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Rb Isotopic Analyses by MC-ICPMS Using Zr as a Fractionation Monitor: Initial Results and Potential Applications to Improved Rb-Sr Geochronology

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The accuracy and precision of Rb-Sr geochronology by thermal ionisation mass spectrometry (TIMS) is primarily limited by the precision of Rb isotopic compositions for isotope dilution determinations. Rb isotopic measurements and concentrations by TIMS have precisions generally no better than ±1%, and this has also made it difficult to accurately determine the ^{87}Rb decay constant. Simple and consistent mass fractionation of similar mass elements during analysis using multiple collector inductively coupled mass spectrometry (MC-ICPMS) makes it possible to measure isotopic ratios of similar elements simultaneously. One possibility is to use Zr to monitor mass fractionation on the Rb isotope ratio.

Mixtures of natural Rb and Zr in variable ratios have been analysed on a VG Axiom high resolution MC-ICPMS. Runs consisting of 200 ratios (acquisition time = 5 minutes) with a typical internal precision of 0.01% (2se), yield a fractionation-corrected value (using ^{90}Zr/^{91}Zr = 4.588) for ^{85}Rb/^{87}Rb of 2.594 ±1 (2sd; n = 48). This corresponds to a ±0.04% (2sd) reproducibility for our standard data. Measurements were carried out over a period of several days, and included interspersed analyses of an ^{87}Rb-spiked sample in order to reproduce realistic analytical situations. Potential interferences on the Rb masses from KrH and Sr were monitored at masses 83 and 88 respectively. Sample input was via a Cetac Aridus desolvating nebuliser with an uptake rate of approximately 0.05µl/min (a 133 ppb Rb solution yielding a ~2V signal on ^{87}Rb). Mass fractionation of Rb is consistently 2.4 ±0.06% (2sd) per a.m.u.; small variations in mass fractionation may result from torch positioning. Good correlations between the measured ^{90}Zr/^{91}Zr and ^{85}Rb/^{87}Rb indicate that the two elements show similar mass fractionation, justifying using the ratio of one element to mass fractionate another of similar mass. Some difficulties were noted achieving complete washout of Rb from the Aridus and this problem will be significant when running isotope dilution samples with variable ^{87}Rb/^{85}Rb. Improvement in the Rb reproducibility is expected with establishing more efficient washout procedures and with the application of on-peak zeroes. No discernible difference in measured isotopic ratios is observed between reasonably ratioed Rb-Zr solutions (i.e. 1:0.5-1:0.1), although analytical errors increase significantly at lower Zr concentrations.

Zr fractionation-corrected Rb isotope analysis allows measurement of considerably more precise ^{87}Rb/^{86}Sr ratios than by TIMS. Combining conventional TIMS or MC-ICPMS Sr isotope and concentration data with MC-ICPMS, Rb isotope dilution data will greatly improve the accuracy and precision of mineral Rb-Sr isochrons, allow for greater resolution of individual ages, highlight possible fine-scale open system behaviour in igneous systems, and extend Rb-Sr dating to younger rocks with less Rb-Sr fractionation. It may also be possible to constrain the ^{87}Rb decay constant more accurately on suitable rocks by comparison with U-Pb dating. We intend to test the MC-ICPMS Rb-Zr technique by applying it to several high level plutonic bodies of both well-known and unknown ages, where the effects of slow cooling, post-crystallisation isotopic disturbance, and initial isotopic heterogeneity are minimal.