

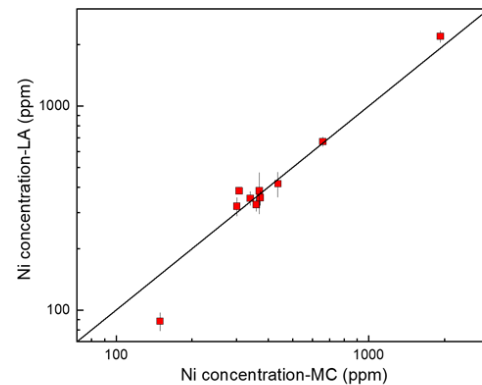
**NICKEL ISOTOPE FRACTIONATION BETWEEN METAL AND SILICATE AT SUPER-LIQUIDUS TEMPERATURE.** B. Yang, Y. Zhang, H. Ni and L. Qin. CAS Key Laboratory of Crust-Mantle Materials and Environments and CAS Center for Excellence in Comparative Planetology, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China (lpqin@ustc.edu.cn).

**Introduction:** The metal-silicate segregation was the most important differentiation event in the early solar system history for terrestrial planets and some small asteroids. Nickel almost quantitatively entered the metal phase during the differentiation. The depletion signature of Ni in the silicate phase was long been used to constrain the condition of core-mantle equilibration [1,2]. Recently, stable isotopes have emerged as powerful tools in understanding planetary formation and evolution [3,4]. If there is resolvable equilibrium Ni isotope fractionation between metal and silicate at high temperature, the Ni isotopic signatures of the silicate portions of differentiated planets would be biased from that of the bulk planets, which could be used to trace the core-mantle segregation process.

Recent studies have revealed a resolvable heavier Ni isotopic composition of the bulk silicate Earth than the chondrites [5,6], which was suggested to be a core formation signature. Nickel isotopic measurements on MG-pallasites also found that Olivines are enriched in heavy Ni isotopes compared to the metals, with  $\Delta^{60}\text{Ni}_{\text{Olivine-Metal}}$  value ranging from  $0.20 \pm 0.09\%$  to  $2.03 \pm 0.15\%$  [7]. However, experimental studies suggested no Ni isotope fractionation between metal and silicate at high temperatures [8,9]. The existing experiments were performed at sub-solidus conditions and may not reflect equilibrium fractionation. To better understand the Ni isotope fractionation during core-mantle segregation, we conducted super-liquidus metal-silicate equilibrium experiments to determine equilibrium Ni isotope fractionation factors between the two phases.

**Methods:** The super-liquidus metal-silicate equilibrium experiments were performed in a piston cylinder apparatus at the University of Science and Technology of China. The starting materials were prepared from mixtures of pure  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ , Fe and Ni powders. The samples were sealed in graphite capsules to maintain closed systems. The experiments were conducted at 1873K and 1GPa with run durations ranging from 0.5 to 8 hours. After quenching, the recovered samples were cut into two pieces, one for elemental analysis and the other one for isotopic analysis. The pieces for isotopic analysis were separated mechanically into metal and silicate fractions. The silicate fractions were crushed and possible contamination from the small metal spheres were

removed with a magnet. The major element concentrations were measured using an electron microprobe at Tongji University and the Ni concentrations in the silicate glasses were measured using an LA-ICP-MS at the University of Science and Technology of China. The Ni isotopic compositions were measured using a  $^{61}\text{Ni}$ - $^{62}\text{Ni}$  double-spike method with a Thermo-Fisher Scientific Neptune Plus MC-ICP-MS at the Hefei University of Technology.

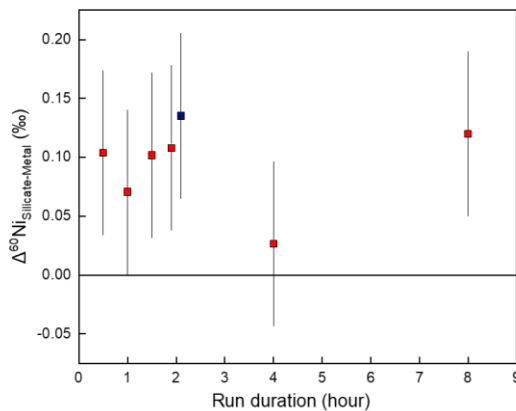


**Figure 1:** Nickel concentrations determined by two different methods.

**Results:** The Ni concentrations in the silicate glasses determined by in-situ LA-ICP-MS were compared with the bulk Ni concentrations of the dissolved silicate glasses determined by MC-ICP-MS (Fig.1). For most samples, the Ni concentrations determined by the two methods fall along a 1:1 line, which reflects the dissolved silicates of these samples free of metal contamination. Only one sample showed obvious elevated Ni concentration determined by MC-ICP-MS compared to the in-situ LA-ICP-MS measurement and this sample was excluded from further discussions. Experiments with the same starting materials but varying run durations from 0.5 to 8 hours have uniform Ni isotope fractionation factors (Fig. 2), indicating that our experiments have reached isotopic equilibrium.

The silicate phases of all our experiments are enriched in heavy Ni isotopes compared to the metal phases, with the  $\Delta^{60}\text{Ni}_{\text{Silicate-Metal}}$  values ranging from  $0.03 \pm 0.07\%$  to  $0.24 \pm 0.07\%$  (Fig. 3). The fractionation factor shows a positive correlation with the Ni

content in the metal phase, and similar observation has been reported for the Fe isotope system [10]. All our available samples have more than 25 wt.% Ni in the metal phases and the only sample with low Ni contents in the metal was excluded because of the possible metal contamination. Therefore, we linearly fitted the data in Fig. 3 and extrapolated the  $\Delta^{60}\text{Ni}_{\text{Silicate-Metal}}$  value to low Ni content in the metal. At a given Ni content of  $\sim 10$  wt.% in the metal phase, the  $\Delta^{60}\text{Ni}_{\text{Silicate-Metal}}$  value is  $\sim 0.03 \pm 0.06\%$  (95% confidence); when the Ni content in the metal phase is  $\sim 5$  wt.%, the  $\Delta^{60}\text{Ni}_{\text{Silicate-Metal}}$  value is  $\sim 0.01 \pm 0.06\%$  (95% confidence), which is unresolvable from zero.

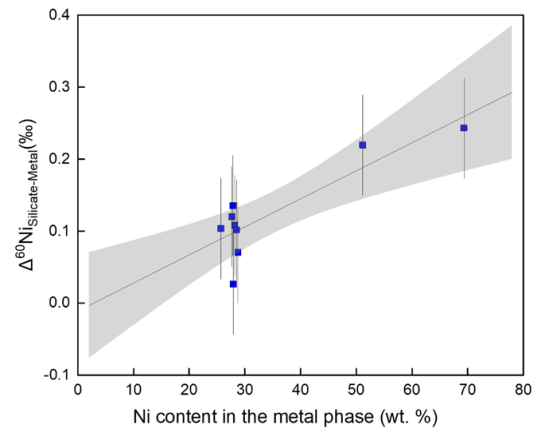


**Figure 2:** Nickel isotope fractionation factors of time series experiments.

**Discussions:** With our experimentally determined equilibrium Ni isotope fractionation factor between metal and silicate, we can evaluate the effects of metal-silicate segregation on the Ni isotopic compositions of different planetary silicate reservoirs. Our experimental conditions most approximate the core formation of asteroids. The Ni contents in the cores of most small differentiated asteroids are between 5 wt.% and 10 wt.%, indicating core formation should not have changed or just slightly have elevated the Ni isotopic compositions of their mantles. Our interpretation is consistent with recent Ni isotopic measurements on lunar samples, Martian meteorites, and eucrites, which have indistinguishable Ni isotopic compositions from chondrites [11].

However, the  $\delta^{60}\text{Ni}$  value of BSE is  $\sim 0.1\%$  lighter than the chondritic value [6], which is difficult to reconcile with our experimental results. The increased pressure under which the Core-Mantle differentiation took place [12] and different chemical composition of the Core [13] may have changed the Ni isotope fractionation factor between the two phases. Other param-

eters such as mantle heterogeneity, chondrite heterogeneity, and isotope fractionation during solar nebula condensation should also be further examined.



**Figure 3:** The relation between Ni fractionation factor and Ni content in the metal.

For pallasites, our experiments indicate that the olivine and metal in Seymchan pallasite might have reached equilibrium at  $\sim 900$ - $1100\text{K}$ , but equilibrium fractionation at reasonable temperature could not explain the Ni isotopic signatures of other pallasites [7]. Our interpretation is consistent with the Ni concentration profiles in the olivines of pallasite, which suggested that some pallasites reached equilibrium between metal and olivine phases but some did not [14].

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