Pergamon

PII: S0191–8141(98)00014–5

*Journal of Structural Geology*, Vol. 20, No. 6, pp. 819 to 821, 1998

0191-8141/98 $19.00 + 0.00

# Brevia
# The tectonic significance of a porphyroblastic blueschist facies overprint during Alpine orogenesis: Sifnos, Aegean Sea, Greece: Discussion

W. J. DUNLAP

Research School of Earth Sciences, The Australian National University, Canberra ACT, 0200, Australia
(jim.dunlap@anu.edu.au)

(*Received* 3 *June* 1997; *accepted in revised form* 18 *February* 1998)

## INTRODUCTION

Lister and Raouzaios (1996) have presented an integrated microstructural, petrologic and geochronologic study of Tertiary blueschist, eclogite and greenschist facies rocks of Sifnos, Greece. Their treatment of the microstructural and petrologic data is commendable and the new knowledge gained will surely further the understanding of the tectonic evolution of Sifnos. Their modelling and interpretation of the geochronologic data are, however, of limited value in my opinion. In this regard, they have based their analysis on assumptions which are contradicted by the available literature on argon diffusion in micas and by the behaviour of micas during laser step-heating under vacuum. Moreover, researchers seeking to understand the evolution of orogenic belts should not be led to believe that theoretical modelling of mica $^{40}Ar/^{39}Ar$ data can provide meaningful *P–T–t* paths at the level of resolution implied by the analysis of Lister and Raouzaios (1996).

Lister and Raouzaios (1996) model previously published $^{40}Ar/^{39}Ar$ laser step-heating age spectra from Sifnos phengites (Wijbrans *et al.*, 1990) with the MacArgon program (Lister and Baldwin, 1996). The blueschist facies rocks contain ~42 Ma phengites, whereas the greenschist facies rocks from an adjacent lithotectonic unit a few kilometres away contain ~32 Ma phengites. They test, through comparison of model and laboratory age spectra, the proposed *P–T–t* paths of Wijbrans *et al.* (1993) and Wijbrans *et al.* (1990) and suggest that these paths are not realistic estimates of the true *P–T–t* paths experienced by the rocks. In modelling the laboratory age spectra, however, they reduce the number of variables controlling argon diffusion by making several simplifying assumptions, and these assumptions bias their models. Key assumptions made by Lister and Raouzaios (1996) are the following.

1. The diffusivity of argon as measured experimentally in, for example, phlogopite (Giletti, 1974) is a reasonable estimate of that for Sifnos phengites.
2. Argon loss from phengite modelled as phlogopite is via cylindrical geometry, whereas argon loss from phengite modelled as muscovite is via slab geometry.
3. Flat $^{40}Ar/^{39}Ar$ age spectra for micas indicate rapid cooling.
4. Micas can effectively be modelled as uniform with respect to argon diffusivity and effective diffusion length scale. I argue below that these underlying assumptions are unwarranted in light of the published literature.

## DIFFUSIVITY UNKNOWN

Assumption 1: The diffusivity of argon as measured experimentally in phlogopite is a reasonable estimate of that for phengite. The main problem with this assumption is that the diffusion parameters for one mineral applied to another can at best be only a first order estimate (Wijbrans and McDougall, 1988), and the use of these parameters for detailed modelling purposes is probably unjustified. The uncertainty in the diffusion data for phlogopite alone limits the validity of the MacArgon modelling to perhaps $\pm 50^{\circ}C$ in closure temperature, yet when crystal-chemical differences between trioctahedral phlogopite and dioctahedral phengite are considered (Dahl, 1996), it must be concluded that there is a less than firm basis for the detailed modelling of Sifnos phengites as theoretical phlogopites.

## INCONSISTENT GEOMETRY

Assumption 2: Lister and Raouzaios (1996) assume that argon loss from phengite modelled as phlogopite is via cylindrical geometry, whereas that from phengite modelled as muscovite is via slab geometry. Is it likely that diffusion paths in phlogopite and muscovite differ significantly? The most sensible approach would be to

assume that the geometry which controls argon diffusion is similar in both phlogopite and muscovite. In fact there is no crystal-chemical reason to expect such a radical difference between two such similar minerals, and the choice of Lister and Raouzaios (1996) to model muscovite as 6 $\mu$m slabs is confounding. The most compelling evidence to date for the geometry which effectively controls argon diffusion in white micas comes from the works of de Jong *et al.* (1992) and Hames and Bowring (1994), which show, in general, that argon concentration in apparently slowly cooled grains decreases radially outward in the cleavage (perpendicular to the *c*-axis), thus supporting the cylindrical geometry model. Similar studies have failed to reveal evidence for smooth argon concentration gradients along the *c*-axis of white micas (e.g. Scaillet *et al.*, 1992). Hames and Bowring (1994) made a case for a much lower diffusivity of argon in muscovite than that proposed by either Lister and Baldwin (1996) or Robbins (1972), despite the three groups using the same experimental data set (cf. Robbins, 1972)! In fact these three estimates are so disparate (partially due to the choice of diffusion geometry) that closure temperatures differing by many tens of degrees Celsius are obtained (for moderate cooling rates); indeed this variation in closure temperature indicates the level of resolution at which $^{40}Ar/^{39}Ar$ data from micas can be interpreted. Lister and Raouzaios (1996) have exceeded this resolution limit in their modelling exercise.

## AGE SPECTRA ARE NOT DIFFUSIVE LOSS PROFILES

Assumption 3: Flat $^{40}Ar/^{39}Ar$ age spectra for micas must be a product of rapid cooling. This assumption is based on the concept that a mica which cools quickly through its closure window for argon diffusion will not develop any significant argon concentration gradient (i.e. an age gradient) due to diffusive loss of argon. The assumption is only valid, however, if the shape of the laboratory-derived age spectrum directly reflects the argon concentration gradient produced in nature. For this assumption to be true we must rely on the step-heating experiment effectively to reverse the closure process experienced in the natural environment. Although homogeneous, slowly cooled, single grains of mica commonly do preserve age gradients, it is unlikely that step heating of whole grains with a laser will reveal such gradients in the form of the age spectrum. Non-uniform heating due to differential laser coupling, and violent dehydroxylation and associated delamination of the mica structure at relatively low temperatures ($\sim$700°C) ensures that any age gradients are likely to be smoothed or destroyed. The result is that flat age spectra may be produced regardless of whether strong argon concentration gradients exist in the starting material (e.g. de Jong *et al.*, 1992; Hodges *et al.*, 1994). For many years it has been recognized that step heating of hydrous minerals under vacuum generally fails to reveal diffusive loss profiles; thus it is misleading for Lister and Raouzaios (1996) to suggest a strong correlation between theoretical diffusive loss models and laboratory step-heating results. Micas that exhibit flat age spectra may or may not have undergone rapid cooling. Thus, it is clear that the form of age spectra for micas is not a good indicator of cooling rate.

## DIFFUSION LENGTH SCALES UNKNOWN

Assumption 4: Micas can effectively be modelled as uniform with respect to argon diffusion parameters (activation energy and frequency factor) and effective diffusion length scale. Lister and Raouzaios (1996) have modelled the Sifnos phengites as homogeneous single domains of uniform diffusivity using fixed diffusion length scales of either 150 $\mu$m (phlogopite) or 6 $\mu$m (muscovite), and the disparate geometries outlined above. It is probably not realistic to expect the Sifnos micas to have behaved as domains of uniform arbitrary length scale, and it also seems unlikely that different grains of phengite will have identical bulk diffusivities for argon. Several studies have shown that single mica grains are not likely to act as single diffusion domains (e.g. Wright *et al.*, 1991), and it seems overly hopeful to expect all grains in a deformed rock mass to have identical diffusion length scales. Each grain analysed by Wijbrans *et al.* (1990) had a distinct composition and likely contained a range of diffusion length scales (probably dominated by one close to the physical grain size). It is also important to note that the phengites measured by Wijbrans *et al.* (1990) were all $>200$ $\mu$m in radius (perpendicular to the *c*-axis). The implication of intragrain diffusion length scale variations is that age gradients may not be uniform across individual grains. In view of this, it is unrealistic to model argon loss by fixing diffusion length scale and diffusion parameters because both are likely to vary significantly. A more appropriate approach would be to vary diffusion length scale and diffusion parameters over a range of reasonable values, and see how this aids the tectonic interpretation.

## CONCLUSIONS

Conclusions 3–5 of Lister and Raouzaios (1996), based almost solely on the MacArgon modelling exercise, find little support in light of the above arguments. Step heating of micas will generally not reveal pronounced age gradients such as those modelled by the MacArgon program. Given the possibility that a flat age spectrum may result even if strong argon concentration gradients exist in a mica, it is not realistic to conclude that the eclogite-blueschist and greenschist

facies rocks on Sifnos have cooled at $>50^{\circ}C/Ma$ just after ~42 Ma and ~32 Ma. It is not within the resolution of the $^{40}Ar/^{39}Ar$ data to make these conclusions. In describing the limitations of their modelling approach Lister and Raouzaios (1996) state that "We accept that future research may show this attempt to have been unjustified". I contend that past research has shown their attempt to be unjustified, but it is my hope that future research will allow another attempt to be made once a more complete understanding of compositional, length scale and geometric controls on argon diffusion in micas is realized.

## REFERENCES


Dahl, P. S. (1996) The crystal-chemical basis for Ar retention in micas: inferences from interlayer partitioning and implications for geochronology. *Contributions to Mineralogy and Petrology* **123,** 22–39.

de Jong, K., Wijbrans, J. R. and Feraud, G. (1992) Repeated thermal resetting of phengites in the Mulhacen Complex (Betic Zone, southeastern Spain) shown by $^{40}Ar/^{39}Ar$ step heating and single grain laser probe dating. *Earth and Planetary Science Letters* **110,** 173–191.

Giletti, B. J. (1974) Studies in diffusion I: Argon in phlogopite mica. In *Geochemical Transport and Kinetics*, eds A. W. Hofmann, B. J. Giletti, H. S. Yoder and R. A. Yund, pp. 107–115. Carnegie Institute of Washington, Publication **634**.

Hames, W. E. and Bowring, S. A. (1994) An empirical evaluation of the argon diffusion geometry in muscovite. *Earth and Planetary Science Letters* **124,** 161–167.

Hodges, K. V., Hames, W. E. and Bowring, S. A. (1994) $^{40}Ar/^{39}Ar$ age gradients in micas from a high-temperature–low-pressure metamorphic terrain: Evidence for very slow cooling and implications for the interpretation of age spectra. *Geology* **22,** 55–58.

Lister, G. S. and Raouzaios, A. (1996) The tectonic significance of a porphyroblastic blueschist facies overprint during Alpine orogenesis: Sifnos, Aegean Sea, Greece. *Journal of Structural Geology* **18,** 1417–1435.

Lister, G. S. and Baldwin, S. L. (1996) Modelling the effect of arbitrary *P–T–t* histories on argon diffusion in minerals using the MacArgon program for the Apple Macintosh. *Tectonophysics* **253,** 83–109.

Robbins, G. A. (1972) Radiogenic argon diffusion in muscovite under hydrothermal conditions. Unpublished MSc thesis. Brown University, Providence.

Scaillet, S., Feraud, G., Ballevre, M. and Amouric, M. (1992) Mg/Fe and [(Mg,Fe) $Si–Al_2$] compositional control on argon behaviour in high-pressure white micas: A $^{40}Ar/^{39}Ar$ continuous laser-probe study from the Dora–Maira nappe of the internal western Alps, Italy. *Geochimica et Cosmochimica Acta* **56,** 2851–2872.

Wijbrans, J. R., Schliestedt, M. and York, D. (1990) Single grain argon laser probe dating on phengites from the blueschist to greenschist transition on Sifnos (Cyclades, Greece). *Contributions to Mineralogy and Petrology* **104,** 582–593.

Wijbrans, J. R., van Wees, J. D., Stephenson, R. A. and Cloetingh, S. A. P. L. (1993) Pressure–temperature–time evolution of the high pressure metamorphic complex of Sifnos, Greece. *Geology* **21,** 443–446.

Wijbrans, J. R. and McDougall, I. (1988) $^{40}Ar/^{39}Ar$ dating of white micas from an Alpine high-pressure metamorphic belt on Naxos (Greece): the resetting of the argon isotopic system. *Contributions to Mineralogy and Petrology* **93,** 187–194.

Wright, N., Layer, P. W. and York, D. (1991) New insights into thermal history from single grain $^{40}Ar/^{39}Ar$ analysis of biotite. *Earth and Planetary Science Letters* **104,** 70–79.