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GEOCHEMISTRY

^{40}Ar–^{39}Ar Dating of a Phlogopite-Bearing Websterite: Evidence for Ancient Metasomatism in the Subcontinental Lithospheric Mantle under the Arabian Shield?

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One of the most interesting and perspective regions to investigate the evolution of the subcontinental lithospheric mantle is the central part of the Arabian–Nubian Shield. Here, Cenozoic rifting and related volcanism led to the formation of the Red Sea. Studies during the last two decades revealed that Red Sea rifting was preceded by intensive volcanism in the Afar region (~30 Ma ago), which is geochemically and geophysically interpreted as the manifestation of a deep mantle plume [e.g., 1, 2]. It was also shown that part of the subcontinental mantle beneath the Saudi Arabian Rift shoulder was subjected to intense metasomatism affecting mineral assemblages and also inducing cryptic metasomatic alterations that can be recognized in trace element patterns [3, 4] including noble gases [5, 6]. Henjes-Kunst *et al.* [3] recognized two stages of metasomatic overprints. The first one (metasomatism 1) led to the formation of intragranular Cr–Al-spinel, intragranular Cr-pargasite and intergranular Ba-phlogopite. After the recrystallization of these minerals, the second metasomatic event (metasomatism 2) occurred, leading to the formation of intragranular amphibole and former melt patches now consisting of olivine, pyroxene, spinel and amphibole. Rb–Sr and Sm–Nd systematics of the xenoliths indicate that both metasomatic events (1 and 2) occurred during the last few million years in interaction with fluids and/or melts similar in Sr and Nd isotopic composition [3]. The age of metasomatism 2 inferred from the ^{40}Ar–^{39}Ar age (3.9 ± 0.4 Ma; Buikin *et al.*, in preparation) of secondary intergranular amphibole formed during metasomatism 2 is consistent with the estimate by Henjes-Kunst *et al.* [3]. Geochronological constraints on the earlier metasomatism 1 have not been presented as yet, except for phlogopite from a websteritic xenolith (SA 84–63), which has a slightly higher ^{87}Sr/^{86}Sr ratio than coexisting clinopyroxene from this sample, suggesting a young age (not more then a few million years) of metasomatism 1 [3].

We present ^{40}Ar–^{39}Ar data on a xenolith (SA 84–63) from the volcanic field Uwayrid (Saudi Arabia) and discuss in particular data on an orthopyroxene mineral separate from this xenolith. This mineral separate still contained minor amounts of intergranular phlogopite and probably intragranular Cr-pargasite (products of metasomatism 1). These minor phases, however, contain the major budget of K and are thus potential carriers of either radiogenic ^{40}Ar from in situ K-decay or of ^{40}Ar trapped from hydrous mantle fluids. Resolving radiogenic and trapped ^{40}Ar components is of crucial importance to deciphering the timing of mantle metasomatism. The SA 84–63 xenolith is an olivine websterite containing a remarkably high quantity of primary intergranular Ba-phlogopite. It should be noted that study of the argon isotopic composition of Uwayrid mantle xenoliths displayed a plethora of radiogenic ^{40}Ar in the SA 84–63 xenolith [7]. Attention was given to this fact, because the ^{40}Ar concentration in other xenoliths was much lower, up to an order of magnitude.

Orthopyroxene was separated under a binocular microscope and then cleaned ultrasonically with diluted HNO_3, deionized water, and ethanol. Mineral separation often turns out to be insufficient to completely separate main minerals from intergranular (and, of course, intragranular) mineral phases. Such secondary phases can contain significant amounts of argon genetically and isotopically different from the argon of the main mineral. Correspondingly, they can severely influence the bulk separate isotopic composition [5, 7], occasionally leading to serious misinterpretations. The ^{40}Ar–^{39}Ar method, applied with high-resolution stepwise heating, allows the separation of mineralogically inseparable phases, because individual minerals have

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characteristic argon release temperatures. For example, the degassing temperature range is 1050–1150°C for amphiboles, 1200–1450°C for pyroxenes (clinopyroxene and orthopyroxene are often hardly separable), and 1500–1650°C for olivine [e.g., 5].

The neutron-irradiated sample was stepwise heated from 350°C to 1700°C (11 temperature steps) with temperature intervals ranging from 70 to 200°C using an induction-heated furnace with ^{40}Ar blank values of 0.01 at 600°C, 0.08 at 1400°C and 0.2 at 1500°C ($x \times 10^{-8}$ cm^3/gSTP, 10 min heating duration). Argon isotopic composition was measured on a CH5 mass-spectrometer at the Mineralogical Institute of the University of Heidelberg (Germany). Apparent ages were calculated using the Steiger and Jäger [8] conventions. Further irradiation details and the experimental method will be described elsewhere (Buikin *et al.*, in preparation].

The argon isotope release pattern is shown in Fig. 1. Both neutron-induced isotopes (^{37}Ar from Ca, ^{38}Ar from Cl, and ^{39}Ar from K) and natural (^{36}Ar and ^{40}Ar) isotopes clearly show two well-defined peaks. The high-temperature (1280–1450°C) high-calcium peak belongs to argon released from pyroxene. The intermediate temperature fractions are dominated by an additional release of potassium- and chlorine-derived argon. Petrographic observations of this xenolith indicate that the dominant hydrous phase is phlogopite rather than amphibole or glass. Both phases are characterized by high ^{40}Ar/^{36}Ar ratios (up to 5000 in phlogopite and 10500 in pyroxene). Low-temperature extractions (from intergranular boundaries and/or secondary alterations) are characterized by very small amounts of argon with ^{40}Ar/^{36}Ar ratios close to atmospheric composition. Note the surprisingly high potassium concentration inferred from ^{39}Ar content in the pyroxene reservoir (120 ppm), which is not characteristic for orthopyroxene (EMPA analyses did not yield measurable amounts of potassium in orthopyroxene lattice). The most feasible explanation is that the K-derived ^{39}Ar in the pyroxene release peak is from mineral grains completely encapsulated in pyroxene. Such minerals were observed previously in [3], e.g., intragranular Cr-pargasite and subordinate intergranular Ba-phlogopite described as characteristic products of metasomatism 1. After formation of hydrous minerals, subsequent recrystallization caused the partial replacement of Cr-pargasite and the formation of less hydrous mineral assemblages.

The age spectrum of the sample is irregular (Fig. 3) if radiogenic argon is corrected for trapped argon of atmospheric composition with ^{40}Ar/^{36}Ar = 295.5. This suggests the presence of excess or mantle argon. Indeed, in a three-isotope diagram (Fig. 2), the data points form three different groups: (1) low-temperature extractions (excluding 900°C) tending to atmospheric argon composition; (2) high-temperature (pyroxene) extractions having the highest ^{40}Ar/^{36}Ar ratios, and (3) intermediate-temperature (phlogopite) extractions forming a straight line pointing to trapped argon with $(^{40}Ar/^{36}Ar)_{trapped} = 2112 \pm 4$. Correction of the age spectrum with this value results in a partial plateau of the phlogopite extractions (over 35% of the ^{39}Ar release) with an age of 786 ± 18 Ma. This value corresponds to the formation time of juvenile Pan-African crust of the Arabian–Nubian Shield (650–850 Ma ago), but it obviously conflicts with the suggestion that metasomatism 1 led to the formation of Ba-phlogopite within the last few million years [3]. If the straight line in Fig. 2 is not accidental and if it is a real isochron rather than a mixing line, two questions arise: (1) how could the K–Ar system remain closed under mantle conditions at temperatures probably a hundred degrees above the closure temperature of phlogopite of ~500°C [9]; and (2) why was argon quantitatively retained by phlogopite, while the Rb–Sr system was open until a few million years ago or reset at that time, allowing nearly complete Sr isotopic equilibration?

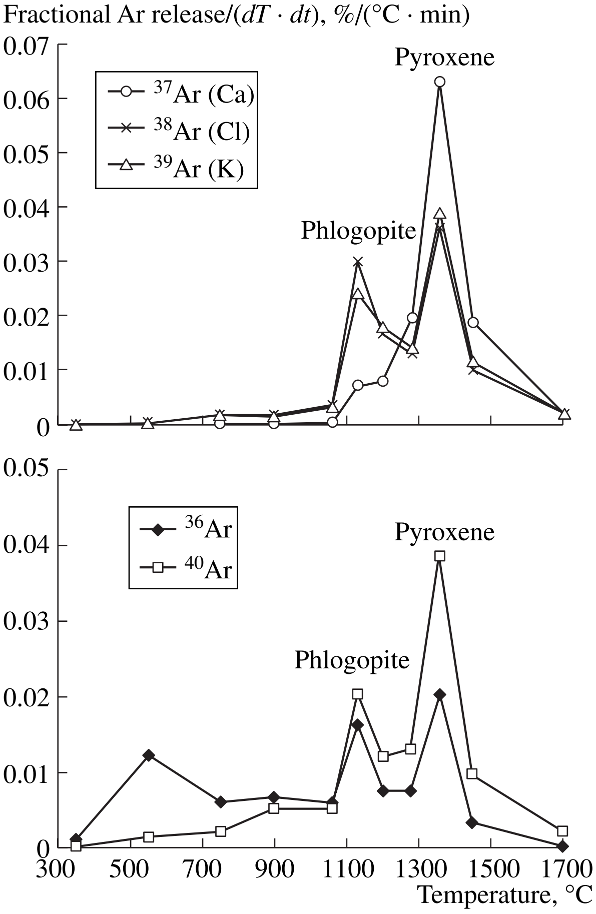

Fig. 1. Degassing pattern of argon isotopes of SA 84–63 Opx. There are two well-separated peaks at intermediate (1060–1200°C) and high (1280–1450°C) temperatures, which indicate the presence of two distinct argon reservoirs in the sample.

To answer the first question, let us refer to the pioneering study of Kelley and Wartho [9]. They have

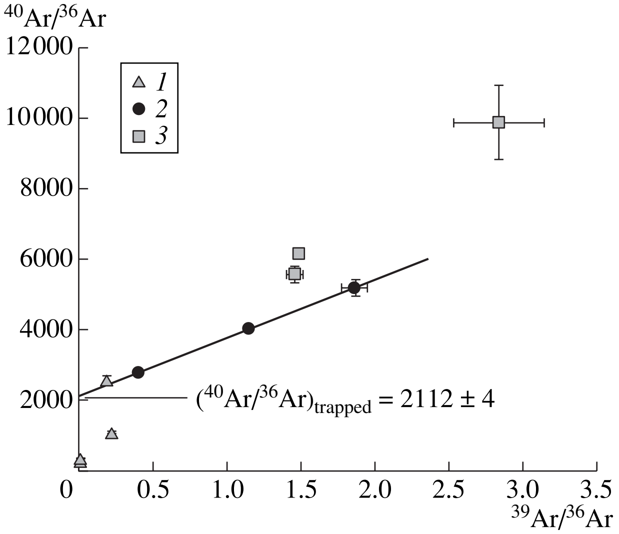

Fig. 2. Argon three-isotope diagram in $^{40}Ar/^{36}Ar$–$^{39}Ar/^{36}Ar$ coordinates. The straight line through three phlogopite extractions points to the trapped argon composition with $(^{40}Ar/^{36}Ar)_{trapped}$ = 2112 ± 4.

1—Low-temperature extractions; *2*—intermediate-temperature extractions; *3*—high-temperature extractions.

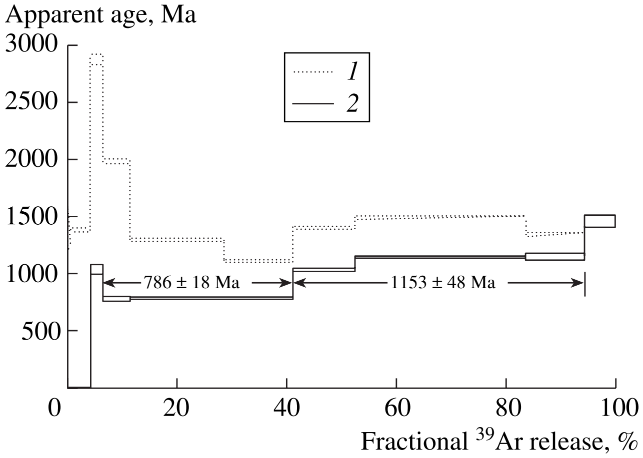

Fig. 3. The age spectrum of the sample SA84–63 Opx. After correction for $(^{40}Ar/^{36}Ar)_{trapped}$ = 2112 ± 4, three phlogopite temperature extractions (more then 35% of ^{39}Ar) form a plateau with the age of 786 ± 18 Ma. *1*—Assuming atmospheric trapped argon; *2*—correct for $(^{40}Ar/^{36}Ar)_{trapped}$ = 2112 ± 4.

shown that phlogopites from xenoliths exhumed by kimberlites and diatremes retained radiogenic argon, although the temperature remained many hundreds of degrees higher than their estimated closure temperatures for long periods of time. Argon seemed to be retained quantitatively, because calculated ages reflected known geological events in the source region of the xenoliths. The only mechanism to cause such an effect seemed to be a lack of argon transfer to other phases or into the grain boundary network. Indeed, at very low concentrations of free fluids (as often is the case for xenoliths from the lithospheric mantle), argon will partition into phlogopite in preference to other more tightly packed mineral lattices such as olivine, garnet, or pyroxene. The only competitive phase could be the grain boundary melt. However, calculations based on argon solubility in silicate melt and phlogopite, and on estimations of the volume of grain boundary networks in the rock show that only 0.2–1% of the radiogenic argon would partition into the grain boundary network at equilibrium [9]. Hence, the mantle phlogopite, being the only potassium-bearing phase (in the neighborhood of olivine, pyroxene, and spinel), and at the same time having the highest argon partition coefficient, is able to retain radiogenic argon quantitatively, with the "excess" argon reflecting storage times in the mantle.

The second question—why are the $^{87}Sr/^{86}Sr$ ratios of the separate Rb-rich phlogopite and coexisting Rb-poor phases very similar, and do they not indicate in situ production of ^{87}Sr over 800 Ma?—may be explained by the presence of mineralogically inseparable intra- and intergranular phases that can introduce a great deal into the phlogopite Sr budget, yielding average isotope signatures similar to Rb-poor phases, such as clinopyroxene. However, 281 ppm Rb in SA 84–63 phlogopite [3] will produce 0.89 ppm ^{87}Sr during the last 800 Ma. Even if all the ^{86}Sr is not in phlogopite but in other phases (clinopyroxene, celsian, etc., making up to 279 ppm total Sr [3]), these phases must have a $^{87}Sr/^{86}Sr$ ratio of 0.69767 in order to yield an average $^{87}Sr/^{86}Sr$ bulk value of 0.703115 reported in [3]. As the value of $^{87}Sr/^{86}Sr = 0.69767$ is far below what has been observed in all samples (minerals) analyzed by Henjes-Kunst *et al.* [3], this seems a quite improbable scenario.

The second possibility to explain similar $^{87}Sr/^{86}Sr$ ratios in phlogopite and coexisting clinopyroxene is episodic or continuous loss of radiogenic ^{87}Sr during the last 800 Ma. At elevated mantle temperatures, Ar and Sr are possibly geochemically fractionated: radiogenic ^{40}Ar preferably stays (due to the higher respective partition coefficient) in phlogopite, where it is continuously produced via K decay (see [9]). In contrast, radiogenic ^{87}Sr most probably partitions into clinopyroxene or grain boundary networks, and is eventually lost from phlogopite. During later metasomatic events, Sr from clinopyroxene or interstitials could well be equilibrated, yielding Sr isotope ratios similar to the metasomatic melts.

If the above described mechanisms are valid, the line connecting phlogopite extractions at intermediate temperatures in Fig. 2 could be interpreted as isochron, indicating closed system behavior of the phlogopite during the last 786 Ma, and incorporation of a mantle fluid with an argon isotopic composition corresponding to the intercept of $(^{40}Ar/^{36}Ar)_{trapped} = 2112 \pm 4$.

The high-temperature or pyroxene extractions (1280–1450°C) in Fig. 2 are not well correlated; however, they can also be connected by a line that yields (within uncertainties) an isotopic composition of trapped argon close to the phlogopite reservoir. If the values are also corrected for $(^{40}Ar/^{36}Ar)_{trapped} = 2112 \pm 4$, the three pyroxene fractions yield a partial plateau with an age of 1153 ± 48 Ma (Fig. 3), which is significantly older than the phlogopite partial plateau. This age is hard to interpret, as we do not know the carrier phase. If the potassium-bearing phase here is intragranular amphibole or an earlier phlogopite generation completely encapsulated in the pyroxene lattice, this value could point to the time of hydrous phase formation and/or enclosure by the pyroxene grains. In principle, this age fits the range of model ages T_{CHUR} and T_{UR} (1.05–1.91 Ga) for most of the Arabian xenoliths [3], and also corresponds to the Pb–Pb ages of whole-rock samples of Zabargad peridotites within uncertainties [10].

The 900°C fraction indicates the presence of excess argon even after correction for trapped argon. A possible reservoir for such argon could be celsian that formed as a scale around rims of phlogopite grains as result of interaction with new portions of melt, thereby trapping the excess argon. Another and probably more likely explanation of the higher apparent age is ^{39}Ar recoil loss from grain boundaries during irradiation. Part of the recoil nuclei could be implanted into the rims of the adjacent pyroxene grains, which could serve as a reasonable explanation of the somewhat lower apparent age of the first pyroxene extraction (1280°C) (Fig. 3).

If the above interpretation of the closed system behavior of phlogopite for 800 Ma is correct, this would imply that the effects previously ascribed to a recent "metasomatism 1" are due to different metasomatic events significantly separated in time: An early metasomatic event triggered the formation of intergranular Ba-phlogopite and intragranular Cr-pargasite much longer ago than suggested in [3] (>800 Ma ago). A later metasomatic event related genetically and temporally to "metasomatism 2" (as it follows from Sr–Nd systematics of the Arabian xenoliths) was responsible for late overprints of subcontinental mantle rocks under the Arabian Plate. In any case, the early metasomatism was an event related to tectonomagmatic processes in the late Pan-African, probably associated with the early stages of juvenile Precambrian crust formation in the Arabian region.

Scenarios describing major lithospheric processes at that time are presented in [11, 12]. Based on stratigraphy, geochronology, secular changes in magma chemistry, and Nd, Sr and Pb isotope ratios, the authors of [12] reconstructed in detail the history of Arabian–Nubian Shield formation. They came to a conclusion about the anomalously rapid generation of both the continental crust of the Arabian–Nubian Shield and its lithospheric mantle root (mainly over ~150 Ma) as a result of the successive processes of oceanic plateau formation by a mantle plume head, subduction and related calc-alkaline magmatism, and the formation of continental crust [12]. The main phase of shield formation—oceanic and then calc-alkaline magmatism—occurred between 875 and 725 Ma. At this stage, the intensive metasomatism in mantle margins and consequent Ba-phlogopite formation are anticipated. Along with subducted material, some part of the atmospheric argon could be introduced into the mantle, which is reflected in the trapped argon isotopic composition (Fig. 2), since $(^{40}Ar/^{36}Ar)_{trapped} = 2112$ is significantly lower than the current estimations for mantle argon (8000 for the Hawaiian plume [13] and >28000 for MORB mantle [i.e., 14, 15]). It is possible that such an argon isotopic composition is typical for supersubduction mantle zones.

It is possible that late metasomatic agents considerably changed the Sr–Nd system of the xenoliths, but they did not severely affect the K–Ar isotope system of pre-existing potassium-bearing minerals, as outlined above. In contrast, the argon isotopic composition of newly-formed minerals (i.e., subordinate intergranular Cr-pargasite or hornblende megacrysts) indicates that the source of late metasomatism 2 contained essentially lower mantle argon concentrations and was strongly contaminated by an atmospheric component. Further investigations of the argon isotopic composition, measured directly in the relict intragranular amphibole and intergranular Ba-phlogopite, e.g., including laser ablation spectra on single grains, should clarify our hypothesis of the phlogopite formation age and also provide insight into the problem of argon retentivity in K-minerals at mantle conditions.

REFERENCES

1. B. Marty, R. Pik, and Y. Gezahegn, Earth Planet. Sci. Lett. **144**, 223 (1996).
2. P. Scarsi and H. Craig, Earth Planet. Sci. Lett. **144**, 505 (1996).
3. F. Henjes-Kunst, R. Altherr, and A. Baumann, Contrib. Min. Petrol. **105**, 460 (1990).
4. G. Kurat, H. Palme, A. Embey-Isztin, *et al.* Mineral. Petrol. **48**, 309 (1993).
5. M. Trieloff, H. W. Weber, G. Kurat, *et al.* Geochim. Cosmochim. Acta **61**, 5065 (1997).
6. J. Hopp, Ph. D. Thesis (Heidelberg Univ., Heidelberg, 2002).

7. A. I. Buikin, E. V. Korochantseva, M. Trieloff, *et al.*, in *Isotope Dating of Geological Processes: New Methods and Results* (Moscow, 2000), pp. 79–81.
8. R. H. Steiger and E. Jäger, Earth Planet. Sci. Lett. **36**, 359 (1977).
9. S. P. Kelley and J.-A. Wartho, Science **289**, 609 (2000).
10. B. Hamelin and C. J. Allègre, Earth Planet Sci Lett. **91**, 117 (1988).
11. M. Stein and A. W. Hofmann, Earth Planet Sci Lett. **114**, 193 (1992).
12. M. Stein and S. L. Goldstein, Nature **382**, 773 (1996).
13. M. Trieloff, J. Kunz, D. H. Harrison, D. A. Clague, and C. J. Allègre, Science **288**, 1036 (2000).
14. M. Trieloff, M. Falter, and E. Jessberger, Geochim. Cosmochim. Acta **67**, 1229 (2003).
15. M. Moreira, J. Kunz, and C. J. Allègre, Science **279**, 1178 (1998).