Subject offered for a contract starting October 2016

SUBJECT TITLE: Dating volatile element depletion in the early solar system using Sr isotopes

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Presentation of the subject: Despite the key role that volatiles play in understanding the evolution of the terrestrial planets, the origin of volatile elements has been a central problem in Earth sciences and is at the core of many current investigations. The major difficulty is that the terrestrial planets formed in the inner solar system close to the young Sun where temperatures were theoretically too high (>1000K) for volatiles to condense. Thus, explaining the presence of volatiles in the inner solar system remains a subject of intense debate, dominated by two competing theories. It has been proposed that the Earth accreted without volatiles (the "dry" Earth hypothesis), and that the present-day inventory of volatiles were brought to Earth after the main stage of planetary accretion and differentiation (i.e. 100-200 Myrs after the formation of the solar system). An alternative explanation is that the volatiles were added to the Earth early, during the main stage of planetary formation, and that the Earth accreted "wet" (e.g., Ringwood 1979, Drake and Righter 2002).

Distinguishing between the hypotheses for the origin of volatile elements in planets requires a detailed knowledge of the timing of volatile addition and depletion. An early (<1 Myr) age would suggest a nebular event, while a later age would indicate a planetary event. The ^{87}Rb-^{87}Sr radioactive decay system (half-life = 4.88×10^{10} years) is one of the best-suited systems for studying the fine-scale relative chronology for volatile element depletion. Rubidium is more volatile than Sr and, during volatilization events, Rb and Sr are fractionated leading to volatile-poor samples with very low Rb/Sr ratios. However, in such samples the precision on the slope is not good enough to use the classical isochron approach for chronological dating. On the other hand, the initial ^{87}Sr/^{86}Sr ratio (the intercept of the isochron with the y-axis) can be determined with a high precision, and for more than four decades (Gray et al., 1973; Papanastassiou and Wasserburg, 1969; Podosek et al., 1991) high precision determination of initial ^{87}Sr/^{86}Sr ratios have been translated into evolutionary timescales using models for ^{87}Sr/^{86}Sr evolution. This chronology, using the initial ratio, depends on the Rb/Sr ratio assumed for the solar system (i.e. the Sun), which is the main source of uncertainty and limits the use of this system to date the volatile element depletion in solar system materials. Since it is impossible to directly measure the Rb/Sr ratio of the Sun precisely, an alternative way must be found.

In this thesis, we will use an original approach of measuring the Rb/Sr of the Sun via the analysis of solar wind implanted at the surface of ilmenites present in lunar regolith material. Because the Moon has no atmosphere and its surface is covered by a fine-grained regolith that is well gardened by meteorite impacts, lunar soils contain a high abundance of implanted solar wind that can be directly analyzed. It has already been shown that the lunar regolith records the history of solar wind irradiation for rare gases (Becker and Pepin, 1989; Frick et al., 1988; Kerridge, 1993; Wieler et al., 1996), Li (Chaussidon and Robert, 1999), O (Hashizume and Chaussidon, 2005; Ireland et al., 2006), C (Hashizume et al., 2004), N (Hashizume et al., 2000), and Cr (Kitts et al., 2003). We will focus on the measurement of the Sr isotopic composition of the surface layers of ilmenite grains from lunar soils to obtain the Sr isotopic composition and Rb/Sr ratio of the solar wind and of the Sun. Our approach is to determine the Rb/Sr ratio of the Sun by simply measuring the Sr isotopic composition of the solar wind as well as the Rb and Sr abundances to correct for ^{87}Rb decays. The strength of this approach is that we do not have to correct for elemental fractionation between the Sun and the solar wind, and possible isotopic fractionation will be corrected by normalizing the isotope ratio to ^{88}Sr/^{86}Sr. In addition, we will use surface etching experiments to separate possible surface contamination from the solar wind implantation based on the fact that solar wind is implanted at a different depth.

The ^{87}Rb–^{87}Sr system involves relatively rapid growth of the radiogenic daughter isotope, yet the disparate geochemical characteristics of Rb and Sr can lead to the formation of Rb-poor phases that essentially record their initial ^{87}Sr/^{88}Sr. Chronology using this initial ratio depends on the Rb/Sr ratio assumed for the solar nebula. If one assumes that the CI chondrite ratio represents the solar nebula (Rb/ Sr = 0.35, or ^{87}Rb/^{86}Sr = 0.85, in the early solar system), the generation of radiogenic ^{87}Sr leads to isotopic compositional growth in ^{87}Sr/^{86}Sr of 0.000013 Ma^{-1}, or about 0.17 ε-unit Ma^{-1}. On the other hand, if one uses the (non-precise) Rb/Sr ratio of the solar photosphere (^{87}Rb/^{86}Sr = 2.48; most recent value from Asplung et al. 2009), the ^{87}Sr/^{86}Sr compositional growth is about 0.50 ε-unit Ma^{-1}. Because the parent element Rb is relatively volatile, and the daughter element Sr is quite refractory, some materials formed in the early solar system are characterized by extremely low Rb/ Sr, as much as four orders of magnitude lower than chondritic materials. In such materials the in situ growth of radiogenic ^{87}Sr over the age of the solar system is small, and so initial ^{87}Sr/^{86}Sr—the ratio in the material from which the Rb-poor, Sr-rich phase was extracted—can be precisely calculated from the measured ratio (Minster et al. 1982; Papanastassiou & Wasserburg 1969; Podosek et al. 1991).

The target substrate will be ilmenite, the mineral in which indigenous Sr is expected to be the lowest. Some lunar regolith sanples, such as 71501 are good candidate for this work (>1 kg total mass, 8% modal ilmenite and an exposure age of 1Ga with high concentrations of solar noble gas implantation; Nichols et al. 1994). The project will start with preparation of leachates from of 71501 ilmenites to refine our analytical protocols. During these tests we will develop the appropriate chemical procedure to etch ilmenite to an average depth of around 0.1 μm, i.e. the characteristic depth in which implanted solar wind resides. This pilot study should also allow for the identification of sample(s) best suited for the full-scale study. We will follow the same approach as described in our previous paper Wang et al. 2012.

One of the objectives of the pilot study will be to determine how much starting material is needed for the full-scale study. We should be able to conduct a successful study on 1 to 3 g of the ilmenite-rich Apollo 17 soils. Using the data from previous work on Cr isotopes study of solar wind implanted in the lunar regolith, we can do a first order estimation of the amount of solar Sr and Rb expected in 1g of regolith by using the relative amount of Sr and Rb compare to Cr. Such estimate yield ~50 ng of Sr and 15ng of Rb. 50ng of Sr is the typical quantity used in high precision MC-ICP-MS and TIMS analysis (50 ppm 2σ precision on the ^{87}Sr/^{86}Sr ratio). Therefore 1-3g of Apollo 17 soils will be enough to obtain very precise measurements with no blank problems (typical Sr blank <0.1 ng).

If a single-stage model of growth in a high-Rb/ Sr reservoir followed by extraction into a low-Rb/Sr reservoir is correct, the time of the assumed chemical differentiation event can be determined from calculated initial ^{87}Sr/^{86}Sr. Following this logic, it has been calculated that Rb/Sr fractionations occurred ~14-16 Myrs (if using the CI Rb/Sr value) after Solar System formation (*e.g.* Minster et al. 1982). This is in disagreement with other radiometric systems such as Mn-Cr, which give younger ages of about 4 Myrs (*e.g.* Trinquier et al. 2007). We have recently found that Sr isotopes were not homogeneously distributed (Moynier et al. 2012) and that refractory inclusions have a ε^{84}Sr deficiency when normalized to ^{88}Sr/^{86}Sr compared to other planetary materials (especially the volatile-poor eucrites from 4-Vesta, as shown in Figure 1).

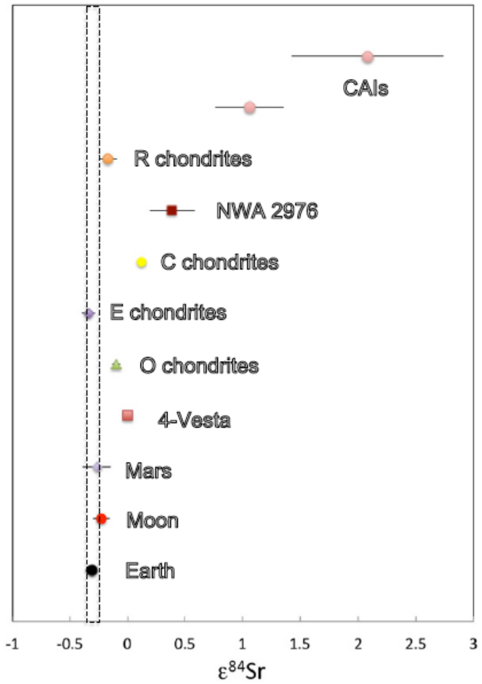

Figure 1. $^{84}Sr/^{86}Sr$ values for different solar system materials. The isotope ratio is expressed in ε per 10,000 units after internal normalization to the $^{88}Sr/^{86}Sr$ ratio and to the standard SRM987. Figure from Moynier et al. (2012).

The heterogeneous distribution of Sr isotopes may indicate that variations in the initial $^{87}Sr/^{86}Sr$ of early solar system materials reflect some isotopic heterogeneity instead of having a chronological significance, as previously interpreted. For example, given the differences in $^{84}Sr/^{86}Sr$ between calcium- and aluminum-rich inclusions and eucrites ($\varepsilon^{84}Sr > 2$), the difference in age between these materials would be ~ 6 Ma shorter (if using the precise CI value) than previously interpreted. This age is in better agreement, but still too young, when compared to other chronometers (*e.g.* Trinquier et al. 2007). The discrepancy between Rb-Sr ages and other chronometers might come from the Rb/Sr ratio assumed for the solar system.

A better-founded value for solar (nebular) Rb/Sr is therefore crucial to a comparison of timescales based on evolution of initial $^{87}Sr/^{86}Sr$ against timescales based on other approaches, *e.g.* decays of short-lived radionuclides and therefore estimate the timing of the volatile element depletion.

In addition, a recent re-investigation of the Rb-Sr ages of early solar system materials (Hans et al. 2014) found that refractory inclusions (All), angrite meteorites (Ador) and eucrite meteorites (BABI) share quasi-similar $^{87}Sr/^{86}Sr$ initial ratios, which is at odd with previous work. We will therefore use the method developed in this project to analyze a variety of early solar system materials, including CAIs, angrites and eucrites for Rb-Sr ages. Since our previous work show that Sr isotopes are heterogeneously distributed we will also analyze the unspiked ^{84}Sr abundances to correct for the isotopic anomalies.

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In summary this PhD thesis will focus on:

1. Measure the Rb/Sr of the Sun via the implanted solar wind at the surface of the Moon
2. Establish the initial Sr isotopic composition of solar system objects
3. Investigate volatile loss and addition mechanisms during solar system formation.

Context of this project at IPGP:

-The IPGP has been one of the first laboratory in the world to develop Rb-Sr chonometry, 50 years ago for the return of the Apollo samples (e.g. Birck and Allegre, 1972; Birck et al. 1975), however this competence has been more or less lost and though this project we will re-instate this method at IPGP and will improve the method trough the determination of the solar Rb/Sr ratio
-Through this PhD thesis we will develop high lever competence in dating methods (principally Rb-Sr, but also Sm-Nd) on small samples that can also be used in geology, but also in the context of future return mission of lunar and martian samples.