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LETTER

Mechanisms of Ar release from Himalayan metamorphic hornblende

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ABSTRACT

Changes in hornblende samples that occur during stepwise $^{39}Ar/^{40}Ar$ analysis were studied experimentally and mineralogically. A complex succession of reactions was seen (hornblende → oxyhornblende → clinopyroxene-structured phase → fine-grained reaction products → glasses) in the temperature range 750–1300 °C. The release of Ar from hornblende in the vacuum furnace appeared to occur by fundamentally different processes from those resulting in Ar loss during metamorphism. Simple diffusional interpretations of the release patterns are, therefore, not capable of revealing the thermal history of samples. In principle, some useful information may be obtained if long-standing fractures and other defects control both natural Ar loss and mineral reactions within the laboratory.

INTRODUCTION

In the $^{39}Ar/^{40}Ar$ stepwise heating method developed by Merrihue and Turner (1966), ^{39}K is converted to ^{39}Ar by neutron irradiation of mineral, rock, or meteorite samples, and values of the ratio $^{39}Ar/^{40}Ar$ are determined for Ar released by in vacuo heating. If the heating process is carried out incrementally (step heating), changes in the $^{39}Ar/^{40}Ar$ ratio may reflect spatial variations in $^{40}K/^{40}Ar$ ratios in the sample resulting from, inter alia, partial loss during its previous history. Turner et al. (1966) and Turner (1968) presented models by which age spectra on meteorite samples could be interpreted as revealing natural Ar diffusion profiles produced as a result of partial degassing of minerals. They showed that their observations were consistent with a log-normal distribution of grain sizes. Harrison and McDougall (1980) subsequently interpreted age spectra on partially degassed hornblende in terms of diffusion from a uniform sphere. Subsequently, Berger and York (1981) treated individual, incremental heating studies of $^{39}Ar/^{40}Ar$ on biotite and hornblende as self-contained Ar diffusion experiments; diffusion parameters based on the loss of ^{39}Ar during step heating were used to infer closure temperatures for ^{40}Ar in the slowly cooled natural samples. These models assume that Ar loss takes place by volume diffusion, both in the laboratory and in nature. More elaborate models have recently been developed by Lovera et al. (1991) and used successfully to determine the cooling history of potassium feldspars. However, in vacuo Ar release from hydrous minerals such as hornblende may be related to other mechanisms including dehydration, melting, phase changes, and structural changes (Gerling et al., 1966; Zimmerman, 1972; Berger, 1975; Hanson et al., 1975; Harrison, 1981, 1983; McDougall and Harrison, 1988; Gaber et al., 1988; Lee et al., 1990). To test which of these processes may affect Ar release, a detailed investigation of the behavior of hornblende during $^{39}Ar/^{40}Ar$ stepwise heating has been instigated.

EXPERIMENTAL STUDIES

Three hornblende samples were investigated. N530 and K507 are both tschermakitic hornblendes (Leake, 1978) taken from coarse-grained hornblendities of the Kamila Shear Zone, northern Pakistan, which cooled through 500 °C by 83 Ma (Treloar et al., 1989). Both samples contained excess Ar but yielded minimum ages of 90–94 m.y. and 92–110 m.y., respectively. The third sample, MMhb-1, is the interlaboratory dating standard, which was separated from a syenite sample 500 m.y. old in the McClure Mountain Complex, Fremont County, Colorado, U.S.A. (Alexander et al., 1978).

Experimental work included (1) a mineralogical investigation of changes in hornblende samples following heating in vacuo and (2) observations of these changes as they occurred by photoemission electron microscopy (PEEM).

Aliquots of unirradiated hornblende (sample N530) were vacuum heated to known temperatures and analyzed using powder camera X-ray diffraction (XRD), electron microprobe analysis, and scanning electron microscopy (SEM). Powder camera X-ray diffractograms of both the unheated sample and of aliquots heated to 960 °C displayed a fairly uniform set of d-values. However, there was a reduction in the d-values with increasing temperature, indicating a contraction of the unit-cell dimensions. This contraction was also noted by Gaber et al. (1988) at temperatures of 700–900 °C. Optical character-

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Fig. 1. Backscattered electron photomicrographs of vacuum heated hornblende separates. (a) N530/1030 °C. Fine-grained reaction products (Mg-rich hedenbergite, plagioclase, and Fe oxides) forming along cleavage traces, fractures, and grain boundaries. The relict material retains the hornblende composition, but possesses a clinopyroxene crystal structure. (b) N530/1090 °C. Complete decomposition of the clinopyroxene-structured phase to fine-grained reaction products. Mg-rich inhomogeneous glasses are also observed along cleavage traces, fractures, and grain boundaries, indicating melting. (c) MMhb-1/1205 °C. Complete melting with the quench formation of plagioclase (Plag) and Fe oxide in a glass matrix.

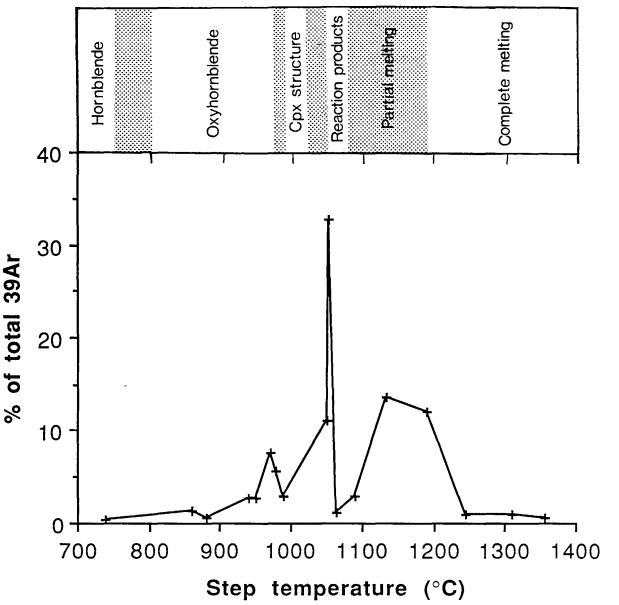

Fig. 2. Percentage of total ^{39}Ar against step temperature for hornblende sample N530. The bar above the graph indicates the observed mineralogical changes at different temperatures, with the shaded zones corresponding to the transitional temperature ranges. "Reaction products" at 1050 °C refers to the fine-grained reaction material shown in Figure 1a.

istics of the phase include a change in color and pleochroism and a decrease in the extinction angle. This suggests that the reaction product is oxyhornblende, which is formed at 750–800 °C (Barnes, 1930; Phillips et al., 1988, 1989) by the release of H and the oxidation of the Fe^{2+} to the ferric state. At higher temperatures (1030 °C and 1090 °C), the diffractograms displayed a completely different set of d-values, indicating the total breakdown of the hornblende crystal structure and the induction of new products, i.e., clinopyroxene (Mg-rich hedenbergite), plagioclase (An_{40-50}), and Fe oxides.

Employing the PEEM at Leeds University (Hammond et al., 1987), a sample of hornblendite 4 mm × 4 mm (K507) was mounted in microscope and heated between 750 and 1000 °C. From 970 to 990 °C an image-contrast front was observed migrating across the surface of the specimen indicating a structural rearrangement of the crystal lattice. Electron microprobe analysis of this reacted phase indicated no change from the original hornblende composition, but XRD analysis showed a new structure, probably that of clinopyroxene. At 1010–1020 °C fine-grained Fe oxides were seen concentrated along fractures and cleavage traces. These PEEM results are consistent with SEM observations on hornblende following vacuum heating to 1030 °C. Figures 1a–1c show successive stages of alteration, from nucleation and growth of new fine-grained reaction products along cleavage planes and fractures (1030 °C) through the beginnings of melting (Fig. 1b) to complete melting with development of phenocrysts on cooling (1205 °C).

Conclusions

Ar release from hornblende is strongly correlated with the sequence of decomposition events (Fig. 2). These relationships may be useful for establishing heating strategies for dating hornblende samples containing excess Ar (i.e., U-shaped age spectra); the minimum age in such spectra is typically found at 1020–1030 °C (±25 °C), which is the temperature at which the clinopyroxene-structured phase breaks down to the fine-grained reaction products. Details will be published elsewhere.

The complex breakdown sequence of hornblende described here shows that Ar release from this mineral within the vacuum furnace cannot be a simple volume diffusion process. These results support the views of Hanson et al. (1975) and Gaber et al. (1988), that a simple diffusional interpretation of $^{39}Ar/^{40}Ar$ release in vacuo is not suitable for quantitative determination of thermal history on hornblende, because the mechanisms of Ar release in vacuo are quite different from those operating during metamorphism. There remains, however, the possibility that the breakdown reactions in vacuo progress from fractures and other defects that have previously controlled volume diffusion in geological conditions; in that case, increases in the $^{39}Ar/^{40}Ar$ ratio during the step-heating procedure may be indirectly related to diffusion gradients developed during metamorphism.

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