K-Ar dating by stepwise dissolution

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Isotopic closure of the K-Ar system is typically considered to be governed by temperature controlled volume diffusion. However, theoretical considerations as well as experimental suggest that fluid-induced evidence metamorphic recrystallisation may be orders of magnitude more important than thermal diffusion in many if not most field settings [1]. This simple concept may explain the irregular release spectra observed in many stepwise heating experiments. We here present a new approach to argon geochronology, inspired by a technological breakthrough which occurred in U-Pb geochronology in the mid-1990s. At that time, it was found that the discordance of zircons suffering from common Pb or apparent Pb-loss is greatly reduced by stepwise dissolution in hydrofluoric acid [2]. Acid etching may be equally effective at removing compositionally distinct zones in other minerals as well. In fact, several workers have successfully removed excess argon from feldspar by acid dissolution before [2]. We have revisited and extended these earlier experiments using a well characterised K-feldspar sample from the Limpopo Belt (South Africa) which yields a typical complex ⁴⁰Ar/³⁹Arrelease spectrum, comprised of an initial 500 Ma phase which steadily rises to a 'plateau' at 1.1 Ga. Six aliquots of the sample were subjected to different degrees of partial dissolution. Combining the K-content of the supernatant with the Arcontent of the corresponding solid residue we obtain a K-Ar age spectrum, which looks strikingly similar to the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ age spectrum. The first leaching is disproportionally rich in K compared to the subsequent steps, resulting in anomalously young K-Ar ages. Interestingly, the molar abundance of argon in the sample is fairly constant across all leaching steps, indicating that the K-rich phases do not host substantial amounts of radiogenic argon. The similarity between the age spectra obtained by stepwise dissolution to the conventional step-heating spectrum indicates that the sample underwent profound chemical changes over the course of its 2 billion year history which cannot be disentangled from its thermal history by stepwise heating alone. It is a necessary condition for the application of argon thermochronometry that chemical effects can be safely ignored. The acid-etching method provides the first robust way to test this assumption, by analysing the chemical composition of the acid wash. The reconstruction of the compositional evolution of K-bearing minerals with time is step towards the an important development of 'hygrochronometry' as an alternative to thermochronology [1].

[1]Villa, I., 2006, *Lithos*, **87**:155–173, 2006. [2]Mattinson, J.M., 1994, *Contrib. Min. Pet.*, **116**: 117–129. [3]Zeitler and Fitz Gerald, 1985, *GCA*, **50**:1185–1199.