Water in granitic minerals: implications for oxygen isotope geothermometry

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Water in nominally anhydrous minerals like quartz, feldspar and magnetite were measured by FTIR and TCEA-MS for a number of granites from South China. The results show its ubiquitous presence in the form of structural hydroxyl in intragrains and intergrains as well as free water in fluid inclusions. They have bulk H_2O concentrations of 350 to 3110 ppm in feldspars, 170 to 780 ppm in quartz, and 1990 to 2620 ppm in magnetite. The water is now suggested to serve as an exchange medium for retrograde O isotope reequilibration during granite cooling, which has been overlooked in application of O isotope geothermometers to granitic minerals.

The common practice in O isotope geothermometry of igneous and metamorphic rocks is to pair quartz with the other coexisting minerals. A regular sequence of O isotope temperatures is often observed for different quartz-mineral pairs in granites, with $T_{Qz-Hb} > T_{Qz-Mt} > T_{Qz-Bi} > T_{Qz-Pl}$. Although the theoretical basis behind this practice remains to develop, a potential assumption is that SiO₂ would would isotopically behave as either an infinite reservoir or an active phase for O isotopic exchange with the other minerals during rock cooling. Furthermore, the O isotope temperatures are sequentially correlated with Dodson closure temperatures (Tc) of O diffusion in the paired minerals, so that this sequence is usually explained by diffusion-controlled O isotope exchange during cooling. However, the closure temperature of quartz is typically above that for biotite and feldspar, so it cannot act as an infinite reservoir during cooling for the lower Tc minerals to exchange according to the Giletti model. Feldspars have the fastest rate of O diffusion among rock-forming minerals, so that they would cease lastly for O isotope exchange in granites. Nevertheless, it is noted that the Tc calculations have employed "wet" O diffusion coefficients that were measured in the presence of water. If "dry" O diffusion coefficients (measured in the presence of CO_2 or O_2) are employed, calculated Tc are too high to be compatible with the O isotope temperatures for the lower Tc minerals. This implies that retrograde O isotope exchange would occur in the presence of water to achieve the O isotopic reequilibration between quartz and the lower Tc minerals. In this regard, the diffusion-controlled exchange of O isotopes between coexisting minerals in granites would proceed in a H₂O-present system, where the O diffusion is accelarated by high mobility of hydroxyl. Together with the high SiO₂ activity in crustal rocks, the water in nominally anhydrous minerals may act as the infinite reservoir for retrograde O isotope reequilibration during cooling.