, 1981; Stakes and Taylor, 1992; Manning et al., 2000; Nicolas et al., 2003; Bosch et al., 2004; Coogan et al., 2006) although the hydrothermal alteration of this ophiolite clearly differs in detail from that of modern oceanic crust (Gillis and Banerjee, 2000). These studies have led to a wide range of models for the role of fluid flow in the lower crust. These range from the existence of very high-temperature fluid flow (>900 °C) distributed in mm-scale fractures with large enough fluid fluxes to lead to significant cooling of the lower crust (Nicolas et al., 2003; Bosch et al., 2004) through to very limited distributed fluid flow with little thermal impact (Manning et al., 1996a, 2000). Alternatively, it has been suggested that most fluid flow in the lower crust is focused in fault zones (Coogan et al., 2006) rather than being evenly distributed through the crust.

To develop a quantitative understanding of the thermal and chemical consequences of fluid flow under amphibolite-facies conditions, we need to know the distribution of fluid-flow channelways, how long these are open, what the fluid flux/es are and the rates and mechanisms of chemical exchange between the fluid and wall-rock. In combination with quantifying the cooling rate within the crust (Coogan et al., 2002b; John et al., 2004; Coogan et al., in revision), and the temperature interval of fluid flow (Manning et al., 1996a, 2000) these data will allow the relative roles of conductive and advective cooling to be better understood.

The most distinctive fingerprint of amphibolite-facies fluid flow in samples of the lower oceanic crust is the existence of amphibole veins, which occur on a range of scales from grain-boundary microfracture networks with very limited wall-rock haloes to macroscopic millimeter-scale vein arrays with broader vein haloes. Microfractures are widespread; these are

~ 20 μm wide on average and can rarely be traced across more than five igneous crystals in thin section (Manning and MacLeod, 1996). Macroscopic veins are typically ~ 1 mm wide but range in width both within an individual vein and between veins. Because macroscopic veins are much wider (~ 50 times) and much more continuous (extending for many meters in outcrop in ophiolites), we expect that fluid flow through these leads to greater heat and mass fluxes than fluid flow in microcracks.

The present work describes the results of a study of macroscopic amphibole veins in gabbros from Hess Deep, which were recovered during ODP Leg 147 (Hole 894G). We characterize the distribution and abundance of amphibole veins, the temperature over which they were sealed and the duration of the fluid-flow event. In combination, the results provide quantitative constraints on the capacity of amphibolite-facies fluid flow in this permeability network to contribute to heat transport in the lower oceanic crust near the ridge axis.

1.1. Geologic background

The Hess Deep submarine rift valley ($101^{\circ}30'$ W, $2^{\circ}15'$ N) lies in ~ 1 m.y.-old East Pacific Rise (EPR) crust. It occurs at the western termination of the Cocos–Nazca spreading center, ~ 50 – 100 km east of the present EPR axis (Lonsdale, 1988; Francheteau et al., 1990). A disrupted section of EPR crust, including pillow lavas, sheeted dikes, gabbroic rocks and ultramafic rocks, is exposed in horst blocks and on the rift valley walls providing a window into the lower oceanic crust. The rocks exposed at Hess Deep formed at the EPR at an inferred half spreading rate of 65 mm yr^{-1} (Francheteau et al., 1990).

Ocean Drilling Program Hole 894G penetrated 154.5 m of upper gabbros with 35% recovery (gabbro, gabbro-norite, and olivine gabbro-norite; (Gillis et al., 1993; Pedersen et al., 1996). Initial metamorphism of the plutonic rocks recovered from Hess Deep occurred in the amphibolite facies (Gillis, 1995) and was associated with a microfracture network filled by calcic amphibole (Manning and MacLeod, 1996). Macroscopic fractures filled by calcic amphibole generally crosscut the microscopic veins, but contain identical minerals. Later vein types are macroscopic chlorite-bearing veins and zeolite–calcite veins. The microscopic and macroscopic amphibole veins record brittle deformation and metamorphism associated with near-ridge fracturing and hydrothermal activity. In contrast, chlorite-bearing and zeolite–calcite veins record deformation and fluid flow during later, unrelated, interaction with the Cocos–

Nazca spreading center (i.e. atypical of the EPR and not considered further here; (Manning and MacLeod, 1996). Amphibole–plagioclase thermometry has been used to infer that fluid flow associated with the microfracturing that occurred over a ≤ 60 °C temperature interval centered at ~ 715 °C; comparison of this temperature range with thermal models suggests that amphibolite facies fluid flow lasted ≤ 6000 yr (Manning et al., 1996a).

Previous O-isotope studies have shown that the upper gabbros are only slightly depleted in ^{18}O (average bulk-rock $\delta^{18}\text{O} \sim 4.9\text{‰}$) relative to fresh MORB ($\delta^{18}\text{O} \sim 5.7\text{‰}$), and samples from deeper in the crust show even less modification of their O-isotope composition (Agrinier et al., 1995; Lecuyer and Gruau, 1996). Plagioclase is generally more depleted in ^{18}O than coexisting pyroxene suggesting a kinetic control on O-isotope exchange between fluid and rock (Lecuyer and Gruau, 1996). A single analysis of amphibole separated from an amphibole vein has a $\delta^{18}\text{O}$ of 3.0‰ (Fruh-Green et al., 1996) which, if it formed at ~ 700 °C, would have been in equilibrium with a fluid with a $\delta^{18}\text{O} \sim 5\text{‰}$.

2. Methods

2.1. Vein distributions

Manning et al. (1996b) report vein distributions in the core from ODP Hole 894G. From this data set, we extracted amphibole vein locations, and recalculated locations in the core by multiplying depth to vein in curated core by the ratio of recovered core to curated core for each core interval. This procedure gives vein positions and abundances in the material actually recovered, which is assumed to be representative of the depth interval that was drilled (154.5 m). The upper 2.7 m of recovered material (Cores 1R-1 to 2R-2) was ignored because it is dominated by a late diabase dike; wash cores were also ignored. Because the overall recovery in this Hole was $\sim 35\%$, this approach is inherently uncertain. Therefore we also present for comparison new amphibole vein-distribution data from the Oman ophiolite, where continuous exposure admits no such uncertainty.

2.2. Petrologic and isotopic studies

We examined a thin section of sample ODP 147-894G-4R2-07 30–40 cm (ODP Leg 147) from the intra-rift ridge at Hess Deep (Gillis et al., 1993). This sample displays amphibolite-facies alteration associated with both microscopic and macroscopic amphibole veins (Fig. 1).

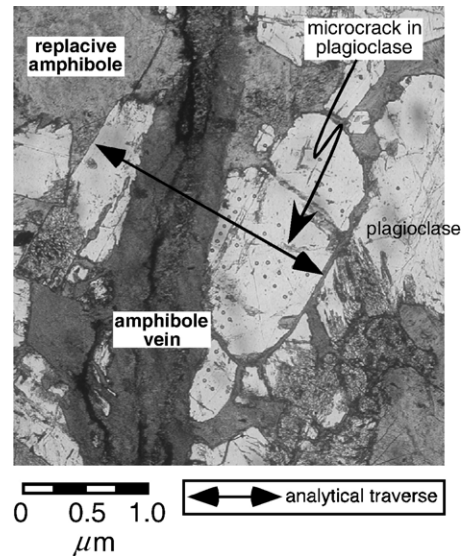


Fig. 1. Photomicrograph of the region of the amphibole vein in sample ODP 147 894G 4R2-07 studied. The plagioclase crystal to the left of the traverse has ragged grain boundaries against the amphibole vein suggesting dissolution along its margin. Note the small fracture within the main plagioclase crystal running horizontally through the image. Small spots in plagioclase are ion microprobe analyses from an aborted attempt to undertake this project using a Cameca 4f ion microprobe. Pits from the Cameca 1270 analyses reported here are too small to see. Further images of the sample are available in the supplementary data in the Appendix.

Major-element analyses were performed on a JEOL 8600S electron microprobe (University of Leicester), using standard operating conditions of 15 kV, 30 nA beam current, and 20 s counting times on peak and background for all elements except K, for which 60 s counting times were used to improve precision.

In situ O-isotope analyses by ion microprobe were conducted on the same sample. Two recent studies of continental hydrothermal systems have used *in situ* analysis of O-isotopes in plagioclase adjacent to paleo-fluid-flow conduits to constrain the duration of paleo-fluid-flow events (Mora et al., 1999; Cole et al., 2004). Because of the large difference between the oxygen-isotopic composition of meteoric water and most rocks relatively large isotopic gradients have been observed ($\sim 15\text{‰}$; (Mora et al., 1999; Cole et al., 2004)) and thus high precision has not been a prerequisite for these studies. In contrast, in high-temperature oceanic hydrothermal systems the expected changes in mineral O-isotope compositions are relatively small (a few per mil) and thus high precision analysis was crucial for this study.

We undertook high-precision, *in situ* O-isotope analysis of plagioclase using the Cameca 1270 ion

microprobe at The University of Edinburgh. Analyses of ^{18}O and ^{16}O were made simultaneously on Faraday Cups for a total of 40 s after ~ 2 min pre-sputtering. Count rates were equivalent to $\sim 10^6$ and $\sim 10^9$ counts per second respectively. An energy window of 40 eV was used with no energy filtering.

Seven in-house plagioclase standards of known O-isotope composition (from conventional analysis) were used to calibrate the instrumental mass fractionation and its variation with plagioclase major-element composition. Fig. 2 shows that the variation of instrumental mass fractionation between albite and anorthite is $\sim 4\%$ — much smaller than the variation observed in Fe-bearing solid solutions (e.g. Eiler et al., 1997). This instrumental mass fractionation was used to calculate the true $\delta^{18}\text{O}$ of each spot analysed based on subsequent measurement of the major element composition of the plagioclase.

During the course of acquiring the O-isotope data replicate analyses of plagioclase standards showed no drift and thus no drift corrections were applied (all data are presented in the supplementary data in the Appendix). The standard deviation of the difference between measured values for the standards and the bulk value measured by conventional methods is 0.5‰. This likely combines both instrumental imprecision and heterogeneity of the plagioclase crystals used as standards, and is therefore interpreted to be an upper

limit of analysis precision. Counting statistics give an average precision of $\pm 0.3\%$ providing a lower limit on the analytical precision. All data are presented relative to SMOW.

3. Results

3.1. Spatial distribution of amphibole veins

The distribution of fluid-flow conduits (e.g. fractures) is expected to play an important role in controlling the heat and mass fluxes associated with fluid flow. Around each fracture, mass can be exchanged between the rock and fluid over limited distances such that reaction haloes form; these are likely to be of different widths for different elements and may be strictly chemical or may be mineralogical too. These haloes slow fluid–rock reaction as they grow. Thus, if fractures are small and evenly distributed then the haloes are least likely to overlap and the mass flux is expected to be maximized (Manning, 1994). If fractures are highly clustered, or fluid flow is channelized, then the mass flux is likely to be minimized due to common overlap of reaction haloes. Heat transport is similar, with heat having to be conducted through impermeable rock towards cooled fractures; again, the shorter the diffusion distance the more extensive the heat exchange. However, on small-scale (e.g., ~ 1 m for a 1 yr fluid-flow event) thermal diffusion is sufficiently rapid that there will be little difference in temperature throughout the rock mass through which fluid is flowing.

We examined the spatial distribution of amphibole veins in Hess Deep gabbros recovered in ODP Hole 894G. As in previous studies of the distribution of veins in the oceanic crust (Manning, 1994; Magde et al., 1995) we constructed a linear traverse by stacking measurements from the archived cores (Cores 147-894G-2R3 through 20R1; Gillis et al., 1993). This contains 43 amphibole veins (Manning et al., 1996b). We then recorded locations of the veins, divided the traverse into bins of constant size (r) and counted the number of bins (N) that contain one or more amphibole veins. This procedure was repeated for r ranging from 0.2 to 10 m.

The average density of amphibole veins is $\sim 1\text{ m}^{-1}$, with widths typically ~ 1 mm. For comparison, the average spacing of amphibole veins in the sheeted dike complex drilled at ODP Hole 504B is 9 cm (Manning, 1994) and in the gabbroic rocks drilled at drilled at ODP Hole 735B (Southwest Indian Ridge) the average spacing of amphibole veins ranges from 5 cm in the uppermost part of the core to >2.5 m at 500 m depth (Magde et al., 1995). Fig. 3 shows the results of the

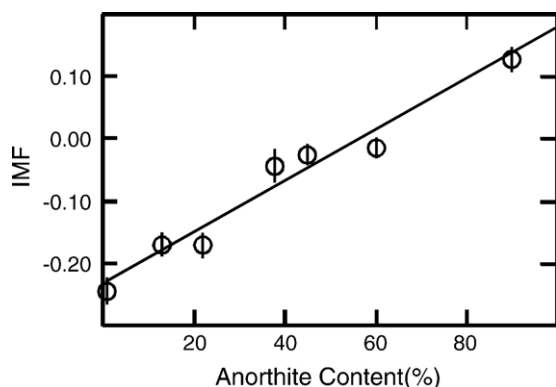


Fig. 2. Instrumental mass fractionation (IMF) as a function of plagioclase major element composition. This is equivalent to $\sim 4\%$ IMF between albite and anorthite. $\text{IMF} = 100 * [((^{18}\text{O}/^{16}\text{O})_{\text{measured}}) - ((^{18}\text{O}/^{16}\text{O})_{\text{true}})] / ((^{18}\text{O}/^{16}\text{O})_{\text{true}})$. Uncertainties in the IMF are shown as the standard error of the mean IMF from between 5 and 15 analyses of each standard. The plagioclase standards are: Amelia albite (An1; $\delta^{18}\text{O} = 10.75$); Ontario feldspar — Harker collection (An13; $\delta^{18}\text{O} = 14.27$); Hawks mice mine (An22; $\delta^{18}\text{O} = 6.72$); Tanzania anorthosite — Harker collection (An38; $\delta^{18}\text{O} = 6.02$); Marcy anorthosite (An45; $\delta^{18}\text{O} = 9.4$); Sierra Leone — Harker collection (An60; $\delta^{18}\text{O} = 6.28$); Mikajima — Japan (An90; $\delta^{18}\text{O} = 6.25$). Conventional analysis was standardized against the UWG-2 standard described by Valley et al. (1995).

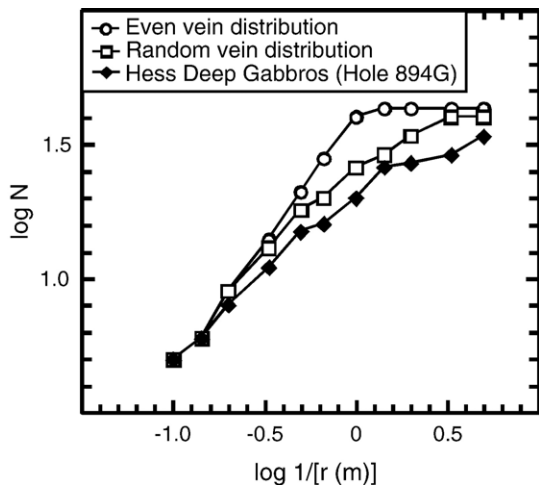


Fig. 3. Measured spatial distribution of 43 amphibole veins in Hole 894G (ODP Leg 147), plotted in terms of $\log(1/r)$ versus $\log(N)$ where r is the bin size and N is the number of bins that contain one or more amphibole veins (see text). Amphibole vein data were taken from Manning et al. (1996b). Also shown are models for both a random and an even vein distribution for the same number of veins existing in the same transect length (43.67 m).

analysis of amphibole vein distribution. The data show that $\log N$ increases nonlinearly with increasing $\log 1/r$ (i.e., decreasing bin size), indicating non-fractal clustering (Manning, 1994). The array is more similar to a random distribution than to an even distribution. However, the smaller number of bins containing at least one amphibole vein for a given bin size compared to a random distribution indicates that veins are somewhat clustered. Similar results have been obtained in linear traverses in the plutonic complex of the Oman ophiolite, where the vein distribution is almost completely random, indicating that uncertainties due to lack of recovery has not significantly biased this analysis (see the supplementary data in the Appendix).

For a given fluid flux and duration of fluid flow the slightly clustered distribution of amphibole veins suggest that fluid flow in this permeability network at amphibolite-facies conditions was less efficient at transporting mass than if veins were evenly distributed. Further, the large average separation of veins suggests that fluid flow through these veins transported mass less efficiently than fluid flow in areas where the average vein spacing is smaller (e.g. the upper portion of ODP Hole 735B). Nevertheless it is possible that the fluid flow through these fractures could have led to significant heat and mass fluxes if the fractures remained open for long times and/or carried large fluid fluxes. This possibility cannot be evaluated by vein

distribution data; rather, it requires information on temperatures and reaction durations, as described below.

3.2. Petrology and geochemistry of amphibole veins and their haloes

The approach used here to understand the duration of fluid flow associated with amphibole vein formation, and the mechanism of fluid–rock exchange, is to study a single vein in detail rather than to examine a large number of veins in less detail. The size and major element composition of the vein are representative of others as is its formation temperature. The advantage of this approach is that a better understanding of the veins history can be developed. However, there is always the possibility that the vein is not representative, which will only become apparent through further study using the methodology developed here.

The amphibole vein in sample ODP147-894G-4R2-07 30–40 cm varies in width between ~ 500 and $800 \mu\text{m}$ (Fig. 1) typical of the amphibole veins in this drill core (Manning and MacLeod, 1996); it is surrounded by a much wider zone (~ 6 mm) in which all mafic phases have been replaced by amphibole and in which there are also some smaller amphibole veins. Partial replacement of the mafic phases by amphibole extends out of the area of the thin section. The vein comes from the upper portion of the drill core where the density of amphibole veins is somewhat higher than at deeper levels.

Plagioclase is also partially replaced by amphibole in some areas, commonly having ragged grain boundaries indicative of dissolution. In other areas it is replaced by hydrothermal plagioclase that can be either more (An_{70-82}) or less (An_{10-12}) calcic than the magmatic plagioclase (An_{50-65}). This hydrothermal plagioclase is significantly depleted in Fe (~ 0.08 versus ~ 0.5 wt.% FeO) and Mg (~ 0 versus ~ 0.04 wt.% MgO) compared to magmatic plagioclase.

In places magmatic plagioclase is preserved adjacent to the amphibole vein (Fig. 1). An electron-microprobe traverse through a plagioclase crystal adjacent to the amphibole vein shows that the anorthite content of plagioclase is within the magmatic range of values (Fig. 4). The plagioclase Fe and Mg concentrations are also within the magmatic ranges (0.45 to 0.65 wt.% FeO and 0.03–0.07 wt.% MgO). This suggests that the plagioclase did not undergo dissolution–reprecipitation reaction during fluid flow. Potassium, in contrast, is depleted adjacent to the amphibole vein (Fig. 4) from a magmatic value of ~ 0.07 wt.% K_2O to ~ 0.03 wt.% K_2O at the edge of the vein. A similar depletion of K in plagioclase is also observed adjacent to a small

amphibole crystal lining a fracture within plagioclase and around an inclusion-rich area of plagioclase (area A in Fig. 4). This is interpreted as principally reflecting

diffusive loss of K into the fluid during the fluid-flow event that formed the amphibole vein.

Amphibole compositions in the vein show a narrow range in composition. The mean composition corresponds to magnesiohornblende (Leake et al., 1997), with a mean Mg mole fraction of 0.64, and atom abundances (relative to 23 O) of $^{IV}Al=0.81$, $Na_B=0.03$, and $(Na+K)_A=0.30$. This compositional range lies within the field defined by amphiboles of the micro-fracture network (Manning and MacLeod, 1996; Manning et al., 1996a, 2000). Fig. 4 shows a compositional profile for aluminium and potassium through the amphibole vein. Calcium, Mg and Fe show smaller relative and absolute variations in abundance than aluminium. Two points should be noted. Firstly, although there are compositional variations, there is no evidence of multiple episodes of vein opening with sharp steps in the amphibole composition; however, the possibility of multiple stages of amphibole growth under similar conditions cannot be discounted. Secondly, there is no zoning of K in the amphibole vein. This suggests that the depletion of K in plagioclase is not due to exchange with the adjacent amphibole after amphibole growth. The only way this could be the case is if K diffusion in amphibole is significantly more rapid than in plagioclase allowing complete equilibration of the amphibole after plagioclase closed to exchange. The scatter in the K concentration in amphibole (Fig. 4) suggests that this is not the case or else these would have been smoothed out by diffusion.

3.3. Temperature of amphibole vein formation

Amphibole–plagioclase thermometry (Holland and Blundy, 1994) was used to determine the temperature at which the amphibole filling the vein crystallized. This gives an average temperature of $725 \text{ }^\circ\text{C} \pm 17 \text{ }^\circ\text{C}$ (1σ , $n=12$). Weston (1998) studied the temperature of

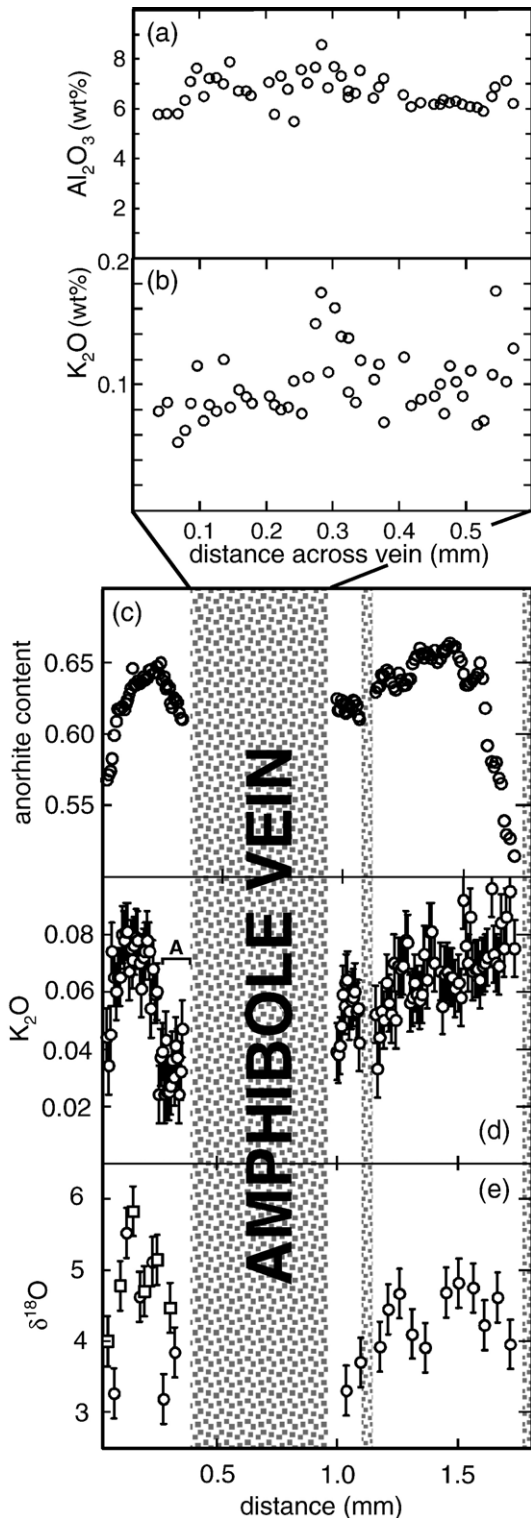


Fig. 4. Compositional zoning across the amphibole vein studied and the wall-rock plagioclase surrounding this (See Fig. 1 for the location of the analytical traverse). (a) Al_2O_3 in amphibole in the vein; (b) K_2O in amphibole in the vein. Note the lack of systematic variation in amphibole composition across the vein; (c) plagioclase anorthite content ($An=Ca/(Ca+Na)$) adjacent to the amphibole vein; (d) plagioclase K_2O adjacent to the amphibole vein. A = area of plagioclase containing many small inclusions which is depleted in potassium; (e) Oxygen isotope variation within plagioclase adjacent to the amphibole vein. The squares denote analyses made in a traverse in the opposite direction across the same plagioclase crystal (see Fig. A1 in the Appendix). Note the decrease in the plagioclase $\delta^{18}O$ adjacent to the main amphibole vein and at the margins against thin amphibole microcracks.

formation of the amphibole-filled micro-fracture network in this sample using the same approach and derived a temperature of $709 \text{ }^\circ\text{C} \pm 30 \text{ }^\circ\text{C}$ (1σ , $n=18$). The narrow range of temperatures implies that fluid flow occurred over a narrow temperature interval (Manning et al., 1996a, 2000). This temperature is representative of temperatures derived from amphibole–plagioclase thermometry for microscopic and macroscopic amphibole veins in the drill core (Manning et al., 1996a; Weston, 1998; Manning et al., 2000). In modeling fluid–rock interaction in the following sections we use a temperature of $720 \text{ }^\circ\text{C}$ as the temperature of amphibole formation in this sample. Below this temperature the permeability is assumed to have become clogged through amphibole precipitation because there is no evidence for lower temperature fluid–rock reaction. Of course, fluids that were not saturated with amphibole could have flowed through the rock at higher-temperatures (McCollom and Shock, 1998).

3.4. O-isotopes in plagioclase around amphibole veins

The O-isotopic composition of the magmatic plagioclase varies systematically away from the amphibole vein (Fig. 4). Adjacent to the vein, and the amphibole-lined grain boundaries along the opposite side of the plagioclase crystals, the plagioclase is depleted from a magmatic value of ~ 5.7 to $\sim 3\%$. The cores of the plagioclase on either side of the vein are less depleted, ranging from 4.5 to 6‰ (Fig. 4). The larger plagioclase crystal is also depleted in $\delta^{18}\text{O}$ in its core. This depletion is associated with a thin fracture along which the plagioclase is partially altered (Figs. 1 and 4). At temperatures of $700\text{--}750 \text{ }^\circ\text{C}$ the equilibrium plagioclase $\delta^{18}\text{O}$ value is slightly ($<1\%$) depleted relative to water (Zheng, 1993a; Matsuhisa et al., 1979). Thus, assuming that the observed depletion in $\delta^{18}\text{O}$ in plagioclase was caused by fluid–rock reaction, the fluid must have had a $\delta^{18}\text{O}$ of $\sim 4\%$ (i.e. significantly rock-buffered) to drive the rim composition of the plagioclase to $\sim 3\%$.

A possible explanation for the variation in $\delta^{18}\text{O}$ in plagioclase is retrograde diffusive exchange between plagioclase and amphibole, with no exchange between plagioclase and fluid. This model is inconsistent with the data in two respects. Firstly, this cannot explain the depletion of $\delta^{18}\text{O}$ in the core of the plagioclase crystal. Instead, if O was significantly mobile after fluid flow ceased then this depletion should have been erased by diffusion. However, this argument could be discounted if the ^{18}O depletion in the core of the plagioclase formed after the amphibole veins. Secondly, O-isotope

fractionation factors (Matsuhisa et al., 1979; Zheng, 1993a,b) show that during cooling ^{18}O will preferentially partition into the plagioclase relative to amphibole. This would lead to $\delta^{18}\text{O}$ -enriched rims on the plagioclase adjacent to the amphibole, not depleted rims as observed. Thus equilibrium growth and retrograde exchange is discounted.

An alternative explanation for the plagioclase O-isotope zoning is that the amphibole grew with low $\delta^{18}\text{O}$ (as observed in Fruh-Green et al., 1996), out of O-isotope exchange equilibrium with the adjacent plagioclase, followed by O-isotope exchange during cooling. To evaluate this possibility we have performed numerical models of this process. We assume that the amphibole initially has a $\delta^{18}\text{O}$ of 0 and the plagioclase has a $\delta^{18}\text{O}$ of 5.7. All parameters in the modeling were set so as to maximize the possible retrograde effects. Because the amphibole is made up of many small amphibole crystals we model O-diffusion in it as a combination of volume and grain boundary diffusion. Using the volume diffusion coefficient of Farver and Giletti (1985) the bulk diffusivity is calculated as (Hart, 1957):

$$D_{\text{bulk}} = \tau[(1 - a)D_{\text{vol}} + aD_{\text{gb}}] \quad (1)$$

where D_{bulk} = bulk diffusion coefficient, τ = tortuosity (here taken as 1), a = volume fraction grain boundaries (here taken as 0.0005 based on a grain size of $10 \text{ }\mu\text{m}$ and a grain boundary width of 5 nm), D_{vol} = volume diffusion coefficient, and D_{gb} = grain boundary diffusion coefficient which is here taken to be 1000 times D_{vol} . The plagioclase diffusion coefficient used in the models for ‘wet’ conditions is an average of the albite and anorthite diffusion coefficients determined by Giletti et al. (1978). The diffusion coefficient for plagioclase under ‘dry’ conditions is from Elphick et al. (1988). The temperature dependence of the equilibrium fractionation of O-isotopes between plagioclase and amphibole is taken from Zheng (1993a,b) assuming that the fractionation in plagioclase is linearly related to the An content (Ganguly, 1982). The hornblende fractionation factor of Zheng (1993b) is used for amphibole but empirical as well as theoretical data suggested that the fractionation factors for different amphibole compositions are similar (Kohn and Valley, 1998).

Using these input parameters explicit finite difference models (e.g., Crank, 1975) were run assuming an initial temperature of $720 \text{ }^\circ\text{C}$ and a cooling rate of $0.01 \text{ }^\circ\text{C yr}^{-1}$. This is based on the lower end of the cooling rates for the upper gabbros from fast-spreading ridges (Coogan et al., 2002b, in revision) in order to

maximize the potential for O-isotope exchange. These models demonstrate that retrograde exchange, assuming initial disequilibrium between plagioclase and amphibole, cannot explain the observations. Under ‘wet’ conditions O-diffusion in plagioclase is much more rapid than in amphibole (Giletti et al., 1978; Farver and Giletti, 1985) and thus the plagioclase internally homogenizes after amphibole closes to exchange (Fig. 5). This clearly did not occur since O-isotope zoning is preserved in plagioclase; i.e. the system must have been effectively ‘dry’ during cooling from 720 °C after amphibole sealed the rock. If exchange between amphibole and plagioclase occurred under ‘dry’ conditions O diffusion in plagioclase is too slow to lead to the extent of O-depletion observed (Fig. 5).

In summary, the observed variation in O-isotope composition in plagioclase requires O-isotope exchange between plagioclase and a fluid under hydrous conditions (where O-diffusion is rapid) followed by amphibole formation and then subsequent cooling under anhydrous conditions (where O-diffusion is slow). This change from ‘wet’ to ‘dry’ conditions is consistent with the lack of evidence for lower temperature fluid–rock reaction in this sample.

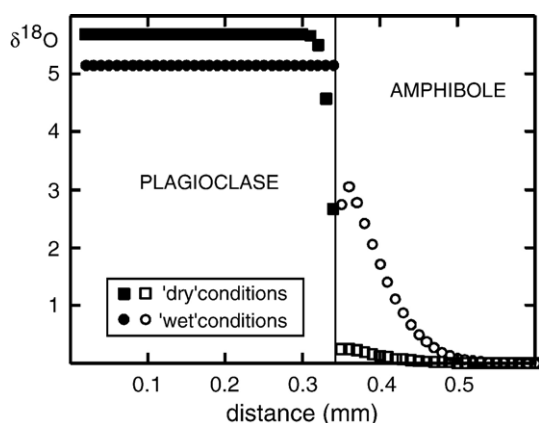


Fig. 5. Numerical models of retrograde O-isotope exchange between plagioclase and amphibole assuming that they were not initially in equilibrium. For simplicity half of the vein and one wall-rock plagioclase is modeled — the other side would be a mirror image. In the model the amphibole initially has a $\delta^{18}\text{O}$ of 0 and the plagioclase has a $\delta^{18}\text{O}$ of 5.7. Models using the ‘wet’ plagioclase diffusion coefficients show that O diffusion in plagioclase is sufficiently rapid that no heterogeneity in plagioclase $\delta^{18}\text{O}$ can be preserved during retrograde exchange. In contrast, models using the diffusion coefficient for O diffusion in plagioclase under ‘dry’ conditions show that diffusion is so slow under these conditions that very little retrograde exchange occurs. Neither model can explain the existence of zoning in $\delta^{18}\text{O}$ in plagioclase.

4. Constraining the duration of fluid flow from diffusion modelling

The duration of the fluid-flow event in which the amphibole vein formed can be estimated using the zoning in O-isotopes and K in plagioclase adjacent to the amphibole vein provided that their zoning was generated by diffusive exchange between the plagioclase and fluid. It is argued above that the lack of significant change of An content, Fe or Mg, in plagioclase adjacent to the amphibole vein indicate that the plagioclase adjacent to the vein was not completely dissolved and then re-precipitated. Based on this, and the relatively smooth zoning profiles, the observed K and ^{18}O depletion in plagioclase are modeled here assuming that they formed entirely due to diffusive exchange between the plagioclase and fluid. If other reaction mechanisms contribute to the exchange of these elements then the calculated durations of exchange based on diffusion models will be over-estimates; i.e. assuming diffusive exchange provides an upper limit on the duration of fluid–rock exchange. Additionally, if the analytical traverse is not perpendicular to the orientation of diffusion then the apparent length of the diffusion profile will be longer than the true length again leading to over-estimates of the duration of diffusive exchange.

The amphibole formed at ~ 720 °C which thus provides a lower limit on the temperature interval of fluid flow. This is a lower limit because amphibole precipitation sealed the system within a narrow temperature interval (Manning et al., 1996a) and fluid flow could have occurred at higher temperatures without amphibole formation. The upper temperature limit of fluid flow cannot be directly constrained. However, based on cooling rates in the upper gabbros formed at fast-spreading ridges of 0.01 to 0.1 °C yr⁻¹ (Coogan et al., 2002b, in revision) the initial temperature of fluid flow, and the duration of the fluid-flow event, can be constrained by numerically simulating the observed zoning profiles.

Depletion of K in plagioclase adjacent to amphibole is most readily modeled because the boundary conditions are simpler to constrain than for O-isotope exchange. Potassium is very soluble in high-temperature fluids and thus the edge of the plagioclase adjacent to amphibole is assumed to have a boundary condition of zero K imposed during fluid flow; i.e., at temperatures > 720 °C the edge of the plagioclase is set to have zero K assuming that K is completely dissolved into the fluid. At temperatures < 720 °C the plagioclase grain boundary is closed to K exchange assuming no exchange with the

adjacent amphibole. Once fluid flow is terminated at 720 °C the K distribution in plagioclase tends to homogenize somewhat allowing the surface K concentration to increase from zero. Giletti and Shanahan (1997) measured the diffusion coefficient of K in plagioclase and showed that it is independent of $P_{\text{H}_2\text{O}}$ and their Arrhenius relationship is used. We assume a cooling rate of 0.1 °C yr⁻¹ with this controlling the change in diffusion coefficient with time both during fluid flow and subsequently.

A series of explicit finite difference models (e.g., Crank, 1975) using these parameters were run with different initial temperatures to determine the initial temperature required to fit the data. An initial temperature of fluid–rock exchange of 730 °C fits most of the data reasonably (Fig. 6). This equates to 100 yr of fluid flow at this cooling rate. However, the fidelity of the zoning profile is too poor to constrain the timescale more accurately. Using slower cooling rates, but the same total duration of fluid flow (e.g. cooling from 721 °C to 720 °C at 0.01 °C yr⁻¹), leads to almost identical integrated K loss from the plagioclase. The only difference is that slower cooling leads to more

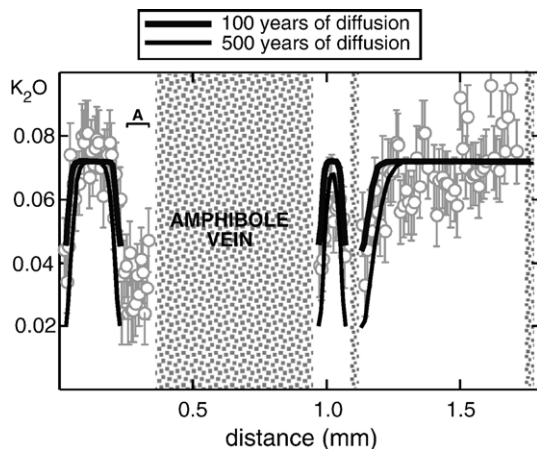


Fig. 6. Numerical model of the zoning in potassium concentration observed in plagioclase adjacent to the amphibole vein. Two models are shown, one for an initial temperature of fluid ingress of 770 °C (500 yr of diffusive exchange) and one for an initial temperature of fluid ingress of 730 °C (100 yr of diffusive exchange). The data precision is insufficient to resolve between these fluid–rock exchange durations. An initial K₂O concentration of 0.072 wt.% K₂O is used based on the measured K content of plagioclase away from the vein. The models assume a boundary condition of zero potassium at the vein between the temperature of fluid ingress and 720 °C at which point amphibole precipitation is assumed to close the plagioclase to further K exchange. Below this temperature the potassium distribution in plagioclase relaxes slightly. The area labeled “A” contains many small mineral inclusions and probably had many small cracks through it at some stage during the fluid-flow event potentially ‘pushing’ the boundary to which K diffused into the crystal.

relaxation of the diffusion profile during cooling from 720 °C. Faster cooling rates require a slightly shorter duration of fluid flow due to the faster diffusion coefficient at higher temperatures. For example, the extremely fast cooling rate of 1 °C yr⁻¹ only requires ~60 yr of fluid flow. More precise K data will be required to resolve the duration of fluid flow and cooling rate more precisely.

The lack of any depletion in K at the amphibole-line microcrack at one end of the analytical traverse (to the right of the profile as shown in Figs. 1, 4 and 6)) suggests that fluid–rock reaction here occurred over too short an interval for diffusive K-loss from plagioclase. This is consistent with a model in which the micro-crack permeability network was open for a shorter time interval than the macroscopic fractures.

Several factors lead to uncertainty in the calculated fluid-flow duration. Firstly, K exchange with the adjacent amphibole after the cessation of fluid flow could lead to some K loss from the plagioclase making 100 yr an over-estimate of the duration of fluid flow. Secondly, the short K diffusion profiles in plagioclase, and imprecision in the data, lead to uncertainty in fitting the zoning profiles. Thirdly, small amphibole (and other?) crystals within the plagioclase indicate that, in detail, diffusion was not the sole process operating.

The ~100 yr required for the K diffusion profiles to form does not require 100 yr of continuous fluid flow. Stagnant fluid may have filled the fractures provided that it could dissolve sufficient K to keep the K concentration at the edge of the plagioclase effectively zero. Alternatively, short-lived episodes of fluid flow may have stripped K from the rim of the plagioclase along the fractures. Interspersed ‘dry’ intervals would allow the K-diffusion profile to grow as the plagioclase internally homogenized.

The zoning in δ¹⁸O in plagioclase provides a complementary data set with which to constrain the duration of fluid flow. The rate of oxygen diffusion in plagioclase is dependent on the presence of water. Oxygen diffusion in plagioclase is fast under hydrous conditions and slow under anhydrous conditions (Giletti et al., 1978; Elphick et al., 1988). Unfortunately, the depletion in δ¹⁸O in the core of the larger plagioclase crystal, as well as at its rims (Fig. 4), complicates the modeling of these data. However, an upper bound on the extent of diffusive ¹⁸O loss to the edge of the crystal can be made by assuming that the depletion in the core of the crystal occurred later.

Using the same approach as used to model the K data we modeled the diffusive exchange of O-isotopes between plagioclase and fluid. We assumed that the edges

of the plagioclase crystals adjacent to the amphibole vein acquired the observed $\delta^{18}\text{O}$ value of 3‰ by reaction with the fluid during fluid flow. Diffusion at temperatures >720 °C was assumed to occur under hydrous conditions. Because O diffusion in plagioclase under anhydrous conditions at <720 °C is very slow, retrograde exchange with the amphibole is ignored (see above). Initial temperatures of fluid–rock reaction of between 721 °C and 730 °C fit the data (10 to 100 yr of exchange; Fig. 7).

Several factors complicate interpretation of the O-isotope data (Table 1). Firstly, as with the K profile, the asymmetry in the zoning of O in the larger plagioclase crystal shown in Fig. 7 is not expected by a simple diffusion model. Again, this can be explained by a shorter duration of fluid–rock reaction along micro-cracks (such as away from the vein at the right side of Fig. 7) than in the main vein. Secondly, the zoning in $\delta^{18}\text{O}$ in the smaller plagioclase crystal analysed occurs over much shorter distances than in the larger crystal (Fig. 7), apparently requiring shorter durations of O-isotope exchange. A plausible explanation for this observation is that dissolution of the edge of the plagioclase crystal removed part of an initially longer diffusion profile. This is supported by the ragged texture

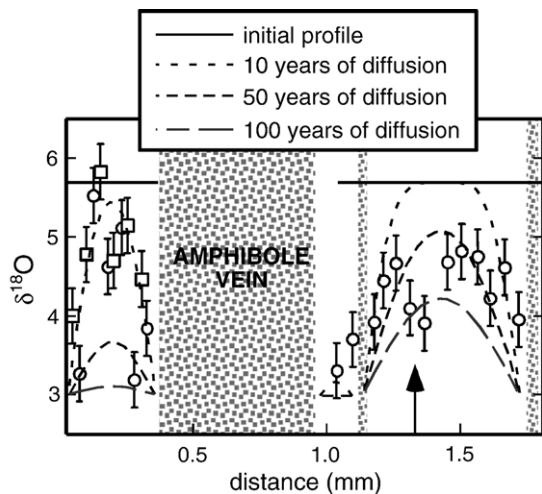


Fig. 7. Numerical model of the zoning of O-isotopes in plagioclase shown in Fig. 4. Three models are shown for fluid ingress at 730 °C (=100 yr of diffusion), 725 °C (50 yr of diffusion), and 721 °C (10 yr of diffusion). These all assume that the initial plagioclase $\delta^{18}\text{O}$ is 5.7‰, that the edge of the plagioclase is set to 3‰ during fluid flow, and a cooling rate of 0.1 °C yr^{-1} . Plagioclase diffusion rates are those for ‘wet’ conditions at temperatures >720 °C and for ‘dry’ conditions for lower temperature. The models span the range in the data reasonably well except the depletion in ^{18}O in the core of the larger plagioclase (two analyses above arrow head) that suggests some fluid flowed through a micro-crack here.

Table 1
O-isotope data

Distance along traverse (mm)	$\delta^{18}\text{O}$
0.03	4.0
0.05	3.3
0.08	4.8
0.11	5.5
0.14	5.8
0.16	4.6
0.18	4.7
0.22	5.1
0.24	5.1
0.26	3.2
0.29	4.5
0.31	3.8
1.03	3.3
1.09	3.7
1.17	3.9
1.20	4.4
1.25	4.7
1.30	4.1
1.35	3.9
1.44	4.7
1.49	4.8
1.56	4.7
1.60	4.2
1.66	4.6
1.71	4.0

at its margin (Fig. 1). Alternatively, the amphibole in the vein may have grown initially at this side suppressing further exchange with the fluid. Irrespective of these details, diffusive O-isotope exchange around the main vein cannot have occurred for more than ~ 100 yr and the data could be explained by an even shorter interval of fluid–rock reaction. Shorter durations of fluid–rock exchange are suggested for micro-fractures.

In summary, zoning in both O-isotopes and K adjacent to the macroscopic amphibole vein can be explained by fluid–rock exchange lasting ≤ 100 yr. Longer durations of fluid–rock exchange are inconsistent with the O-isotope data. Significantly shorter durations cannot be ruled out if either diffusion was not the only exchange mechanism or if healed microcracks allowed fluids to react more pervasively with the plagioclase.

5. Discussion

5.1. Duration of amphibolite facies fluid flow in mm-scale fractures

This study provides the first quantitative constraint on the duration of fluid flow through millimeter-scale

fractures under amphibolite-facies conditions in the lower oceanic crust. The methodology outlined should enable future studies to rapidly increase the number of veins for which we have such data.

Based on detailed study of an amphibole vein, and the plagioclase surrounding it, diffusive fluid–rock exchange occurred over an interval of ≤ 100 yr. Fluid flow in micro-cracks occurred over an even shorter time interval. The data do not require that fluid flow occurred continuously for this duration. Instead episodic fluid-flow events may have occurred; alternatively, a stagnant fluid may have filled the fracture for a portion of the time. During this time amphibole may or may not have been replacing clinopyroxene in the groundmass. However, as shown by McCollom and Shock (1998) there is no requirement for any secondary minerals to form during high-temperature fluid flow and geochemical tracers may be the only indicators that remain of this. The fluid became saturated with amphibole when temperature dropped to ~ 720 °C; at this point amphibole growth apparently filled the fractures sealing the rock.

Assuming that the replacive amphibole formed over the entire duration of fluid flow, and taking the upper estimate of the duration of fluid flow, a minimum ‘amphibole-forming’ reaction rate can be calculated. For individual mm-scale clinopyroxene crystals to be completely replaced by amphibole in ≤ 100 yr reaction rates must have been $\geq 5 \times 10^{-4}$ g cm $^{-2}$ yr $^{-1}$. This reaction rate is consistent with laboratory studies at ~ 700 °C (e.g. Wood and Walther, 1983).

5.2. Amphibolite facies fluid flow in the lower oceanic crust

Future studies are necessary to determine whether the duration of fluid flow determined here is representative of all veins in the upper gabbros at fast-spreading ridges and whether the duration of fluid flow changes with depth in the crust. Assuming that our results are representative of the duration of fluid flow in mm-scale fractures in the lower crust they have important implications for the cooling of the lower crust at fast-spreading ridges. The short duration of amphibolite facies fluid flow (≤ 100 yr), and the small temperature interval over which amphibole is precipitated (Manning et al., 1996a, 2000), suggest that amphibolite facies fluid flow in this permeability network is not efficient at removing heat from the lower oceanic crust. If this fluid flow efficiently removed heat from the crust then either: (i) the amphibole would form over a wide temperature interval, or (ii) fluid flow would be initiated at much

higher temperatures than amphibole vein precipitation. Hydrothermal amphibole forms over a relatively narrow temperature interval (Manning et al., 1996a) consistent with either a small temperature interval of fluid flow or amphibole becoming a stable phase over a small temperature interval. In the latter case there could be substantial fluid flow prior to amphibole becoming stable (McCollom and Shock, 1998). However, the short duration of fluid flow required by the zoning of K and O-isotopes in plagioclase indicates that this is not the case; instead, amphibolite-facies fluid flow occurred over a narrow temperature interval and short time interval, prior to amphibole growth. Thus, little heat was removed by this fluid-flow event.

Geophysical data suggest that, at least at some times and/or places, the lower crust at fast-spreading ridges is much cooler near the axis than it could be if it cooled conductively (Dunn et al., 2000; Crawford and Webb, 2002). If the missing heat cannot be removed by fluid flow in mm-scale fractures, as suggested by its very short duration and the limited temperature interval over which this occurred, then an alternative explanation is required. Taking the interpretation of a cool lower crust near the ridge axis (Dunn et al., 2000) at face value, the simplest explanation is that the missing heat is extracted by channelized fluid flow in the lower crust. In this model fluid flow would be focused in large channels, such as faults, as described in the Oman ophiolite (Coogan et al., 2006). High-permeability channels through which large fluid fluxes can be carried are likely to be associated with faults and will probably occur at irregular spacings leading to heterogeneous cooling of the lower oceanic crust in the near-axis environment. This is consistent with the asymmetric distribution of melt in the lower crust described by Crawford and Webb (2002); i.e. where there is a deeply penetrating fault fluid flow through it cools the lower crust and freezes any melt near the axis but where there are no faults a broader mush zone can exist.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2007.06.013](https://doi.org/10.1016/j.epsl.2007.06.013).

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