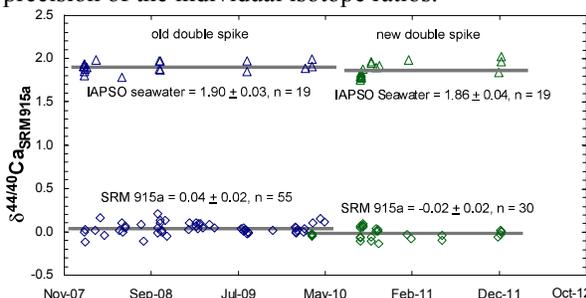


**PRECISE DETERMINATION OF CALCIUM ISOTOPE VARIATIONS IN METEORITIC AND PLANETARY MATERIALS.** R. Parai<sup>1</sup>, S. Huang<sup>1</sup> and S. B. Jacobsen<sup>1</sup>, <sup>1</sup>Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, MA, USA. Email: parai@fas.harvard.edu.

**Introduction:** Calcium has 6 isotopes (<sup>40</sup>Ca, <sup>42</sup>Ca, <sup>43</sup>Ca, <sup>44</sup>Ca, <sup>46</sup>Ca and <sup>48</sup>Ca) that exhibit both mass-dependent and mass-independent isotope effects in nature. Very large mass-dependent variations have been reported in CAIs as well as smaller mass-independent effects [1-3]. Bulk chondrites also exhibit a substantial range in both mass-dependent and mass-independent effects. Among major elements, Ca is second only to O in the size and range of isotope effects displayed in meteoritic materials [4]. Smaller fractionation effects have been reported for igneous minerals, but there has also been extensive use of Ca isotopes in low-temperature geochemistry. This work all demonstrates the importance of fully exploiting the potential of Ca isotopes in the future with the best possible measurements. This lab has already demonstrated long-term reproducibility of  $\delta^{44/40}\text{Ca}$  to very high precision (Fig. 1), but there are still many problems that need to be resolved. Here we report a numerical analysis of what improvements may be achieved as a function of the mass spectrometric precision of the individual isotope ratios.



**Fig. 1** Long-term reproducibility of  $\delta^{44/40}\text{Ca}$  in NIST SRM 915a and IAPSO seawater in this lab since 2007. Two double spikes have been used.

**Ca double spike techniques:** Double spike techniques have been used [1,5-6] to correct for mass-dependent fractionation that occurs during analysis (due to instrumental fractionation and ion exchange chromatography). A mixture of two relatively pure nuclides (the “double spike”) is added to the sample. After column chemistry, purified Ca is loaded onto one side filament of a Re triple filament assembly and measured on a GV IsoProbeT TIMS. An iterative correction algorithm improved from [1,5-6] is applied to the measured values to determine sample isotopic compositions by correction for instrumental fractionation (including fractionation caused by column chemistry if the yield is not 100%). The precision that can be achieved in the corrected values

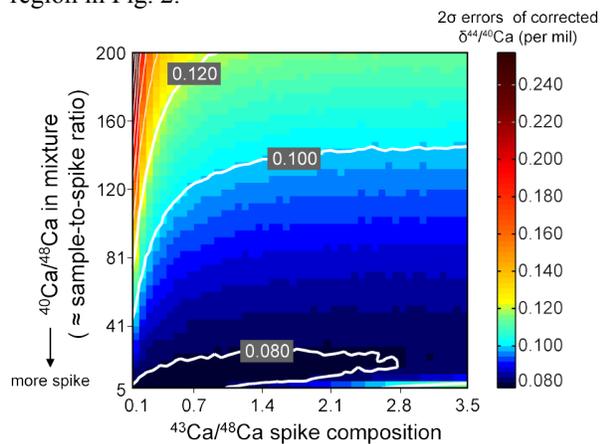
is a function of the double spike composition and the proportion of spike in the sample-spike mixture. In principle, a spiked measurement and an unspiked measurement of a given sample are required to correctly calculate  $\delta$ -values in the sample. However, the majority of Ca isotope effects in terrestrial samples are mass-dependent, since low K/Ca ratios make radiogenic <sup>40</sup>Ca excesses in general small. Consequently, some universally accepted “normal” Ca isotopic compositions have been used in the double spike correction algorithm in place of an unspiked measurement [e.g., 6]. However, Heuser et al. [6] report that calculated  $\delta$ -values are dependent on the “normal” Ca isotopic compositions selected in place of an unspiked measurement. We use a Monte Carlo model to: (1) identify optimal double spike parameters by exploring error magnification as a function of spike composition and sample-to-spike ratios, i.e., explore the precision of double spike techniques; and (2) evaluate the dependence of the calculated  $\delta$ -values on the choice of the “normal” Ca isotopic compositions, i.e., explore the accuracy of double spike techniques.

**Monte Carlo simulations:** (1) Based on the isotopic compositions of a <sup>43</sup>Ca-rich and a <sup>48</sup>Ca-rich spike, we compute isotopic ratios for a range of double spike compositions, with <sup>43</sup>Ca/<sup>48</sup>Ca ranging from 0.1 to 3.5. We then add the hypothetical double spikes in varying proportions to a hypothetical sample with isotopic composition identical to the standard NIST SRM 915a measured at Harvard [7]. For a given spike composition, we vary the proportion of spike in the sample-spike mixture to produce <sup>40</sup>Ca/<sup>48</sup>Ca in the mixture ranging from 5 to 200 (lower <sup>40</sup>Ca/<sup>48</sup>Ca reflects a higher proportion of double spike in the mixture). We simulate instrumental mass-dependent fractionation following an exponential law with a fractionation factor of 0.5 per mil per amu. We then simulate analytical uncertainty by adding normally distributed 2 $\sigma$  errors of 60 ppm, 60 ppm, 45 ppm and 28 ppm to the instrumentally-fractionated <sup>40</sup>Ca/<sup>48</sup>Ca, <sup>42</sup>Ca/<sup>48</sup>Ca, <sup>43</sup>Ca/<sup>48</sup>Ca and <sup>44</sup>Ca/<sup>48</sup>Ca ratios, respectively. The “measured” values are then run through a double spike correction algorithm using an exponential law to compute  $\delta^{44/40}\text{Ca}$  values relative to NIST SRM 915a as measured by this lab [7]. The means and 2 $\sigma$  errors of corrected  $\delta^{44/40}\text{Ca}$  values are determined as a function of spike composition and sample-to-spike ratio.

(2) To test the dependence of the corrected  $\delta^{44/40}\text{Ca}$  values on the choice of “normal” Ca isotopic

compositions, we repeat the procedure but use the “normal” values from Russell et al. [1] for the double spike correction algorithm and  $\delta^{44/40}\text{Ca}$  calculation.

**Results:** Corrected  $\delta^{44/40}\text{Ca}$  values are distributed around 0 with  $2\sigma$  errors plotted in Fig. 2. We find a broad region of parameter space that optimizes precision on the corrected  $\delta^{44/40}\text{Ca}$  (<80 ppm). The lowest standard deviation (77 ppm) is achieved with double spike  $^{43}\text{Ca}/^{48}\text{Ca} = 0.3$  and mixture  $^{40}\text{Ca}/^{48}\text{Ca} = 5$ . However,  $2\sigma$  errors of corrected  $\delta^{44/40}\text{Ca}$  values remain more or less flat throughout the dark blue region in Fig. 2.

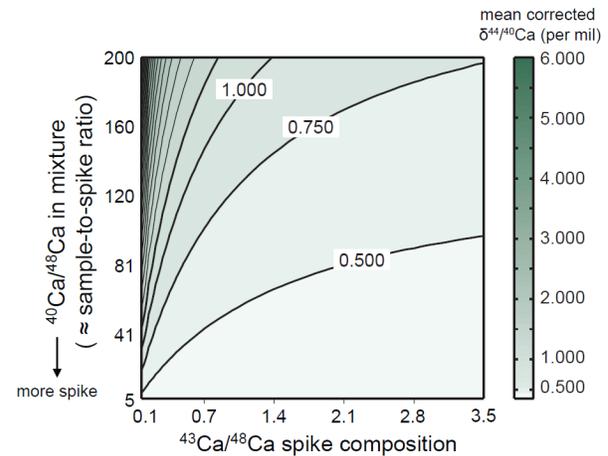


**Fig. 2.**  $2\sigma$  errors of corrected  $\delta^{44/40}\text{Ca}$  values as a function of double spike composition and sample-to-spike ratio.

The mean corrected  $\delta^{44/40}\text{Ca}$  values are within 1 ppm of 0 across the entire parameter space; that is, for all double spike parameters explored, the correction algorithm recovers the hypothetical sample isotopic composition identical to the measured [7] standard NIST SRM 915a with high accuracy. If the “normal” values of [1] are used instead of [7] in the correction algorithm, substantial offsets are generated in the mean corrected  $\delta^{44/40}\text{Ca}$  values (with  $\delta^{44/40}\text{Ca}$  calculated relative to [1]). The magnitude of the offset depends on the double spike composition and the sample-to-spike ratio, and varies between  $\sim +350$  ppm and  $+6200$  ppm in the parameter space explored (Fig. 3). Fig. 3 indicates that an unspiked run within the same lab is necessary for the double spike correction to yield accurate corrected  $\delta^{44/40}\text{Ca}$ .

**Discussion:** The accuracy and precision of the double spike technique are both dependent on how well we can correct for contributions from the double spike in the spiked sample measurement. Ideally, the double spike would not contain any naturally occurring nuclides and the measured samples would not contain any spiked nuclides, so that no double spike correction would be required and the precision of double spike

measurement would be totally controlled by counting statistics (e.g., the  $^{233}\text{U}$ - $^{236}\text{U}$  double spike for U isotopic measurement and the  $^{202}\text{Pb}$ - $^{205}\text{Pb}$  double spike for Pb isotopic measurement [8], in which the double spike nuclides are all short-lived). In contrast, in routine double spike or triple spike Pb techniques [9-10], naturally-occurring Pb nuclides are used in the spike. Consequently, removing the double spike contribution from the spiked sample measurement becomes critical, and the precision is very sensitive to the spike parameters.



**Fig. 3** Magnitude of the offset from 0 in the mean corrected  $\delta^{44/40}\text{Ca}$  if the standard values of [1] are used instead of the standard values measured within the same lab [7].

In our case, the two spiked nuclides,  $^{43}\text{Ca}$  and  $^{48}\text{Ca}$ , are both minor isotopes in natural samples (0.14% and 0.19%, respectively), and the three measured nuclides,  $^{40}\text{Ca}$ ,  $^{42}\text{Ca}$  and  $^{44}\text{Ca}$ , are at least 3 times as abundant. The region of double spike parameter space with minimal error magnification (dark blue region in Fig. 2) corresponds to sample-spike mixtures with low contributions of  $^{40}\text{Ca}$ ,  $^{42}\text{Ca}$  and  $^{44}\text{Ca}$  from the double spike and low contributions of  $^{43}\text{Ca}$  and  $^{48}\text{Ca}$  from the sample. Consequently, in this parameter space the double spike corrections are small and the precision is not very sensitive to the spike composition and the sample-to-spike ratio (Fig. 2).

**References:** [1] Russell et al. (1978) *GCA* 42, 1075-1090. [2] Simon and DePaolo (2010) *EPSL* 289, 457-466. [3] Huang et al. (2012) *GCA* 77, 252-265. [4] Huang and Jacobsen (2012) *43rd LPSC*, Abstract #1334. [5] Eugster et al. (1969) *JGR* 74, 3897-3908. [6] Heuser et al. (2002) *Int J Mass Spectrom* 220, 387-399. [7] Huang et al. (2010) *EPSL* 292 337-344. [8] Amelin et al. (2010) *EPSL* 300, 343-350. [9] Galer (1999) *Chem Geol* 157, 255-274. [10] Baker et al. (2004) *Chem Geol* 211, 275-303.