⁴⁰Ar/³⁹Ar DATING OF MANTLE METASOMATISM: A NOBLE APPROACH OR ALL HOT AIR?

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INTRODUCTION

Studies of mantle xenoliths, transported to the Earth's surface by deep-seated volcanics, demonstrate that the mantle lithosphere beneath many continental regions (e.g.Kaapvaal craton) is depleted in crustal components, but has been re-fertilised (metasomatised) by repeated fluid/melt influxes from the underlying mantle. One of the challenges in Earth Science is relating magmatism and tectonism in the crust to similar processes in the mantle. A demonstration of coincidence in the timing of such events would provide clear links between crustal events and mantle processes. Unfortunately, attempts to accurately date mantle metasomatic events by traditional methods (U-Pb, Sm-Nd, Rb-Sr) have met with limited success, due to incomplete resetting of isotopic clocks, and/or unsuitable mineral assemblages (e.g. Hawkesworth et al., 1990). Recent work on mantle xenoliths has led to suggestions that argon is quantitatively retained by metasomatic phlogopite and that the ⁴⁰Ar/³⁹Ar dating method can provide reliable constraints on the timing of metasomatic events in the mantle (e.g. Kelley and Wartho, 2000; Kempton et al., 2001). In this study, we test this hypothesis using wellconstrained metasomatic xenoliths from the Kimberley kimberlites (~85 Ma) that have been dated using other isotopic methods (Rb-Sr, Sm-Nd, U-Pb) (e.g. Hawkesworth et al., 1990; Konzett et al., 1998). Phlogopite is a common metasomatic phase and a positive outcome would provide a simple, widely applicable method for dating mantle metasomatism.

PREVIOUS WORK

The determination of absolute timeframes for mantle metasomatism is non-trivial, as most mantle minerals reside at temperatures well above the closure temperatures of commonly used isotopic dating techniques. As a result, these minerals typically yield the time of intrusion of the transporting magma. For systems with higher closure temperatures, the selective growth or replacement of minerals may produce disequilibrium isotopic compositions, resulting in mixed ages (e.g. Rudnick et al., 1999). The U-Pb zircon dating method has one of the highest closure temperatures (>900°C) and is widely used for dating

lower crustal rocks. Unfortunately, zircon is a rare in mantle xenoliths and there are few published dates for metasomatic zircons (e.g. Konzett et al., 1998; Rudnick et al., 1999). In contrast, potassium-bearing phases (e.g. phlogopite) are relatively common metasomatic minerals and are ideal candidates for 40 Ar/ 39 Ar dating. However, the closure temperature for argon diffusion in phlogopite (~400 C) is well below typical mantle temperatures (>800 C). Therefore, argon isotopic systematics in phlogopite should be reset within ~1000 years. Nonetheless, several studies have shown that mantle phlogopite commonly gives ⁴⁰Ar/³⁹Ar results that are considerably older than host eruption ages (e.g. Kaneoka and Aoki, 1978; Phillips and Onstott, 1989; Phillips, 1991). In situ laser probe analyses have confirmed that phlogopite usually contains elevated radiogenic argon (⁴⁰Ar*) contents in grain cores, with levels decreasing towards grain edges due to partial argon loss during the eruption process. These studies attributed the anomalously old core ages to high argon partial pressures in the mantle and/or during the initial stages of eruption. Under this interpretation, these ages would have minimal age significance. In contrast, Kelley and Wartho (2000) and Kempton et al. (2001) have suggested that it is possible to accurately date metasomatic phlogopite using the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ laser probe technique, due to the high solubility of argon in phlogopite, minimal intergranular porosity and negligible interstitial melt, which combine to achieve 'closed system' behaviour. Where phlogopite is the sole potassium-bearing phase in a xenolith, these authors suggest that argon will be quantitatively retained by phlogopite. Unfortunately, these conclusions are based on results from only two xenoliths from Malaita (Solomon Islands) and Elvoy island (Kola Peninsula), which yielded ⁴⁰Ar/³⁹Ar results coincident with other isotopic constraints (Rb-Sr, Pb-Pb, Sm-Nd) on the timing of metasomatism in these areas (Kelley & Wartho, 2000). Crucially, results from other studies have been ignored - for example, a Kamfersdam xenolith (Kaapvaal craton) analysed by Pearson et al. (1997) produced Ar-Ar ages up to 500 Ma, which are significantly older than the accepted time of mantle metasomatism in the region (140 - 180 Ma). Clearly, additional evidence from other well-constrained metasomatised xenoliths is required to resolve this critical question.

SAMPLES AND METHODS

A number of dating methods have been used to date metasomatism in the Kimberley xenoliths, including U-Pb zircon (Konzett et al., 1998), Rb-Sr, Sm-Nd and Pb-Pb whole rock (Hawkesworth et al., 1990) and Re-Os (Pearson et al., 1995) techniques. All these methods indicate a widespread mantle metasomatic event at $\sim 140 - 180$ Ma that affected large parts of the Kaapvaal lithosphere. The Kimberley kimberlites were intruded at ~85 Ma. To test the hypothesis that ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ techniques can be used to date mantle metasomatism, we carried out in situ laser probe analyses of phlogopite grains from three metasomatised Kimberley xenoliths that have been dated previously by Hawkesworth et al. (1990). Two xenoliths are phlogopite peridotites and the third is a garnet-phlogopite peridotite. Phlogopite is the *sole* potassium-bearing phase in all three xenoliths. Single phlogopite grains were extracted from each xenolith, ultrasonically cleaned, and irradiated in the McMaster University reactor together with the fluence monitor GA1550 (98.8 \pm 0.5 Ma; Renne et al., 1998). Laser ablation pits were induced using a pulsed laser and ⁴⁰Ar/³⁹Ar analyses were carried out on a 5400 mass spectrometer using a Daly detector.

RESULTS

If Kelley and Wartho (2000) are correct, then laser probe analyses of the cores of phlogopite grains should yield ages that approximate the time of mantle metasomatism. Partial loss of argon during eruption causes reduced ⁴⁰Ar* contents towards grain boundaries, with rim ages usually approaching kimberlite ages. In the current study, core to rim ⁴⁰Ar/³⁹Ar laser probe analyses were conducted on three phlogopite grains from each of the Kimberley xenoliths. Apparent age traverses across the cleavage surfaces of two phlogopite grains are shown in figure 1. In both cases, the margins of the grains are characterized by younger apparent ages, with values generally increasing towards the core. In the case of sample AJE333/4, the dip in apparent ages towards the centre of this grain is likely related to a fracture that transects the grain. With the exception of analyses close to the rims of the two grains, the remaining apparent ages are distinctly older than the inferred time of mantle metasomatism. Maximum core ages from nine phlogopite grains are illustrated in figure 2 and range from 275 ± 2 Ma (AJE213/1) to 949 ± 10 Ma (AJE207/2). Rim ages vary from 123 ± 2 Ma to 359 ± 2 Ma, consistent with partial argon loss from grain margins during kimberlite eruption and cooling. Thus, all apparent ages are older



Figure 1: Laser probe traverses showing variations in ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ apparent ages across the cleavage surfaces of two phlogopite grains from metasomatised Kimberley peridotites. Horizontal bars show times of kimberlite emplacement and mantle metasomatism. The vertical dashed bar represents a fracture cutting one grain. Horizontal 'error' bars reflect laser pit dimensions; errors in ages are smaller than symbol sizes.



Figure 2: Maximum 40 Ar/ 39 Ar apparent ages recorded from the cores of three phlogopite grains from each of three metasomatised peridotite xenoliths.

than the age of kimberlite intrusion (~85 Ma). More importantly, all core ages are distinctly older than the maximum expected limit for mantle metasomatism in the region (180 Ma) (Fig. 2). Furthermore, the core ages recorded from each xenolith are quite different, with AJE213 phlogopite characterized by fairly reproducible core ages of ~280 Ma, whereas grains from AJE239 and AJE207 exhibit older apparent ages of 300 – 600 Ma and 500 – 950 Ma, respectively.

DISCUSSION

The first order conclusion from the above results is that the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ dating method cannot be used to date

(all?) mantle metasomatic events. As the core ages are older than the accepted time of mantle metasomatism in the Kimberley area, the elevated ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ ages are attributed to excess argon contamination. There are two possible sources: First, noble gases behave as highly incompatible trace elements that partition strongly into metasomatic fluids/melts. Therefore, excess argon may have been incorporated from the argon-rich metasomatic fluids/melts responsible for phlogopite crystallisation. This option requires that some portion of the excess argon component is retained by phlogopite in the mantle for 50-100 Ma until kimberlite eruption, a scenario that is still consistent with the 'closed system' model of Kelley and Wartho (2000). Support for this argument comes from studies of some high-pressure (dry) rocks, which show incomplete resetting of argon isotopic systematics during thermal overprinting events (cf. Kelley, 2002). An alternative explanation is that excess argon partitions into phlogopite due to interaction with volatile-rich proto-kimberlite or kimberlite magmas. The presence of excess argon in phlogopite phenocrysts attests to high argon concentrations in kimberlitic melts. However, it is unclear whether the eruption process allows sufficient time for significant ingress of excess argon into phlogopite. Even if kimberlite magmas do not contribute appreciable amounts of excess argon. elevated argon concentrations in the magma would inhibit loss of argon - consequently, attempts to determine eruption rates from argon loss profiles (e.g. Kelley and Wartho, 2000) may underestimate actual timeframes. In all likelihood, the ultimate concentration gradients of argon in mantle minerals are controlled by a combination of processes including interaction with metasomatic and, kimberlitic magmas/fluids, diffusion parameters (e.g. grain size), duration of eruption, timing of melt devolatilisation and cooling rate.

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