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## Geochronology of Heterogeneous Minerals: Biotites from the Larderello Geothermal Field

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In the previous examples (amphiboles and feldspars) it was shown that release of Ar isotopes produced from Ca, Cl and K carries the chemical information required to diagnose the presence of successive, heterochemical mineral zonations. Minerals have long been known to be frequently inhomogeneous, which makes them suitable as thermobarometers (e.g. amphiboles). Micas also show compositional zonations; muscovite inhomogeneity is a geobarometer. Biotite enjoys a much more limited popularity because in most rocks it is completely homogenized and petrographic relics are not preserved. An uncommon exception is represented by the granites from a deep well in the Larderello-Travale geothermal field. Plutons with different chemical composition are present underneath all of the geothermal field. In well Carboli C bis, muscovite-biotite-tourmaline granite was cored between the depths of 4200 and 4300 m; in-hole temperatures are around 400 °C, in a range where biotite and muscovite are almost perfectly closed to isotopic exchange. We analysed the coexisting biotite-muscovite pairs from the top and the bottom of the core (samples CA 4200 and CA 4300, respectively) both by <sup>39</sup>Ar-<sup>40</sup>Ar stepwise heating and by electron microprobe on thin sections and on grain mounts from the dated separate. The <sup>39</sup>Ar-<sup>40</sup>Ar stepwise heating results show common patterns to all four minerals. Ages range from 0.3 to 1.0 Ma, and are substantially younger than any other mica from Larderello sampled at similar and higher temperatures. These are therefore not regional cooling ages but rather reveal that the Carboli twomica granite is Pleistocene, while all other granites known so far are Pliocene. Highest Cl/K ratios correspond to youngest step ages. This anti-correlation was recognized by Villa et al. (1997) as due to a Cl-rich hydrothermal white mica overgrowing the Cl-poorer magmatic one. In the present case, it is not only the white mica which displays two or more populations, but also the biotite. The overall picture given by the 4 minerals is: Cl-poor magmatic micas yield ca. 1.0 Ma ages; they are best preserved in muscovite. Fe+Cl-rich overgrowths, most clearly visible in biotite, formed between 0.25 and 0.4 Ma, probably not as an instantaneous event but rather as a protracted and/or episodic growth. This age is identical to the age of a regional climax of extensional tectonics deduced from the peak of volcanic activity in Latium and Tuscany (Barberi et al., 1994). The younger bulk ages of biotite, compared to muscovite, are demonstrated to be due to larger modal abundance of hydrothermal mica and only subordinately, if at all, to a "closure temperature" difference. The higher reactivity of biotite in hydrothermal reactions is well-known (Lasaga et al., 1994; Dahl, 1996). An essential confirmation of this interpretation is provided by the electron microprobe (EMP) analyses. Muscovites contain <100 ppm Cl and the EMP data are not very significant; on the other hand, the muscovite system is quite well understood (Villa et al., 1997) so the Cl concentrations in muscovite are not really a novel issue. The biotite EMP data, on the other hand, show Cl concentrations between 700 and 1300 ppm; BSE images show a patchy texture typical of replacement reactions, as are all too easily predicted in an active geothermal field. Texturally, the Fe+Cl-richest biotite is late. We observe both high-Cl patches and a correlation between high-Cl degassing steps and young step ages. Our interpretation of the observation is that a texturally young, Cl-rich biotite overgrew a Cl-poor older one. This represents a first indication that biotite is not an exceptional mineral Ar-wise and behaves exactly like amphiboles, K-feldspar and muscovite, in that it is possible to recognize the presence of texturally and chemically resolvable generations by Ar isotope systematics and to assign each generation an age. We thank ERGA SpA (ENEL group) for providing samples and for help and assistance.

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