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The tectonic significance of a blueschist overprint during Alpine orogenesis: Sifnos, Aegean Sea, Greece: Reply

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Dunlap asserts that it is not within the resolution of the ^{40}Ar/^{39}Ar technique to allow the conclusions that were made to be drawn by Lister and Raouzaios (1996), and points to specific difficulties: (1) in estimating the retentivity of argon based on limited experimental data; (2) in making assumptions about the details of the geometry of individual diffusion domains; (3) in interpreting the significance of relatively flat age spectra in phengitic white mica; and (4) in assuming that it is possible to neglect complexity in terms of heterogeneous diffusivity and size in the distribution of diffusion domains. His sentiment is that only when we have "a more complete understanding of compositional, length-scale and geometric controls on argon diffusion" will we be in a position to carry out a modelling exercise.

Some of the commentary offered by Dunlap can be safely ignored, although Dunlap is not alone in his criticism of the attempt made by Lister and Raouzaios (1996) to model the *P–T–t* histories of the rocks from Sifnos. The only rejoinder I will offer is to focus the attention of the scientific community on the potential validity of the hypotheses that have been offered as a result of this research, and to encourage other workers similarly to use MacArgon to aid in the interpretation of ^{40}Ar/^{39}Ar apparent age spectra. Continuing work in the Aegean supports the hypothesis made by Lister and Raouzaios (1996) in respect to the tectonic significance of the blueschist overprint on Sifnos, and these results can be taken to apply throughout the entire Cycladic archipelago. It is clear that the eclogite-blueschist belt of the Cyclades was exhumed early in the history of Alpine orogenesis (e.g. see Baldwin, 1996) and then subjected to a sequence of thermal events, some of demonstrably short duration (e.g. Wijbrans and McDougall, 1986, 1988; Baldwin and Lister, in press). The major conclusions of this study therefore remain!

Note that the ~42 Ma and the ~32 Ma phengitic white micas occur in two rock slices separated by an areally significant detachment fault (Avigad, 1993), and it is not surprising that each slice should exhibit a distinct tectonothermal evolution.

Lister and Raouzaios (1996) made some choices, based on previous work (Wijbrans and McDougall, 1986, 1988; Wijbrans *et al*., 1990, 1993). Phengitic white mica is probably more retentive than muscovite but less retentive than phlogopite. Therefore the extensive sequence of numerical experiments that was conducted was based on the diffusion data available for these two minerals. It really does not matter that there is a wide variation in estimated closure temperature within this range, as long as in the limit, phengitic white mica is less retentive than the model phlogopite used in the calculations.

The phlogopite 'end member' was chosen simply because the assumption had already been made in the published literature (Wijbrans and McDougall, 1986, 1988). We presumed that phengite in nature is in fact less retentive than the 'phlogopite model', and step-heating experiments on co-existing K-feldspar tend to support this presumption (Baldwin and Lister, in press). The key issue is that the behaviour of phengitic white mica in nature is assumed to have been bracketed by the experimentally available data as to retentivity, for a minimum estimate using the data obtained from muscovite (Robbins, 1972), and for a maximum estimate, using the data obtained from phlogopite (Giletti, 1974). If the retentivity of phengite in nature is closer to the 'muscovite model' than to the 'phlogopite model', the conclusions made by Lister and Raouzaios (1996) are reinforced, not diminished.

Dunlap describes the choice as to the geometry of the diffusion domains as "confounding". However these two different geometries come attached to different diffusion parameters (see McDougall and Harrison, 1986; Lister and Baldwin, 1996; p. 105). Laboratory experiments provide information in respect to argon loss, temperature and time. From such data it is possible to estimate frequency factor and activation energy, for a particular diffusion geometry, but this geometry must be assumed. If a cylinder-shaped geometry is to be assumed, then we will obtain a different estimate as to frequency factor than if we had assumed a slab-shaped geometry. The values of frequency factor for the two different geometrical models are constrained by the same set of experimental data! The essential retentivity is the same.

The reader can run MacArgon experiments to confirm this statement (MacArgon is freely available on the internet at address: http://www.earth.monash.edu.au/macargon/). This aspect of the argument put by Dunlap is not relevant to the outcome. It is utterly inconsequential as to whether a cylindrical or a slab-shaped geometry is used in the numerical modelling. It is essential to understand this point.

It is correct to point out that Hames and Bowring (1994) and Lister and Baldwin (1996, p. 105) analysed the same dataset (Robbins, 1972) and arrived at different conclusions. In respect to the analysis made by Lister and Baldwin (1996, p. 105), the key observation is that these authors rejected a significant fraction of the available data, for example because some experiments overestimated diffusivity (grain dimensions less than the inferred diffusion dimension). This was hardly worth the fuss and bother, perhaps? Let me suggest that two decades have passed, during which time it has been evident that argon diffusion in white mica is an important and fundamental variable to the science of ^{40}Ar/^{39}Ar geochronology. The relevant equipment is readily available, in particular in the research institution at which Dunlap now resides. Instead of debating the analysis of Robbins (1972) data (an unpublished MSc thesis, reporting data from a block of muscovite chopped up in a meat blender) it might be more useful to make new measurements in material of appropriate composition.

Dunlap challenges the assumption that the apparent age spectra can be modelled by assuming that only one type of diffusion domain exists within the mica grain. I have nothing to say in respect to this criticism except again to repeat that the approach adopted by Lister and Raouzaios (1996) had more to do with developing the constraints offered by assuming that the answer lies somewhere between the results obtained using a retentive ‘phlogopite-model’ in comparison to a much less retentive ‘muscovite model’. In terms of numerical analysis this seems to make more sense than assuming the existence of a multitude of diffusion domains, each with different retentivity, for which no experimental evidence exists. The MacArgon program offers the potential for more complex modelling, but I suspect the answer obtained would be similar to the conclusions reached by Lister and Raouzaios (1996).

Laser work on natural muscovites (Hames and Bowring, 1994; Hodges *et al.*, 1994) has been interpreted to indicate that diffusion in muscovite occurs principally along the (001) plane (i.e. according to a cylindrical geometry). However these observations do not unequivocally demonstrate that the geometry of the diffusion domains in muscovite is that of a cylinder. It is equally plausible that there is systematic lateral variation in the thickness of slab-shaped diffusion domains, for example because of crystal defect structure induced during mica growth. We do not have enough information to make a decision as to the appropriate geometry.

If a cylindrical geometry is the answer then large muscovites found in pegmatites should be highly retentive and capable of preserving old ages through a multitude of subsequent thermal events. Small grains should be incapable of recording anything very old at all! This does not seem to be the case, so is there a problem with this assumption? The same difficulty is not faced by a ‘model muscovite’ with diffusion domains based on the alternative slab geometry. Careful analysis of Robbins (1972) dataset (see appendix of Lister and Baldwin, 1996) supported a slab-shaped geometry, based on the few experimental data that provided relevant information.

To test variation in concentration gradients along the *c*-axis of mica in the same way as proposed by Scaillet *et al.* (1992) in fact requires a laser spot size of $\sim$0.1–0.5 μm, which is beyond the limits of available technology. Equivalent diffusion domain models have rather different dimensions. A ‘cylinder’ model would have a radius of $\sim$150 μm whereas the ‘slab’ model needs to have a half-thickness of $\sim$7 μm to have equivalent retentivity, based on the parameters obtained by the analysis of Robbins (1972) (see Lister and Baldwin, 1996, p. 105).

The most serious difficulties relate to the dehydroxylation of mica in the vacuum, during a step-heating experiment. It is correct to state that the work reported by Lister and Raouzaios (1996) is invalidated if the shape of apparent age spectra reported for phengitic white mica cannot be related (at least in part) to progressive release of argon as the result of solid state diffusion during step-heating *in vacuo*. This limitation was clearly stated by the authors. The only escape from this conclusion is a cautious qualification as follows. To obtain meaningful results, it is only necessary that the internal distribution of argon within the diffusion domains be mimicked by the pattern of gas release during the sequence of lower temperature steps at the beginning of the experiment. The debate hangs on the validity of this prescription.

There are good reasons to persist with sample applications of diffusion theory in attempting to explain the evolution of ^{40}Ar/^{39}Ar apparent age spectra in phengitic white mica. Phengitic white mica seems to yield results *in vacuo* in a quite different way to muscovite. It seems that it is possible to extract meaningful (?) Arrhenius data (over a limited temperature range) and the apparent age spectra that result resemble theoretical apparent age spectra obtained using the same assumptions that Dunlap has so forcefully rejected. It is not all clear why this should be so.

It is true that laser step-heating suffers from several disadvantages when it comes to the exactness required for determining progressive gas release, and work in progress has confirmed this conjecture. Nevertheless Wijbrans *et al.* (1993) have been careful with their experimental technique, and therefore they were able to obtain apparent age spectra that are capable of theoretical analysis. Progressive step-heating in a furnace yields better results. Dehydroxylation in phengitic white mica seems to accelerate at significantly higher temperatures than appears to be the case for muscovite. Based on the pessimistic assessment provided by Dunlap, there might seem little value in step-heating experiments using muscovite. A note of cautious optimism might be inserted in respect to phengitic white mica however.

Dunlap provides a statement of doctrine when he writes that "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)". My reply is that the reader might also consider the alternative possibility, namely that the constraints on *P–T–t* paths developed by Lister and Raouzaios (1996) are indeed meaningful, and within the limits of resolution provided by the $^{40}Ar/^{39}Ar$ technique applied to the analysis of phengitic white mica. In this case the published work has considerable implications in respect to the evolution of metamorphic terranes in general. Similar conclusions might apply to other terranes, including the ancient orogenic terranes in Central Australia with which Dunlap is perhaps more familiar.

I do not advocate the modelling of $^{40}Ar/^{39}Ar$ geochronological data without careful attention to the many pitfalls and shortcomings inherent in the technique at the present stage of its development. More importantly, I would not advocate the modelling of $^{40}Ar/^{39}Ar$ geochronological data without careful attention to the details of the fabrics and microstructures from which the sample is derived. Dunlap has drawn attention to the difficulties. Nevertheless there is a certain validity in the approach that we should "see what existing diffusion models predict", especially when it comes to the analysis of phengitic white mica. It is important to bring absolute time into the question of the tectonic evolution of young orogenic terranes. Structural geology will be much the poorer if we do not eventually succeed. Therefore I would strongly encourage the continued development of analytical techniques applied to the results of $^{40}Ar/^{39}Ar$ geochronological data.

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