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Radiometric Dating of Young MORB Using the ^{40}Ar-^{39}Ar Incremental Heating Method

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Abstract. Determination of reliable crystallization ages by K-Ar methods for young (<1 Ma), fresh basalts from the seafloor has been frustrated by several effects. The small amounts of radiogenic ^{40}Ar developed over these timescales in such low-K rocks are difficult to resolve from predominantly atmospheric ^{40}Ar. An additional concern is that mantle-derived ^{40}Ar may not be totally outgassed when magmas quench at seafloor hydrostatic pressures. We have developed a successful strategy for partially separating atmospheric from radiogenic ^{40}Ar in ^{40}Ar-^{39}Ar incremental heating experiments on mid-ocean ridge basalts, from the East Pacific Rise near the Clipperton Fracture Zone. Pre-heating samples to 400°C removes surficial atmospheric ^{40}Ar, while subsequent heating at 600°-1000°C produces favorable proportions of radiogenic ^{40}Ar. Experiments using "zero-age" glassy and holocrystalline samples show that mantle-derived ^{40}Ar is retained only in the outermost few cm of rapidly cooled pillow basalts.

Introduction

Detailed, quantitative understanding of magmatic and tectonic processes of crustal accretion at mid-ocean spreading ridges requires accurate and precise radiometric age determinations for young (<1 Ma) mid-ocean ridge basalts (MORB). Until very recently, however, no direct dating methods have promised much success. With increased capability to map the bathymetry, image deeper structures of spreading ridges, and collect well-located samples by precise dredging, submersible, and bare-rock drilling, reliable and generally applicable dating methods have become a top priority.

The most promising radiometric methods for direct dating of MORB are K-Ar and U-decay series systems (Batiza et al., 1988). Additional methods include thermoluminescence (TL) and fission track dating of basalts. However, TL studies of feldspar and MORB glass have not found measurable signals (Karsten et al., 1990), while fission track dating is severely limited by very low U-contents of MORB glasses and track fading over geologic time.

Goldstein et al. (1989) have demonstrated U-Th isotopic disequilibrium for MORB glasses near the Juan de Fuca, Gorda and Endeavour Ridges implying ages between 0 and 350 ka. Ages calculated from these data (assuming constant initial $^{230}Th/^{232}Th$ for each ridge segment) increase with distance from the axis of spreading. The consistency of these ages with those predicted from spreading rates based on magnetic anomalies supports the assumption of uniform initial $^{230}Th/^{232}Th$ during the last 200 ka for these segments. However, other ridge segments (e.g., East Pacific Rise, 9°30'N, Langmuir et al., 1986) show considerable variation in melt compositions and this assumption needs to be carefully evaluated for each sample suite.

Conventional K-Ar dating using the Cassignol technique (Gillot and Cornette, 1986) has provided precise dating of very young (>10 ka) subaerial, K-rich volcanic rocks. This technique employs an essentially dynamic mode of comparing a standard (atmospheric) reservoir composition with the sample Ar composition. Amounts of radiogenic ^{40}Ar as small as ~0.1% of the total ^{40}Ar can be detected. A Juan de Fuca basalt of estimated age 350-440 ka yielded a measured age of 474 ± 78 ka (Karsten et al., 1990). However, because of the large sample sizes required (5-10 g) this procedure has limited application.

This paper reports the first successful application of the ^{40}Ar-^{39}Ar incremental heating method to dating of MORB. We have tested this method with a geologically-controlled suite of basaltic samples from the axial spreading center out to the Brunhes-Matuyama magnetic polarity boundary at the East Pacific Rise near the Clipperton Fracture Zone. Previous difficulties in dating MORB by K-Ar methods can be largely overcome by applying ^{40}Ar-^{39}Ar incremental heating techniques to suitable samples using the new generation of high sensitivity rare gas mass spectrometers and ultra-clean Ar-extraction systems.

^{40}Ar-^{39}Ar Incremental Heating Methodology

Historically the radiometric method of choice for directly determining crystallization ages of volcanic rocks is K-Ar geochronology (Dalrymple and Lanphere, 1969). This is because K is a common (if minor) element in all volcanic rocks, analytical methods are well tested, and measurements can be made to analytical uncertainties of <1%. K-Ar dating of young MORB has been unsuccessful, however, because of 1) the low K-contents of MORB and small decay constant for ^{40}K (5.543×10^{-10} yr^{-1}), and 2) the retention of mantle-derived, non-atmospheric ^{40}Ar (sometimes called "excess" or "inherited"). The first condition means that only very small amounts of radiogenic ^{40}Ar will be generated in periods of interest (10^4 to 10^6 yr); the second condition means that the initial $^{40}Ar/^{36}Ar$ isotopic composition of the sample may be greater than the atmospheric ratio (in the case of quenched, glassy MORB) and, assuming an atmospheric initial ratio as in conventional K-Ar dating, an erroneously old age is calculated.

In the ^{40}Ar-^{39}Ar method of K-Ar dating, geologic samples are irradiated with fast neutrons to induce the reaction ^{39}K (n,p) ^{39}Ar (Dalrymple et al., 1981a). The age of the samples is then calculated from the $^{40}Ar/^{39}Ar$ ratio after appropriate corrections for interfering Ar isotopes from other neutron reactions with

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Ca and K, and subtraction of the atmospheric contribution to total ^{40}Ar. The main advantage of this method over conventional K-Ar dating is in the ability to incrementally heat samples to examine the isotopic composition of Ar diffusing from minerals or rocks as a function of temperature. Thus, it is possible to separate the contributions to total ^{40}Ar from inherited ^{40}Ar (mantle-derived and quenched in glass or vesicles at high hydrostatic pressures), radiogenic ^{40}Ar accumulated since crystallization, and atmospheric ^{40}Ar by taking advantage of the variable Ar-diffusion rates from different K sites within volcanic materials.

The mantle-derived, non-atmospheric ^{40}Ar component can be largely avoided by analyzing only the well-crystallized interiors of submarine basalt flows. Dalrymple and Moore (1968) showed that this component is present only in the glassy rims of pillow basalts erupted at water depths greater than about 1,500 m. The more slowly crystallized pillow interiors apparently completely equilibrate their initial Ar compositions with atmosphere (seawater) at the time of cooling. We have experimented with a large (20 cm) pillow basalt fragment (PH62-1) dredged from the spreading axis of the East Pacific Rise. We cut mini-cores at cm-intervals from the glassy margin into the holocrystalline interior of the block. We then heated each of the 14 cores in 5-6 temperature steps, from 400°C to 1400°C and measured $^{40}Ar/^{36}Ar$. In accord with previous results, mantle-derived ^{40}Ar was found in the glassy margin but decreased smoothly and disappeared within the outermost 3 cm. Cores taken from the deeper interior gave uniformly atmospheric $^{40}Ar/^{36}Ar$. Thus, sampling for age determinations was directed at block interiors at least 4-5 cm from margins.

Hall and York (1978) recognized that atmospheric ^{40}Ar is not homogeneously distributed through basaltic samples. From incremental heating experiments on a young (~45 ka) subaerial basalt they showed that the composition of Ar released at high temperatures was essentially atmospheric. The lowest temperature step also produced largely atmospheric ^{40}Ar, probably desorbed from sample surfaces. However, at temperatures around 700-1000°C significant amounts of radiogenic ^{40}Ar were released. This means that atmospheric and radiogenic ^{40}Ar can be effectively separated and more precise ages can be measured from the radiogenic steps, compared with whole rock total fusion ages. More recently, Pringle et al. (1992) have used a similar incremental heating method to increase radiogenic ^{40}Ar yields in Quaternary volcanic ash deposits from the Taupo province (New Zealand).

We have repeated the Hall and York (1978) experiment for a young (~340 ka), subaerial basalt from the Southeast Rift Zone of Iceland. The K-content (0.90%K) is somewhat above the normal MORB range, and the texture is fine-grained and holocrystalline. The same Ar-release pattern developed: largely atmospheric ^{40}Ar at high temperatures (≥1200°C), which we can ascribe mostly to outgassing of the heating furnace, and at low temperatures (≤600°C), but significantly more radiogenic ^{40}Ar released in between. The 900°C step yielded 70-80% radiogenic ^{40}Ar. Hence, the precision on the 900°C step age improved to ± 1-2% (1s) over the whole rock age, ± 11% (1s). These results point the way to an analytical strategy for maximizing the radiogenic ^{40}Ar component by abbreviated step-heating experiments.

The Hall and York (1978) experiment was achieved with a 10 g sample, while our experiment required 0.2 g. Recent improvements in the sensitivity and resolution of mass spectrometers, and the development of ultra-clean, small volume argon extraction systems allow much smaller samples (1 to 200 mg) to be analyzed. Our mass spectrometer (Mass Analyser Products model MAP 215-50) is a 90° sector direction-focusing instrument with a radius of 15 cm and a Nier-type source. It employs an electron multiplier for increased sensitivity and electrostatic analyzer with adjustable collector slit for resolution (~600) of Ar peaks from small hydrocarbon peaks (m/z near 36 and 39). The total volume of the mass spectrometer is 1500 cc.

We have assembled an all-metal (stainless steel) extraction system (~1000 cc volume), connected directly to the mass spectrometer inlet valve. For incremental heating we use a low-blank, double-vacuum resistance furnace. Irradiated samples, either whole rock mini-cores or Cu-foil wrapped chips/minerals, are loaded into a sample manifold that feeds into a Ta-crucible with a Mo-liner. Temperatures are precisely controlled at the bottom of the crucible with a programmable power supply thermocouple system. Gas is expanded through the extraction system with a series of bakeable valves, and active gases are removed with a series of Zr-V-Fe and Zr-Al getters. The final cleaned-up Ar gas can be concentrated at a LN_2 trap prior to admission to the mass spectrometer.

Ion beam currents are measured with an electron multiplier at m/z = 35, 36, 37, 38, 39 and 40, and intervening baselines. Counting times, peak and baseline positions, data acquisition and storage are controlled by microcomputer. Peak decay is typically <10% during an analysis and regressed peak heights against time follow a first or second order polynomial.

The background for the mass spectrometer is 1.5×10^{-18} mol at m/z = 36, 2×10^{-18} mol at m/z = 39, and 1.5×10^{-16} mol at m/z = 40. A typical line blank, which includes running the resistance furnace up to 800°C is 2×10^{-18} mol at m/z = 36, 4×10^{-18} mol at m/z = 39, and 7×10^{-16} mol at m/z = 40. Mass discrimination is monitored using zero-age basalts run in the same way as older samples. Samples are irradiated at the TRIGA reactor at Oregon State University for 2 hr at 1 MW power. ^{39}Ar production is monitored with small amounts (~10 mg) of biotite standard FCT-3 biotite spaced at regular intervals with the basalt mini-cores or foil packets.

Initial Results

We have first used the ^{40}Ar-^{39}Ar incremental heating procedure to analyze several subaerially-erupted basalts whose ages are well-determined by conventional K-Ar methods. Sample BB-6 is a Quaternary alkali basalt (1.7% K_2O) whose reported age is 441 ± 13 ka (n = 16)(Jager et al., 1985). Our own K-Ar laboratory measurement of its age is 448 ± 10 ka (n=4). An 8-step incremental heating of 0.2 g of BB-6 basalt produced a weighted mean of plateau steps of 422 ± 12 ka, in agreement with the K-Ar measurements. We have also investigated a suite of stratigraphically well-described basaltic lava flows from the eastern neovolcanic zone of Iceland, which produce ages from 40 to 800 ka.

Our initial effort to extend the ^{40}Ar-^{39}Ar incremental heating procedure to dating young ocean floor basalts has focused on a suite of samples from the East Pacific Rise (9°30'N to 11°20'N). Pillow basalt fragments were dredged from the ocean floor along three morphologically distinct flow-lines, perpendicular to spreading segments, from the axial spreading center out to the Brunhes-Matuyama boundary on both sides of the ridge, at roughly 2 km spacing (Phoenix-02 cruise of the R/V Melville, R. Batiza, chief scientist).

Table 1. ^{40}Ar-^{39}Ar Incremental Heating Age Determinations for Basalts from the East Pacific Rise (9° 30' N to 11° 20' N)

Sample No.	Distance from Axis (km, +E, -W)	Model Age (ka)	%K_2O	Age (ka, ± 1 s)
PH62-1	0.0	0	0.19	
PH103-1	0.0	5	0.19	-112 ± 122
PH92-2	11.6	208	0.50	293 ± 417
PH90-3	15.6	295	0.55	195 ± 71
				201 ± 48
PH90-4	15.6	295	0.12	341 ± 23
				313 ± 26
PH117-2	-16.0	304	1.06	348 ± 35
				385 ± 19
PH49-2	20.9	427	0.28	446 ± 54
				423 ± 96
PH39-2	-31.9	585	0.15	538 ± 48
				574 ± 51
PH78-7	28.0	509	0.40	599 ± 84
PH19-4	39.8	780	0.18	780 ± 39
				745 ± 28
PH124-1	-41.2	800	0.22	946 ± 77
				752 ± 42

We first attempted dating basalts collected near the Brunhes-Matuyama magnetic boundary because of the age tie with the magnetic reversal timescale (780 ka; Baksi et al., 1992) and greatest expected accumulation of radiogenic ^{40}Ar within this sample suite. Basalts PH19-4 and PH124-1 are N-MORB that produced measured ages (780 ± 39; 745 ± 28 ka and 946 ± 77; 752 ± 42 ka) close to the expected crystallization ages (Table 1).These, and younger samples, show typical Ar release patterns (Figure 1), similar to those based on incremental heating of subaerial basalts. In these cases the 800° to 1000°C step ages contain much of the sample ^{39}Ar and proportions of radiogenic ^{40}Ar (5 to 10%) are maximized. Step ages for this middle-temperature portion of the ^{39}Ar release spectra are concordant and dominate the weighted mean estimates of crystallization ages.

We plot measured ages against distance from the EPR spreading axis in Figure 2. In general, ages match those estimated from the long-term spreading rate (55 km/m.y. half

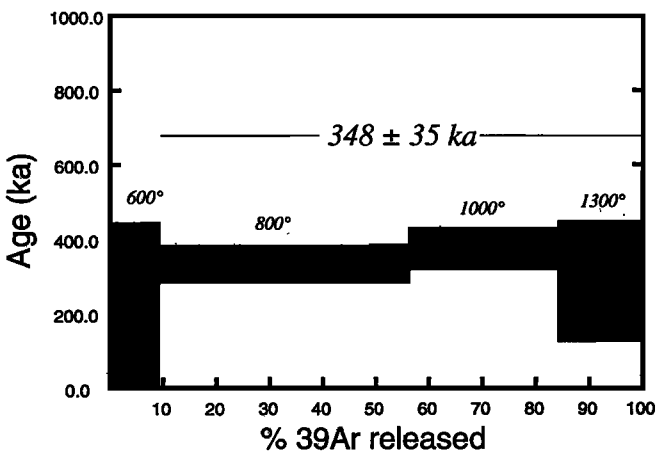

Figure 1. Age spectrum for incremental heating of submarine basalt PH117-2 from the East Pacific Rise (9° 30'N to 11° 20'N). Largely atmospheric Ar outgassed at low and high temperatures, while higher proportions of radiogenic ^{40}Ar were released at 800 ± 200°C.

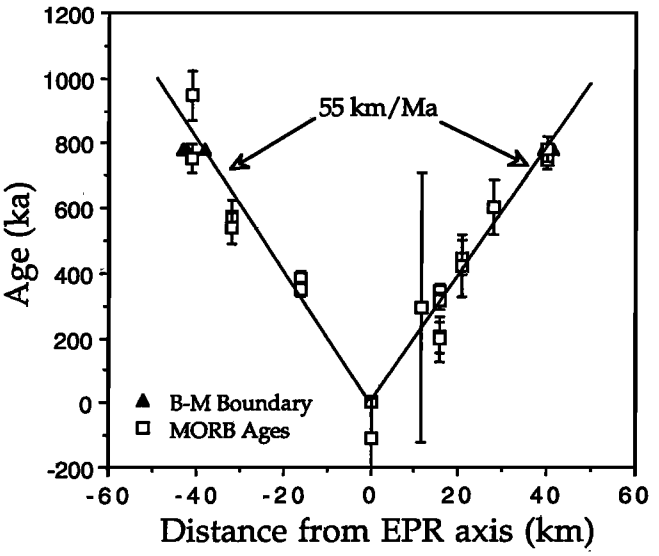

Figure 2. Radiometric ages measured by ^{40}Ar-^{39}Ar incremental heating experiments plotted against distance from the East Pacific Rise. In general, sample ages are concordant with those expected from location and the spreading rate, or interpolation between the Brunhes-Matuyama boundary and the spreading axis.

rate, Carbotte and Macdonald, 1992). Sample PH103-1, collected from the spreading axis, gave a measured age within analytical uncertainty of zero ka.

There is considerable minor and incompatible element variability among the basalts erupted in the 9° 30'N segment, leading Perfit et al. (1993) to speculate that eruptions have occurred over a broad crestal region from small, isolated magma bodies, as well as from the axial summit caldera. Goldstein et al. (1994) have measured ^{238}U-^{230}Th and ^{235}U-^{231}Pa disequilibrium ages for basaltic glasses from the 9° 30' N segment, and found that some are younger (by up to 70 ka) than ages inferred from eruption at the spreading axis and so imply eruption "off-axis", over a ~8 km wide crestal plateau. In contrast, Niu and Batiza (1993) report ridge-symmetric compositional patterns (e.g., FeO, K_2O, Mg-number) for the three segments, which they claim reflects eruption within a very narrow neovolcanic zone with long term (300-600 ka) changes in the balance between magma supply and crustal cooling. Some of the basalts we have analyzed (e.g., PH92-2, PH90-3 and PH117-2, from the 11° 20'N segment) are relatively K-rich and Ti-rich and might, from compositional considerations, be possible off-axis eruptions from evolved (low magma supply) chambers. However, only PH90-3 produced an age younger (by 120 ± 50 ka) than expected, and thus erupted outside the axial zone onto older crust; the age of PH92-2 is poorly resolved but that of PH117-2 places it at the present position of the ridge axis at ~370 ka. Clearly, the significance of "off-axis" eruptions to crustal accretion at the EPR may vary from segment to segment.

Table 1 lists about one-half of the whole rock samples we have tried to date. The others yielded no useful results because large amounts of atmospheric ^{40}Ar swamped radiogenic ^{40}Ar at all temperature steps. This was apparent in the large concentrations of total ^{40}Ar. This problem does not appear to be a function of K-content, as both high and low-K basalts give good results. Instead, atmospheric ^{40}Ar is probably related to rock texture (crystallinity, micro-vesicles) or

incipient alteration (hydration fronts). If so, separating a mineral phase such as plagioclase feldspar for dating would make sense. Unfortunately, less than 10% of the dredged basalts contain separable feldspar. So, while some of these samples might be dated using feldspar, this will not be possible for the majority of MORB. Another consideration is that plagioclase feldspar in MORB usually contains less K than the whole rock, so the optimum material for dating (if the atmospheric ^{40}Ar problem can be overcome by crushing) is the fine-grained rock matrix.

Conclusions

Our initial results indicate that it is possible to measure crystallization ages for MORB in the age range 0.2 to 1.0 Ma with ±10% (1s) uncertainty (Table 1). We believe that this is a significant achievement and confirms the utility of the ^{40}Ar-^{39}Ar incremental heating method for dating young volcanic rocks. We have not, however, attempted to date many samples less than 350 ka, where correlation with U-Th disequilibrium ages can be tested. This is certainly a high priority and will be done with the new EPR sample suite.

Successful intercalibration and concordant ages will produce confidence in both of these methods which cover different age ranges, and so are complementary. Routine, reliable absolute radiometric dating by these methods will provide time scales for Brunhes-age volcanic and tectonic processes in the neovolcanic zones of spreading ridges. Some of the obvious applications will be to quantify periodicities and rates of magma supply, fractionation, and eruption, the timing of rift propagation events, definition of the width of the accretionary zone, the temporal persistence of axial magmatic units, and the age relations of near-ridge seamounts.

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