



"Excess Ar" by artificial alteration of biotite

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Many biotite phenocrysts from submarine tephra layers have substoichiometric K concentrations and alkali occupation $\ll 2.0$ atoms per formula unit. Diagenetic alteration is an expected effect of exposure of "fresh" magmatic minerals to interstitial water and brine intrusions after the rapid deposition and burial of sediments.

Miocene sediments in the East Pisco Basin (Peru) record carbonate dissolution/precipitation and contain diagenetic gypsum, anhydrite and Mn minerals (Gioncada et al., *J South Am Earth Sci* 81 (2018) 141). Primary volcanic air-fall deposits are interbedded with these sediments. Volcanic feldspars have invariably discordant age spectra, high Cl/K ($^{38}Ar/^{39}Ar$) ratios diagnostic of alteration, and give apparent ages several Ma older than the coexisting biotite. Biotite mostly gives flat age spectra and low Ca/K ratios. The 2 sigma age difference between two stratigraphically equivalent tephra layers was 0.071 ± 0.046 Ma. The biotite with low K concentration gave both a higher age and higher Cl/K , suggesting that alteration increases the apparent K-Ar age.

To test this, we irradiated and stepheated one untreated Fish Canyon biotite ($t = 28.2$ Ma) and one aliquot leached in HCl for 30 min. Artificial alteration caused loss of K (down to 3.7 wt%), age spectrum discordance, high step ages (all > 30 Ma, total gas age 33.6 Ma), Ar release at much lower oven temperature, higher Cl/K , and a slight increase in ^{36}Ar concentration. We conclude that ^{40}K decay partly implants radiogenic Ar^* into the T-O-T phyllosilicate layer, where Ar^* is shielded from interlayer leaching, which thus preferentially removes K. This effect is one explanation why biotite from tephra layers affected by diagenesis, such as those from the Miocene deposits in the East Pisco Basin, can show an excess of radiogenic Ar^* .