Using white mica $^{40}\text{Ar}/^{39}\text{Ar}$ data as a tracer for fluid flow and permeability under high-P conditions: Tauern Window, Eastern Alps


ABSTRACT

New single-grain–fusion muscovite and paragonite $^{40}\text{Ar}/^{39}\text{Ar}$ data from eclogite and blueschist units exposed in the Tauern Window, Eastern Alps yield a range of apparent ages from 90 to 23 Ma. These apparent ages are generally older than expected for $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages, given constraints from other geochronological systems such as Rb-Sr and U-Pb. Numerical Ar-in-muscovite diffusion model for Tauern Window nappe $P$-$T$ paths in an open system suggest that $^{40}\text{Ar}/^{39}\text{Ar}$ ages should lie between 29-24 Ma, and that they should constrain cooling and decompression following the post high pressure Barrovian overprint. The measured ranges of apparent $^{40}\text{Ar}/^{39}\text{Ar}$ dates suggest that the assumption of open system behaviour is not valid for this region. The local and/or regional generation of fluid during exhumation promoted pervasive recrystallization of high pressure lithologies throughout the Tauern Window to greenschist and amphibolite facies assemblages. The old apparent $^{40}\text{Ar}/^{39}\text{Ar}$ white mica dates in all lithologies are therefore interpreted as being due to inefficient removal of grain boundary Ar by the grain boundary fluids during the Barrovian overprint, due to high Ar concentrations or limited connectivity or both. This caused spatially (mm-scale) and temporally variable fluxes of Ar out of, and probably into, white mica in both metasedimentary and metabasic lithologies.

SUPPORTING INFORMATION: Appendix S1. Analytical Methods
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Electron Microprobe Analyses

Major-element compositions of micas from the CWT samples and ASA35b were analysed on the Open University JEOL SX-100 5 wavelength-dispersive spectrometer Electron Microprobe using a defocused beam with spot size of 10µm, and conditions of 15kV, 20nA and 30s collection time. Natural standards were used for calibration and analyses were corrected using a ZAF matrix correction routine. Analyses were bracketed by analyses of secondary standards to check for major element reproducibility of 1%. Major-element compositions of mica from the remaining ASA samples and N45b were acquired using the Cambridge University Cameca SX-100 5 wavelength-dispersive spectrometer electron microprobe, operated using a 15kV accelerating voltage, a 10nA beam current and 20s data collection time. Natural and synthetic minerals and oxides were used as standards. Calculation of Fe$^{3+}$ in the mica analyses was performed using AX software (Holland, available at http://www.esc.cam.ac.uk/research/research-groups/holland/ax), which estimates ferric iron assuming a tetrahedral cation sum of 12.10 for white mica normalised to 22 oxygens. Many of the mica grains contained negligible Fe$^{3+}$.

$^{40}$Ar/$^{39}$Ar Analyses

Samples were crushed, washed and sieved and the largest, least-deformed, most inclusion-free muscovite was picked from each sample. Grains were washed in acetone, methanol and water before packing into foil packets for irradiation. An additional cold 0.2M HCl wash was applied to mica picked from calcareous rocks to remove any carbonate dust.

All samples were irradiated at McMaster University in Canada. Irradiation flux was monitored using the GA1550 biotite standard with an age of 98.79 ± 0.54 Ma (Renne et al., 1998). Sample J values were calculated by linear interpolation between two bracketing standards (Table S2); a standard was included between every 8-10 samples in the irradiation tube. Standard analyses were corrected for background and neutron-induced interference reactions. Typical background measurements (which bracket every 1-2 standard and sample measurements) are included for each sample and sample run in Table S2; tabled data are background corrected. Muscovite analyses and standards were corrected for ($^{40}$Ar/$^{39}$Ar)K = 0.0085 based on analyses K salts. Analyses were also corrected for mass spectrometer discrimination using a value of 283.

In common with other small-sample studies, $^{36}$Ar sample and blank measurements approached detection limits, and were commonly within error of each other. The correction for atmospheric Ar magnifies errors on the $^{36}$Ar measurement and results in anomalously high analytical errors on the final $^{40}$Ar/$^{39}$Ar age (Sherlock et al., 2005; Warren et al., 2011). Atmospheric Ar contents were measurable on larger samples and were generally <5% of the total Ar (Table S2). Samples were therefore only corrected for atmospheric Ar where the $^{36}$Ar measurement was >2x the $^{36}$Ar blank and outside the blank measurement uncertainty (indicated in the data table). Samples that were not corrected for atmospheric Ar had the uncertainty on the calculated age doubled in compensation (Sherlock et al., 2005, 2008; Warren et al., 2011).

Samples were loaded into an ultra-high-vacuum laser port and placed under a heat lamp for eight hours to reduce atmospheric blank levels. Total fusion of single grains was achieved using a Nd-YAG 1064 nm infra-red laser coupled to an automated gas handling vacuum system and admitted into an MAP 215-50 noble gas mass spectrometer. Gases were gettered for 5 minutes using two SAES getters (at 450°C and room temperature respectively), and a liquid nitrogen cold trap before inlet into the mass spectrometer. Baselines and peaks from $^{36}$Ar to $^{40}$Ar were scanned 10 times each and amounts were extrapolated back to the inlet time. Data were reduced using an in-house software package (ArMaDiLo) developed by J. Schwanethal.

Compared with step-heating experiments, which in general use multiple grains in a single experiment and for which repeated analyses are rarely presented, single grain fusion data have the advantage of rapidly showing the range of apparent $^{40}$Ar/$^{39}$Ar ages in a population of 10-20 muscovite grains picked from a single ~1 cm$^3$ volume of sample. This method therefore allows us to
compare spatial variability of mica Ar concentration across small rock volumes and between samples of different lithology. It is assumed that variations in age due to variations in the picked grain size population are negligible, and that whole grains were picked rather than fragments (mica does not easily crack across cleavage planes). By using this method any variation in age caused by diffusion profiles across grains is ignored. Ideally, the UV laserprobe would allow spatial variability in Ar concentrations (and hence apparent ages) to be determined from single spots within muscovite crystals in a similar manner to using the SHRIMP or laser ablation to date zircon by U-Pb (Sherlock & Kelley 2002; Putlitz et al., 2005; Warren et al., 2011). However if all the uncertainties in the analytical data (including the uncertainty in the J value) are propagated through rigorously, the age resolution that results from such small-volume analysis is currently insufficient to resolve intra-grain differences outside uncertainty in such young (c. 30 Ma) white mica.

**Diffusion Modelling**

The time integration in DiffArgP was performed with a Crank-Nicholson solver, using a recommended time step that is 10 times larger than the value suggested for a stable fully-explicit method (Wheeler, 1996). The direct calculation results in DiffArg are profiles of apparent age (as a proxy for Ar concentration) as a function of distance from the grain centre. The model uses Simpson’s rule over the radial mesh to calculate the final apparent bulk (integrated) grain age. The numerical error on this age is proportional to the size of the radial grid spacing specified in the input. We minimize this error in DiffArgP by regressing the integrated (bulk) age yielded by calculations at different mesh sizes to the zero mesh-size intercept (corresponding to an infinite mesh density). The errors resulting from the finite precision of Simpson's integration rule over the remainder of the grain are negligible by comparison.

**REFERENCES**


