Argon geochronology and phengites: a story of excess argon, diagrams and paradoxes

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Among the most debated questions in the world of metamorphic dating is certainly that of high pressure metamorphism which ultimately underpins most geodynamical reconstructions and mechanisms of orogenesis. Applying argon dating to high pressure material brings both good news and possibly bad. The good news is that during the HP peak potassium rich phases are likely to crystallise in most pelitic but also in many magmatic systems. This is often represented by the crystallisation of the silica rich white mica: phengites. On the other hand the bad news is that the dating of such a ubiquitous and highly valuable phase has lead to a growing controversy. Many authors suspect that large quantities of excess argon can be incorporated during the growth of phengite leading to anomalously old ages. Moreover several flaws in the analyses protocol or the graphical tools usually used often prohibit the identification and correction of the incorporated excess argon. However only rarely can clear evidence of that artefact be isolated and the controversy rises from contradictory interpretations of age data. Below we expose a geological case in which field data and independent age constraints lead to the proposal of either the presence of excess argon, or very unusual diffusion characteristics for phengite. This in turn implies geological consequences which can be tested. Finally we discuss the possible directions of research which should lead to a definitive assessment of the role of phengite in dating HP terrains.

Suspicious circumstances: how many ages can we have for a single event?

In 25 years more than 50 ages have been published for the high-pressure metamorphic event from Alps, essentially the Dora Maira, Gran Paradiso and Sesia regions. Aside from the wide scatter in 40Ar-39Ar phengite ages, a single K-feldspar shows most of the range in ages found in other minerals. A second and more recently highlighted example is from the Tavsanli Zone of NW Turkey, a belt of high-pressure metamorphic rocks which have yielded 40Ar-39Ar phengite and glaucophane ages of 88 to 108 Ma (Okay and Kelley, 1994; Harris *et al.*, 1995) and 72 to 124 Ma A single sample, 96/134, has yielded a range of isotopic ages for the single high-pressure metamorphic event, with a Rb-Sr mineral age of 80.2 \pm 1.6 Ma. for the same sample ultra-violet laser ablation microprobe (UVLAMP) white mica analyses are in the range 78 \pm 2 to 109 \pm 3 Ma and classical furnace step heating yielded a convincing plateau age of 107 \pm 2 Ma (Fig. 1), consistent with many of the oldest UVLAMP ages but 25 Ma older than the Rb-Sr age for the same mineral.

Micro analysis and spatial distribution of ages at the grain scale: excess argon or unusual retentivity characteristics?

Arnaud and Kelley (1995) show that single grains of alpine phengites from a Hercynian metagranite yielded variable ages ranging from 600 Ma to 45-50 Ma and demonstrated in that sample that excess argon was indeed present. Other studies show a restricted fluid flow in such an environment, such a scatter in age for a single deformation peak is highly suggestive of artefacts in the argon concentration gradient. Such geologically impossible ages from the Alps is by far the best indication of the existence of



FIG. 1. Flat plateau of furnace step-heated white mica sample 96/134 (from Sherlock and Arnaud, subm.).



FIG. 2. With an inflated y-axis scale resembling a mineral spectrum contaminated with excess Ar.

excess argon. This is an exceptional case and more often the problem arises for scattered but geologically meaningful ages at the grain scale. The reasoning behind this is complex and by no means clear, two possibilities are: (1) Tc is much higher in Si-rich phengites; (2) The plateau is incorrect and an artefact of excess argon.

The first hypothesis has been suggested and discussed by several authors, the second hypothesis we will discuss more fully below.

The geological proof

High Tc or excess argon? For sample 96/134 in the Tavsanli Zone the Tc is approximately 380°C based on the kinetic data of Hames and Bowring (1994) and the equations of Dodson (1973), and is some 120°C lower than Tc for Rb-Sr. If the ⁴⁰Ar-³⁹Ar age of 107 Ma is real, then based on the PT history and an average cooling rate of 10°C/km and an Rb-Sr age of 80 Ma, then the difference in age would suggest a Tc for argon in phengite in the region of 800°C (Sherlock and Arnaud, subm). In view of the maximum temperature of 550°C proposed for the Tavsanli Zone a Tc of 800°C is implausible. Conversely, if a cooling rate of 1°C/km is assumed then the Tc for Ar-Ar and Rb-Sr are only separated by 20°C, however this would require a thermal stasis of approaching 30 Ma which again is implausible based on the exhumation history of the Tavsanli Zone. The second hypothesis requires a critical examination of the plateau.

Graphical identification of excess argon or emphasis of artefacts?

Plateaus and inverse isochrons have largely been



FIG. 3. Inverse isochron correlation diagram for sample 96/134 (from Sherlock and Arnaud, subm.).

used as statistical tools in identifying meaningful successions of steps and heterogeneous reservoirs of excess argon. This has been partially successful in Alpine high-pressure metamorphism in identifying an age gradient in the plateaus with the inverse isochron suggesting that this is an artifact. The inverse isochron diagram of Arnaud and Kelley (1995) for all minerals illustrates radiogenic growth of a variable mix of excess and atmospheric argon. In the case of the Tavsanli Zone the seemingly flat plateau resembles more the spectra of a mineral contaminated with excess argon when the scale on the y-axis is inflated (Fig 2), however the inverse isochron diagram indicates that there is no contamination by excess argon (Fig 3).

The paradox is clearly that the apparently perfect plateau age is 27 Ma older than the Rb-Sr age, and the supporting inverse isochron diagram suggests that there is no excess argon.

A definitive test of these hypotheses...

From the geological evidence it is clear that in the case of theTavsanli Zone geochronology it is implausible to suggest that the Tc of argon in high-Si micas is significantly higher than that of Rb-Sr. It is also clear that the plateau age, inverse isochron diagram and Rb-Sr ages are irreconcileable and that indeed there is a problem with the statistical tools and graphical representation of this data. To look to a definitive answer it is first necessary to rule out the posibility of higher Tc in all high-Si micas in all HP regions which can only be achieved by experimental petrology and dilligent diffusion studies. Secondly there is the necessity to look towards new statistical tools to enable us to examine more realistically such data as is presented here.