THE APPLICATION OF MICROANALYTICAL TECHNIQUES IN ISOTOPE GEOCHEMISTRY: 1. SINGLE CRYSTAL $^{40}Ar/^{39}Ar$ DATING OF RHYOLITES IN THE JEMEZ VOLCANIC FIELD, NEW MEXICO, WITH IMPLICATIONS FOR EVOLUTION OF THE MAGMA SYSTEM. 2. TOWARDS DEVELOPMENT OF A LASER MICROPROBE FOURIER TRANSFORM MASS SPECTROMETER FOR ISOTOPIC ANALYSIS OF GEOLOGIC SAMPLES

by

Terry L. Spell

A Dissertation

Submitted to the State University of New York at Albany

in Partial Fulfillment of

the Requirements for the Degree of

Doctor of Philosophy

College of Sciences and Mathematics

Department of Geological Sciences

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ABSTRACT

Dating of single crystals from rhyolites in the Jemez Mountains volcanic field (JMVF) by the laser fusion $^{40}Ar/^{39}Ar$ technique reveals phenocryst populations dominated by juvenile crystals, but often containing xenocrystic and altered crystals. Isochron plots of single crystal analyses allow identification of the eruptive age and trapped Ar in the sample. Explosive caldera forming events commenced in the JMVF at 1.78 Ma with eruption of the San Diego Canyon ignimbrites. Xenocrystic material in these units was apparently responsible for the anomalously old K-Ar ages (2.84-3.64 Ma) previously obtained. Further caldera collapse events occurred with eruption of the lower Bandelier Tuff at 1.51 Ma (Toledo Caldera) and the upper Bandelier Tuff at 1.14 Ma (Valles Caldera). These eruptions record the chemical evolution of a large, open system, upper crustal, silicic magma chamber. Postcollapse rhyolites of the Valles Caldera were erupted over an ~1 Ma interval from immediately following caldera formation until ~200 ka. Volcanism was periodic with eruptive activity at ~1.133 Ma, 973-915 ka, 800-787 ka, 557-521 ka, and ~300-170 ka. Most samples contain trapped atmospheric Ar, however several have apparent $^{40}Ar/^{36}Ar$ ranging from 282 to 325. Approximately 30% of the postcollapse rhyolites yield $^{40}Ar/^{39}Ar$ dates significantly older than previous K-Ar dates. This is most likely due to incomplete extraction of $^{40}Ar^*$ from high-temperature alkali feldspars. Variations in petrographic, geochemical, and isotopic characteristics indicate that the discrete intervals of volcanic activity are related to the emplacement of shallow upper crustal magma chambers. Magmas erupted at 973-787 ka and 557-521 ka record differentiation sequences controlled by crystal-liquid fraction and minor assimilation, whereas those vented at 1.133 Ma and ~300-170 ka were distinct compositionally but show no differention. Nd isotopic compositions (ϵ_{Nd} = -2.7 to -4.6) indicate that ~20-65% of these rhyolitic magmas was of mantle-derived origin. Sr isotopic values as low as 0.70464 and calculated magmatic $\delta^{18}O$ of +6.6-7.0 $^o/_{oo}$ suggest that granulitic lower crust of igneous origin was assimilated by basaltic magmas.

Work on the development of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer has established a performance baseline for the initial goal of *in situ* isotopic analysis. The levels of precision for isotope ratio measurements of Kr gas using electron beam ionization provide a measure of the capabilities of FT-ICR under ideal conditions. Ratios of major isotopes are measured to better than ± 0.1%, whereas those involving minor isotopes are reproducible to ± 0.4%. Laser ionization (LI) experiments yield significantly lower levels of precision due to variations in ion number from shot to shot, mass fractionation at the sample surface, and a larger spread in ion kinetic energy. LI experiments involving isotope ratios of abundant elements (metallic Ti) give precisions on the order of 1-4%, whereas those involving trace elements (Pb in zircon or monazite) are measured at 9-12%. The application of the SWIFT excitation technique to eject more abundant ions should allow measurement of trace element isotope ratios with precision approaching that seen for abundant elements.

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A dissertation such as this is a product of the combined efforts of many people. Most of the work can obviously be attributed to myself, however, no single person could likely undertake such a project and complete it on their own. I suspect that many who look at a dissertation do not fully appreciate the importance of the scientific, financial, and emotional encouragement and support from others unless they have experienced it for themselves.

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