

**PRECISE AND ACCURATE DETERMINATION OF STRONTIUM ISOTOPE COMPOSITIONS USING MC-ICPMS.** V. K. Rai<sup>1</sup>, G. S. Franco<sup>1</sup>, R. Hines<sup>1</sup>, and M. Wadhwa<sup>1</sup>, <sup>1</sup>School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85281, USA (vkrai@asu.edu).

**Introduction:** Strontium is an alkaline earth metal with an atomic number of 38 and four stable isotopes [<sup>84</sup>Sr (0.56%); <sup>86</sup>Sr (9.86%); <sup>87</sup>Sr (7%) and <sup>88</sup>Sr (82.58%)] formed by the p-, s- and r- nucleosynthetic processes. Among these isotopes, <sup>87</sup>Sr is the only one that is also radiogenic (produced by the decay of <sup>87</sup>Rb). As such, over the last several decades, measurements of variations in <sup>87</sup>Sr/<sup>86</sup>Sr have been used widely for a range of geological and environmental applications (e.g., [1-4]), primarily using thermal ionization mass spectrometry (TIMS). Such measurements have typically utilized the <sup>88</sup>Sr/<sup>86</sup>Sr ratio for internal mass bias correction, and so cannot be used to determine stable isotope variations in Sr isotopes; use of a double spike is required for constraining such variations using TIMS. Also, until recently, measurement of Sr isotope ratios involving <sup>84</sup>Sr in particular was limited due to its very low abundance. However, in the last decade or so, TIMS measurements of mass-independent isotopic anomalies in <sup>84</sup>Sr have been reported in primitive meteorites on a scale ranging from mm-sized objects (CAIs) to planetesimals [5-9]. Such anomalies can provide insights into the delivery of stellar materials to the early solar nebula and the extent of homogenization during accretion and subsequent evolution of larger planetary bodies.

In the last decade or so, the advent of multicollector inductively coupled mass spectrometry (MC-ICPMS) has greatly enabled studies of natural variations in the stable isotopes of Sr, as accurate mass bias correction can be performed using Zr doping and/or sample-standard bracketing [5,10-12]. Nevertheless, these measurements have been challenging because a small amount of Kr is always present in the Ar gas required for MC-ICPMS analyses, which is enough to generate isobaric interferences on <sup>84</sup>Sr and <sup>86</sup>Sr and results in poor precision. In addition, impurities due to inefficient column purification of the analyte solution can also affect the measurement precision and accuracy. In the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) at ASU, we have developed analytical protocols using MC-ICPMS to determine mass-dependent variations in <sup>88</sup>Sr/<sup>86</sup>Sr (expressed relative to a standard in parts per 1000, i.e.,  $\delta^{88}\text{Sr}$ ), as well as mass-independent variations in <sup>84</sup>Sr/<sup>86</sup>Sr (expressed relative to a standard in parts per 10<sup>4</sup>, i.e.,  $\epsilon^{84}\text{Sr}$ ) and <sup>87</sup>Sr/<sup>86</sup>Sr (expressed relative to a standard in parts per 1000, i.e.,  $\delta^{87}\text{Sr}^*$ ) accurately and with precision comparable to TIMS. This implies that MC-ICPMS

methods can be advantageous for making precise and accurate measurements of Sr isotope compositions of planetary materials, especially given the potential high sample throughput of MC-ICPMS compared to TIMS.

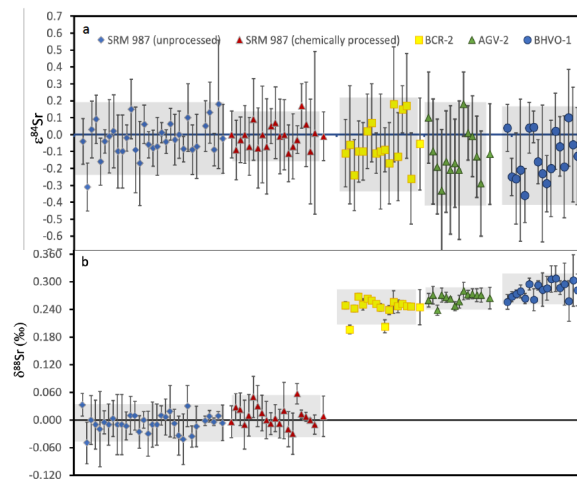
**Analytical Methods:** Several USGS rock standards (BCR-2, AGV-2, BHVO-1) were digested in 3:1 HF-HNO<sub>3</sub> in high-pressure Parr vessels, followed by treatment with 6M HCl to dissolve any remaining fluoride precipitate. Samples were then re-dissolved in 3M HNO<sub>3</sub> for column loading following the procedure modified after [13]. In addition to the solutions of the USGS rock standards, we also chemically processed the NIST SRM987 Sr solution using the same procedure described below to assess whether there was any resolvable isotopic fractionation resulting from our chemical purification procedures.

Solutions with 2 micrograms of Sr were loaded onto 0.3 ml of precleaned Eichrom Sr resin in 1 ml BioRad columns. Prior to loading, resin was cleaned with 6 ml of ultrapure water, followed by a preconditioning step of 1.5 ml of 3M HNO<sub>3</sub>. Most of the alkali and alkaline metals were eluted in 2.5 ml of 3M HNO<sub>3</sub>, followed by elution of Ba in 5 ml of 8M HNO<sub>3</sub>. More than 99% of Ba and other matrix elements was eluted in these two steps. Barium removal is crucial to obtaining high-precision Sr isotope data [14]. Subsequently, Sr was quantitatively eluted in 5 ml of warm MilliQ water. The Sr solution was further treated with H<sub>2</sub>O<sub>2</sub>-HNO<sub>3</sub> to remove organics before preparing a final solution of 200 ppb of Sr in 3% HNO<sub>3</sub>-0.01M HF. This solution was doped with 75 ppb of Zr for external mass bias correction. Isotopic measurements were performed on a Thermo Neptune MC-ICPMS in dry plasma mode using an ARIDUS II in the ICGL at ASU. All the data reduction was performed offline and isotopic data are reported relative to NIST SRM987.

*Kr interference on Sr and correction procedure:* During the development phase of our analytical protocols, we performed controlled doping experiments for a variety of elements that could be present as impurities (such as Na, Ca, and Ba), and determined that Ba was the only one that measurably affected the accuracy and precision of Sr isotopic measurements at the levels present in our purified analyte solutions. We observed that  $\epsilon^{84}\text{Sr}$  values were resolvably affected if Ba/Sr > 0.5, whereas  $\delta^{87}\text{Sr}^*$  values are affected for Ba/Sr > 0.025;  $\delta^{88}\text{Sr}$  values were not resolvably affected for Ba/Sr up to ~1. Therefore, we modified our column cleaning procedure (see “Analytical Methods” above) to

remove Ba efficiently such that Ba/Sr was reliably  $<0.025$  without affecting the Sr yield. In addition, the Kr interference correction procedure was also modified. In the new data reduction procedure, we used the average of  $^{82}\text{Kr}$  intensities measured from the bracketing standards (NIST SRM 987) to correct Kr interferences from  $^{84}\text{Sr}$  and  $^{86}\text{Sr}$ . All the data reduction was performed offline using the Iolite software [15]. Use of relatively high  $\text{N}_2$  flow ( $<5\text{ml}$ ) in ARIDUS II was also found to be helpful in reducing the Kr signal intensity.

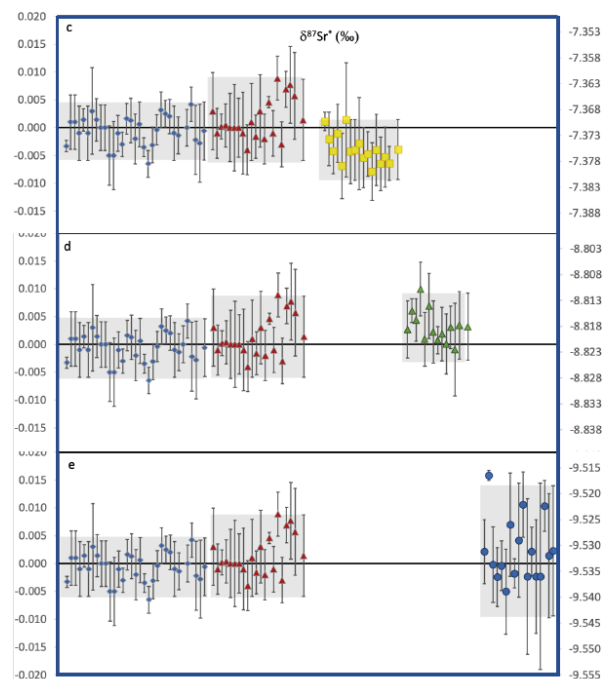
**Results:** Data for the three USGS rock standards, BCR-2, AGV-2, and BHVO-1, are reported in this study. We also report data for NIST SRM987 Sr solution purified through column chemistry. The chemically processed SRM987 yielded the following average values for Sr isotope compositions:  $\epsilon^{84}\text{Sr} = -0.011 \pm 0.144$ ,  $\delta^{87}\text{Sr}^* = 0.001 \pm 0.007$  ‰, and  $\delta^{88}\text{Sr} = 0.008 \pm 0.044$  ‰, (N=20, errors are  $\pm 2\text{SD}$ ). These are indistinguishable from corresponding values for unprocessed SRM987 ( $\epsilon^{84}\text{Sr} = -0.025 \pm 0.203$ ,  $\delta^{87}\text{Sr}^* = -0.001 \pm 0.005$  ‰, and  $\delta^{88}\text{Sr} = -0.007 \pm 0.039$  ‰; N=31, errors are  $\pm 2\text{SD}$ ). The average  $\epsilon^{84}\text{Sr}$  values for BCR-2 (N=16), AGV-2 (N=12) and BHVO-1 (N=16) are  $-0.055 \pm 0.272$ ,  $-0.116 \pm 0.298$  and  $-0.127 \pm 0.287$ , respectively (Fig 1a). This is the first report of  $\epsilon^{84}\text{Sr}$  values measured by MC-ICPMS; these are comparable in precision to the literature data for TIMS analyses [7,10,12,16].



**Fig. 1.** (a) Mass-independent variations in  $^{84}\text{Sr}$  (expressed as  $\epsilon^{84}\text{Sr}$ ) and (b) mass-dependent variations in  $\delta^{88}\text{Sr}$  in synthetic (NIST SRM987) and natural rock (BCR-2, AGV-2, and BHVO-1) standards. Error bars on individual data points are 2SE (N=6), whereas the shaded gray bars represent 2SD uncertainties on the mean for each standard.

To accurately characterize mass-dependent fractionation of  $^{88}\text{Sr}/^{86}\text{Sr}$ , quantitative recovery of Sr after processing through chemical purification procedures is essential. Our Sr yield after such chemical processing was typically  $>98\%$ . The average  $\delta^{88}\text{Sr}$  values measured for BCR-2, AGV-2 and BHVO-1 are  $0.245 \pm 0.039$  ‰,  $0.265 \pm 0.023$  ‰, and  $-0.282 \pm 0.034$  ‰ respectively (Fig 1b). These results are similar to literature values within uncertainty [6,10-12,16].

The mean values for mass-independent variations in  $^{87}\text{Sr}$  (expressed as  $\delta^{87}\text{Sr}^*$ ) for BCR-2, AGV-2 and BHVO-1 are  $-7.376 \pm 0.006$  ‰,  $-8.818 \pm 0.006$  ‰, and  $-9.531 \pm 0.013$  ‰, respectively (Fig 2). Both  $\epsilon^{84}\text{Sr}$  and  $\delta^{87}\text{Sr}^*$  obtained in this study are similar to previously reported literature values.[7-8,10,16].



**Fig. 2.**  $\delta^{87}\text{Sr}^*$  of the USGS rock standards and SRM987 passed through column. Error bars on individual data points are 2SE (N=6) whereas the shaded gray bars represent 2SD uncertainties on the mean for each standard. For rock standards, refer to right Y-axis.

**References:** [1] Allegre et al. (1979) *Physics of Earth Interiors* 19, 293. [2] DePaolo and Wasserburg (1979) *GCA* 43, 615. [3] Pearce et al. *GCA* 157, 125. [4] Veizer (1989) *Ann. Rev. Earth Planet. Sci.* 17, 141. [5] Moynier et al. (2012) *Ap. J.* 758 (45) 7pp. [6] Hans et al. (2013) *EPSL* 204. [7] Charlier et al. (2017) *Geochem. Persp. Lett.* 4, 35. [8] Charlier et al. (2019) *GCA* 265, 413. [9] Paton et al. (2013) *Ap. J.* 763 (L40) 6pp. [10] Moynier et al., (2010) *EPSL* 300, 359. [11] JinLong et al., 2013, doi: 10.1007/s11434-013-5803-5 [12] Liu et al., *Talanta* 88, 338 [13] Yobregat et al., (2017) *JAAS* 32, 1388. [14] Scher et al. (2014) *Geochem. Geophys., Geosys.* 15, 499. [15] Paton et al. (2011) *JAAS* 12, DOI: 10.1039/c1ja10172b. [16] Amsellem (2020) *Chem. Geol.* 339, 113.