

**A NEW METHOD FOR COUPLED INVESTIGATION OF SILICON AND IRON ISOTOPES IN THE SAME SAMPLE: APPLICATION TO UNDERSTANDING ACCRETION AND DIFFERENTIATION PROCESSES ON METEORITE PARENT BODIES.** S. Ray, V. K. Rai and M. Wadhwa, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA.

**Introduction:** The condensation temperature range of the three most abundant rock-forming elements, i.e., Mg, Si, and Fe, separates the volatile elements from the refractory ones [1]. Enrichment of heavy isotopes of Mg, Si, and Fe in planetary materials has been attributed to the role of evaporation in accreting planetesimals [2-5]. Moreover, condensation from the nebula [6] and core formation [7-10] have also been invoked to explain at least the Fe and Si isotope compositions of various planetary materials. At the high temperatures expected during core formation, the fractionation of Mg isotopes between metal and silicates is expected to be negligible (e.g., [4]). However, there has been a long-standing debate about the fractionation of Fe and Si isotopes during metal-silicate equilibration.

Based on first principles, core formation and metal-silicate equilibration should be accompanied by a temperature dependent fractionation of Fe isotopes [11]. In pallasites, which are considered to be the core-mantle boundary of differentiated asteroids, heavy Fe isotope composition of metal compared to co-existing silicates and sulfides was suggested to provide evidence for Fe isotope fractionation during core formation [12]. This has subsequently either been corroborated or challenged by experiments [8-10,13,14], analyses of meteorites [15-17] and nuclear resonant inelastic X-Ray spectroscopy of multi-anvil charges [18].

Silicon, which is typically a rock-forming or lithophile element, exhibits siderophile behavior and enters the metallic phase under conditions of low oxygen fugacity, high pressure and high temperature [19-21]. Just as for Fe isotopes, mass-dependent variations in Si isotopes have been reported to be present in a variety of planetary materials. Si isotope variation is interpreted to reflect either incorporation of Si into the core of a differentiated body [7, 22-24], volatile depletion during impact processes [3], or equilibrium fractionation between forsterite ( $Mg_2SiO_4$ ) and gaseous SiO in the solar nebula [6].

It is clear from the above discussion that the Fe and Si isotope compositions of a variety of meteoritic materials have been previously reported. Nevertheless, a coupled investigation of Fe and Si isotopes in the same aliquots of the same samples has not been attempted. This is because the common method of rock digestion (for isotopic analysis of a variety of elements including Fe) involves using an acid mixture that contains HF, which breaks down the silicate

structure. However, volatile  $SiF_4$  formed during the reaction between the silicates and HF is lost, thereby precluding the measurement of Si isotopes in samples that are digested in this manner. For the analysis of Si isotopes in rocky samples, the alkali fusion method is instead the method of choice [3,6,23,25-29]. As such, typically Fe and Si isotopes have to be measured on separate aliquots of samples that may be heterogeneous on the scale of such analyses.

A coupled investigation of both Fe and Si isotopes in bulk meteorites and mineral separates could provide important constraints on processes occurring during the accretion and differentiation of meteorite parent bodies. In this study, we report a new method for the purification of Fe and Si from the same aliquots of digested and dissolved samples.

**Analytical Methods:** The samples analyzed here for Fe and Si isotopes include the Allende CV3 meteorite, and 3 terrestrial rock standards, i.e., the basalts BCR-2 and BHVO-1, and the andesite AGV-2. In addition, Si isotopes were also measured in the diatomaceous earth standard. All chemical and mass spectrometric procedures were conducted in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) at Arizona State University (ASU). To digest the above samples, ~1 mg of each of the powdered and homogenized samples was mixed with ~200 mg NaOH.H<sub>2</sub>O flakes in a Teflon beaker, and heated at ~250°C for 96 hours to ensure complete digestion. This alkali fusion technique is adapted from and modified after [30]. After a fused cake was formed, appropriate volume of concentrated HCl and Milli-Q® water was added to neutralize the alkali and make 10 ml of final solution with pH ~2.

Solutions containing ~25 µg of Si (and proportional concentrations of other elements including Fe), were loaded onto columns with 1.8 ml of AG50W-X8 (200-400 mesh) cation exchange resin. Since Si occurs as neutral or negative ions, it is not exchanged on the cation exchange resin, facilitating its elution using incremental volumes of a total 15 ml of Milli-Q® water. Elements such as Fe exist as cations in the solution and are adsorbed onto the cation exchange resin. Silicon yields for this chemical separation procedure were always better than ~99%. Final solutions of purified Si with a concentration of 1 ppm in 0.05 N HCl were made up and were used for the measurement of Si isotopes.

After elution of Si from the cation exchange resin column, another column containing 1 ml of AG1-X8

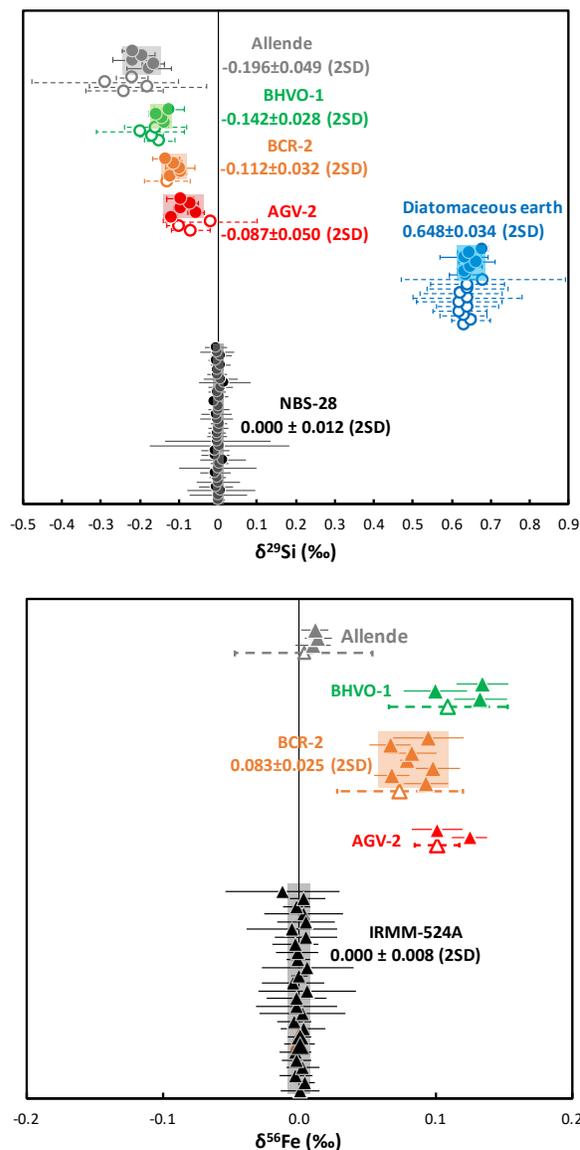
(200-400 mesh) anion exchange resin was placed under it. To elute the cations adsorbed on the cation exchange resin, 22 ml of 6N HCl was passed through it. After being eluted from the cation exchange resin, Fe gets adsorbed on the anion exchange resin placed below. Following this, the column with the cation exchange resin was removed and Fe separation procedure (modified after [31]) was carried out on the Fe adsorbed on the anion exchange resin column. Specifically, 24 ml of 6N HCl was passed through the column to elute cations (such as Na, Mg, Al, Ca, Ti, V, Cr, Ni, and Cu) followed by 14 ml of 0.5 N HCl to elute Fe. Iron yields for this separation procedure were always better than ~99%. The purified Fe was made up into a 500 ppb concentration solution in 2% HNO<sub>3</sub> for isotope measurement. The isotope compositions of the purified Si and Fe solutions were measured using the Thermo Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) in the ICGL in high- and medium-resolution mode, respectively. Isotope ratios are reported as  $\delta^{29}\text{Si}$  (parts per mil deviation of  $^{29}\text{Si}/^{28}\text{Si}$  ratio relative to the NBS-28 standard) and  $\delta^{56}\text{Fe}$  (parts per mil deviation of  $^{56}\text{Fe}/^{54}\text{Fe}$  ratio relative to the IRMM-524A standard).

**Results and Discussion:** The results of our Fe and Si isotope analyses of the same aliquots of the Allende CV3 chondrite and several terrestrial rock standards are shown (as solid symbols) in Fig. 1. For comparison, previously published data for these samples (where Fe and Si isotopes were measured in different studies and thus on different aliquots) are also shown (open symbols) in Fig. 1. The accuracy and precision of the measurements reported here demonstrate that this method can be reliably applied towards measuring the Fe and Si isotopes in the same aliquot of a given sample. We are currently in the process of measuring Fe and Si isotope compositions for several achondritic meteorites, and plan to report these.

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**Fig 1** :  $\delta^{29}\text{Si}$  (top) and  $\delta^{56}\text{Fe}$  (bottom) compositions of Allende CV3 chondrite and terrestrial standards. Solid symbols: this study; open symbols: literature data [2,12,15,22-27,29,30,32-45]. Colored boxes denote the average  $\pm 2\text{SD}$  for our data.