Description of Ph.D. Research

During my Ph.D., my research topics covered the surface processes that shaped the early earth and early Mars, and the formation of the Moon. I use non-traditional stable isotopes as my primary tool, combing with other interdisciplinary techniques, to investigate, interrogate and solve complex questions in the realm of geochemistry and cosmochemistry.

In the beginning of my Ph.D., I explored the behavior of the Fe isotopic system in aqueous Fe oxidation-precipitation processes, for a better understanding of the mechanisms responsible for the formation of two of the most unique Fe entities involving large quantities of Fe transport: banded iron formations (BIFs) and Martian hematite spherules (MHS). Their iron sources were thought to be aqueous Fe(II) from hydrothermal vents for BIFs, and leached Fe(II) from basalts for MHS. Ferrous iron from the sources was oxidized to Fe(III), and due to the much lower solubility, Fe(III) precipitated to form BIFs and MHS. The oxidizing mechanism, since ancient Earth and Mars lacked oxygenated atmospheres, had been suggested to be either bioactivity (i.e., oxygen produced by photosynthesis of cyanobacteria [1], [2], or anoxygenic photosynthesis of bacteria [3]) or UV photo-oxidation [4], [5].

My study was focused on testing the possibility of UV photo-oxidation causing the precipitation of BIFs and MHS. Definitive evidence of life on Earth during the formation of the earliest BIFs (~3.8 Gyr) was non-existent. UV photo-oxidation mechanism, which does not involve life, had been largely ignored in literature despite the fact that ancient Earth could have allowed about 5 times more UV light than the present penetrate through the thin atmosphere and oxidize the surface. I tested the UV photo-oxidation hypothesis from two aspects: (i) Is the Fe isotope fractionation during UV photo-oxidation consistent with the isotope signature of BIFs? (ii) Is UV photo-oxidation efficient enough to oxidize such large quantities of Fe? The latter is of great importance for testing the photo-oxidation hypothesis for MHS, considering samples of MHS are not available yet for isotope measurement.

To answer question (i), I designed and performed lab photo-chemical experiments to mimic UV photo-oxidation, and measured the isotope evolution of the system. A broad-spectrum UV lamp for mimicking the early sun was used to irradiate and oxidize aqueous Fe(II) [$Fe(II)_{aq}$] to Fe(III) precipitate [$Fe(III)_{ppt}$] under anoxic conditions. $Fe(II)_{aq}$ and $Fe(III)_{ppt}$ were sampled at certain time intervals during the experiment. The samples were run through Fe chromatography and measured for Fe isotopic compositions ($\delta^{56/54}Fe$) using the MC-ICP-MS in our lab. With the isotope data, I constrained the $Fe(III)_{ppt}$-$Fe(II)_{aq}$ isotope fractionation factor during UV photo-oxidation. The factor could explain the Fe isotopic variation observed in BIFs. In addition, I measured carefully the mass-dependent isotope fractionation law (i.e., the relationship between $\varepsilon^{56/54}Fe$ and $\delta^{57/54}Fe$) of UV photo-oxidation products. The expectation was that different processes would follow a slightly different mass dependent fractionation law (e.g., [6]). If photo-oxidation was responsible for BIF precipitation, the photo-oxidation products and BIFs should follow the same law. The method has not been widely used, because these measurements examining the very small differences between two laws are very analytically challenging. Interestingly, the measured BIF sample and the photo-oxidation run products did follow the same law. This provides further evidence that photo-oxidation is consistent with BIF precipitation (the laws for microbial-involved oxidations have not been measured and could not be compared with). To further test the scenario, I collaborated with Richard Greenwood from Open University, to measure oxygen isotopes of the UV photo-oxidation experiment products. Oxygen was known to show some peculiar isotopic effects (mass-independent fractionation) during some processes involving UV lights (e.g., [7]-[9]).

If photo-oxidation produces mass-independent oxygen isotope fractionation, it would not be consistent with BIF formation, because mass-independent oxygen isotopes have not been observed in BIFs. We did not observe mass-independent oxygen isotope fractionation in the photo-oxidation products, substantiating that UV photo-oxidation is a possible mechanism accounting for BIF precipitation.

To answer the question (ii), I created a mathematical model to calculate rates and timescales for photo-oxidation of Fe in lakes with various depths. Photo-oxidation rate of Fe is a function of many parameters, such as Fe(II) concentrations, water depths, UV wavelengths and flux, Fe speciation, Fe molar absorptivity and quantum yield. My model aimed to be more realistic than previous models by using more accurate values for the parameters (e.g., I used the quantum yield determined in my experiments) and by taking into account the details that could affect the result such as solar incident angle, the distance of Mars from the Sun, water pH change as Fe gets oxidized, diurnal effect and so on. As a result, more realistic timescales were obtained (For example, it would take ~40 years to oxidize the Fe(II) in a lake with a depth of 100 m in my model vs. 50 days obtained in previous calculations). This model suggested that photo-oxidation could be very effective, compared with the normal lifetime of a lake and with the timescale of oxidation by oxygen (due to the low oxygen content of Martian atmosphere, oxidizing a lake could be extremely slow). The main conclusion of the work was that photo-oxidation was a viable oxidation mechanism to form BIFs and MHS. This work was published in Earth and Planetary Science Letters [10].

After studying the UV photo-oxidation mechanism, I was excited to learn more about the detailed MHS formation processes, i.e., how was Fe transferred from the source (presumably basalts) to eventually form hematite spherules. Since MHS were not available, I studied a terrestrial analogue, hematite spherules and associated lithologies from Hawaii, using Fe isotopes and elemental concentrations. I compared various types of alteration the Hawaii samples experienced (acid-sulfate alteration, low-T and high-T hydrolytic alteration, and hydrothermal alteration under neutral to basic condition) and found that acid-sulfate alteration was the only process among them that could effectively leach Fe from basalts. The Fe isotope fractionation factor during acid-sulfate alteration was constrained very precisely for the first time by looking at rock slabs from a heterogeneously altered basalt. Furthermore, by studying the Fe isotopes of acid-sulfate altered rocks, tephras, and individual hematite spherules, the detailed hematite formation processes of Fe leaching, transport, mixing, precipitation and enrichment were reconstructed. The work provides valuable insights into MHS formation, and a prospective study for the future returned Martian samples. This work is currently in revision.

Using Fe isotopes to trace detailed geological processes is sometimes limited by our knowledge of the equilibrium Fe isotope fractionation factors between different phases. For example, the study above on the reconstructing of hematite formation processes suffered from the lack of the knowledge of the exact equilibrium fractionation factors between Fe phases such as Fe oxides. Therefore, I initiated a project to precisely constrain equilibrium Fe isotope fractionation factors between several common rock-forming minerals (garnet, ilmenite, biotite, plagioclase and tourmaline). Constraining equilibrium fractionation factors is fundamental in isotope geochemistry but is far from straightforward, and studies using different methods sometimes give contradicting results. Equilibrium fractionation factors are normally constrained using four methods: (i) measuring natural minerals that are in isotope equilibrium at known temperatures, (ii) measuring the isotopic compositions of lab experimental run products where two phases are allowed to exchange isotopes to reach equilibrium, (iii) measuring the strength of the bonds in phases by

NRIXS (Nuclear Resonant Inelastic X-ray Scattering spectroscopy), and (iv) ab-initio calculations. Natural minerals generally involve equilibration over longer timescales, so they can more closely approach equilibrium than phases in lab experiments, but the exact equilibration temperatures are usually unknown (equilibrium isotope fractionation is a function of temperature). The NRIXS method is relatively new and more studies are needed to ascertain its reliability. Ab-initio calculations may suffer from systematic biases.

I planned my study such that accurate equilibrium fractionation factors between minerals could be obtained, and meanwhile, the consistency among different methods could be tested. In my study, a unique metamorphic rock (a schist) from Mt. Moosilauke was selected, because the minerals were in chemical equilibrium and the metamorphic condition was precisely at aluminosilicate triple point (i.e., the temperature and pressure were well known; [11]). I crushed the rock, carefully picked the cleanest minerals individually under a microscope (which took me about a month since minerals intergrew during the metamorphism), measured the Fe isotopic compositions and calculated the equilibrium fractionation factors between them. To confirm that the obtained factors reflected equilibrium isotope fractionation, I performed NRIXS measurements at Argonne National Lab to obtain the factors independently, and also collaborated with a colleague at U of Chicago who does ab-initio calculations to obtain the theoretical fractionation factors. Through the comparison among the three methods, I was able to constrain very precisely the equilibrium isotope fractionation factors that were not available before, and to test the reliability of each method. The work is in preparation for a peer-reviewed journal, and it will be useful for future Fe isotope studies in that it provides fundamental equilibrium isotope fractionation data for Fe isotope interpretations and presents methods for obtaining accurate data.

Another dream of mine during my Ph.D. was to investigate the Moon formation. Although the giant impact hypothesis is very good in explaining many features of the Moon, there remain questions concerning the hypothesis. One of the most outstanding questions is regarding the volatile element depletion of the Moon. The Moon is very similar to the Earth in concentrations and isotopic compositions of refractory elements, but has very low contents of volatile elements such as Zn, K and Rb (depletion by a factor of ~5). This volatile element depletion has been considered to be due to volatile loss during the giant impact [12]-[14]. However, the isotopic compositions of these volatile elements in the Moon do not match quantitatively the extents of volatile loss based on evaporation theories, and the specific temperature and pressure conditions under which the Moon lost its volatiles are to a large extent unconstrained. To better understand the processes, I decided to investigate the Earth-Moon system using a novel isotopic system, Rb, for that Rb is volatile and very sensitive to volatilization, and that it makes a good comparison with the recently reported K isotopic system in the Earth-Moon system [13] due to the very similar chemical behaviors of the two elements. Developing the separation and isotope measurement method of Rb was a major challenge, and not much work had been done for Rb isotopes. Rubidium is a trace element and behaves very similarly to K, separating it from major elements especially from K is extremely difficult. For the past several years, in parallel with the Fe projects above, I have been experimenting with various types of resins and performing numerous analytical tests to determine the best way to achieve pure Rb separation. I was able to develop two methods, and both methods yielded same results in high data quality. My methods also allow for complete K separation from the same samples. Rubidium separation is much more painful and time-consuming compared with chromatography for other elements, and therefore the work is still ongoing, but is in its final stage and will be finished in one or two months.

Directions of Future Work

The Rb isotopic system is very recent and emerging, and not much data has been reported. Alkali metals such as K and Rb have been of great interests to scientists since very early but studying of them has been limited by analytical techniques. For my postdoc research, I would like to take advantage of my newly developed method, to measure correlated Rb and K isotopes (the two elements make a unique and powerful pair) in other planetary bodies, and to compare with that of the Earth-Moon system, for a better understanding of the universal volatile element depletion signature among terrestrial planetary bodies (see the Research Plans). Another future direction I am interested in pursuing is to apply the two elements to paleoclimate records, as they are both very sensitive to weathering. The two isotopic compositions are likely to vary with weathering intensity, and can provide insights into different geological and even biological processes with respect to paleoenvironmental change.

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