

In-Situ $^{87}\text{Sr}/^{86}\text{Sr}$ Analyses of Clinopyroxene from Mantle Xenoliths by Laser Ablation MC-ICP-MS

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Introduction: The micro-drilling (<1 mm scale) and isotopic analysis of plagioclase phenocrysts has recently demonstrated its effective use in documenting large intra-crystal $^{87}\text{Sr}/^{86}\text{Sr}$ variations attributed to open-system magmatic processes (1, 2). A similar approach using laser ablation (~200 μm spot sizes) coupled to a magnetic sector, MC-ICP-MS has also shown great potential for similar type of petrogenetic studies (3). Here we present Sr isotopic data obtained by laser ablation coupled to an Isoprobe instrument (MC-ICP-MS) from Micromass for clinopyroxene from mantle xenoliths (metasomatized to various degrees) from two localities: the Nikos kimberlite pipe (Arctic Canada) and the Kakanui volcanic complex (New Zealand). The objectives of this study are to determine both the feasibility of this method to other Sr-bearing (low-Rb) minerals, and document possible $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic variations within individual clinopyroxene grains and between grains from the same sample. For several samples, the Sr isotopic data obtained here are compared to those representing a population of grains (~100 milligrams) measured by TIMS.

Methodology: All Sr isotopic data were obtained in the static, multi-collection mode using solely Faraday collectors. The Isoprobe is coupled to a 193 nm (ArF) excimer laser (Compex 102) and optics system designed by New Wave Research. Laser pulse energies were in the order of 190 mJ and 15 Hz resulting in energy densities of ~21 J/cm². All ablation experiments were conducted using 150 μm spots since the Sr concentrations for most of the clinopyroxenes ranged from 100 to 500 ppm. As noted in previous studies (3), there is an inevitable trade-off between spot size and ion beam intensity (for a given Sr concentration), which also controls the internal precision. Prior to the laser ablation, a 100 ppb solution of NBS 987 was aspirated (~50 $\mu\text{l}/\text{min}$) into the ICP source using an ARIDUS micro-concentric nebuliser, and the average $^{87}\text{Sr}/^{86}\text{Sr}$ value obtained is 0.71023 ± 5 (n=21; ratios normalized to $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$). The "sample-out" line from the ARIDUS was ("y-") connected to the "sample-out" line from the laser ablation cell outside the torch box. This set-up permits to evaluate the mass bias induced during the laser ablation process, since after exiting the ablation cell both particulate and liquid aerosols travel along the same tubing before entering the torch. Following the analysis of the NBS standard in liquid mode,

nebulizer gas flow rates to both the ablation cell and ARIDUS were adjusted in order to maximize the ion beam intensity.

Results: Ion beam intensities varied from ~0.3 to 1.2×10^{-11} A of ^{88}Sr for concentrations of ~100 to ~500 ppm, respectively. The ^{85}Rb peak was monitored during ablation and this value was either nil or negligible for the clinopyroxenes analysed. Data acquisition consisted of a 50 seconds on-peak baseline measurement prior to ablation and 1 block (50 scans; 2 second integration) resulting in internal precisions ranging from 0.02 to 0.1% (2 σ). Comparison of the measured $^{86}\text{Sr}/^{88}\text{Sr}$ ratios (i.e. mass bias correction ~2.5% amu⁻¹) between the ablation runs to those obtained for the NBS 987 standard in solution mode yield near identical values for a majority of the analyses. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the clinopyroxenes (n=67 analyses for 38 grains) for the eight mantle xenoliths from the Nikos kimberlite pipe define a large range (average values from 0.7035 to 0.7078), both on the scale of individual grains and for crystals from the same sample. Compared to their TIMS values, the latter clearly represent weighted average Sr isotopic ratios. Moreover, the Sr isotopic ratios measured by laser ablation correlate well with the P-T conditions of last equilibration, and the large variation may be attributed to interaction between the xenoliths and host kimberlitic melt. Sr isotope analysis (n=16 analyses from 13 grains) of clinopyroxenes for mantle xenoliths (n=5) from Kakanui also indicate a large variation (average values from 0.7030 to 0.7064) within individual samples. However, these clinopyroxene analyses were somewhat less reproducible due to their much higher content of FeO (~8 to 9 wt%) compared to those for the xenoliths from the Nikos kimberlite (~2 to 3 wt%). We believe that the Fe-to-Sr ratio is an important limitation in this application since Fe-oxide interferences (masses 86 and 88) are formed during the ablation process and affect the mass bias correction based on the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio.

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