Lu-Hf Chronology in Chondrites and the Role of Phosphates.

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Introduction: The ^{176}Lu-^{176}Hf isotopic system is extensively used for dating cosmochemical and geological processes, and for studying planetary evolution. However, two uncertainties in the Lu-Hf systematics need to be sorted out. First, there are hints of apparently faster decay of ^{176}Lu in the early Solar System compared to the well established decay rate of this nuclide. Recent direct-counting experiments and age comparisons performed on terrestrial geological objects gave similar values for λ^{176}Lu ("terrestrial" average of ~1.864-1.867 x 10^{-11} [1-5]), whereas the values obtained on chondrites and achondrites are higher ("meteoritic" average of ~1.95 x 10^{-11} [6-8]). Various processes have been proposed to explain this discrepancy, such as astrophysical processes that may have occurred only at the beginning of the solar system (e.g., irradiation by, γ-rays and cosmic rays [9,10] and branched decay of ^{176}Lu [11]). Whether such irradiation event indeed occurred or not still remains to be tested [12].

Second, unlike the well constrained Sm/Nd value to within 2% for chondritic uniform reservoir (CHUR) [5,13], the Lu/Hf ratios in chondrites vary up to 18% [2,5], hence the CHUR value for Lu/Hf is hard to constrain. This problem have been addressed by Bouvier et al. [14] who suggested that only type 3 chondrites with lowest metamorphic grade should be used to determine the Lu decay constant and the CHUR values. They proposed a more precise estimation of the CHUR values within 3% and a new Lu decay constant of 1.884 ± 0.060 x10^{-11}, which is intermediate between the "terrestrial" and "meteoritic" values and has a large uncertainty. Meanwhile, the discrepant "meteoritic" λ^{176}Lu remains unexplained.

In order to better understand the Lu-Hf systematics of chondrites, we analyzed various mineral fractions from the Richardton H5 chondrite to construct an internal Lu-Hf isochron. The different fractions have been obtained by magnetic separation after sieving. Lu and Hf have been chemically purified at the Université Libre de Bruxelles using the procedure described in [15], without any leaching. Hf cuts and spiked Lu and Hf cuts have been measured at ULB on Nu-Plasma MC-ICP-MS equipped with a DSN-100 desolvating nebulizer.

Results: The isochron yields an age of 4647±210 millions years (Ma) (MSWD= 9.4) (Fig. 1). Low precision is caused by relatively small spread the ^{176}Lu/^{177}Hf ratios from 0.02 to 0.05, and by scatter of the data points exceeding analytical uncertainty.

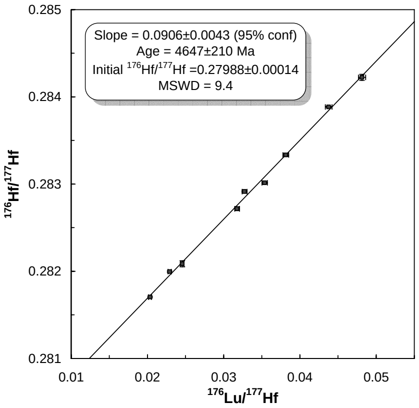

Figure 1: Lu-Hf isochron diagram obtained on nine fractions of Richardton, using λ^{176}Lu=1.867 x 10^{-11} [16]. Error bars are 2σ.

Discussion: The age of 4647±210 Ma agrees, within its large uncertainty limits, with the currently accepted age of the solar system. The slope of our isochron is also consistent with the slope of the Lu-Hf isochron defined by multiple fractions of phosphate minerals apatite and merrillite from the Richardton meteorite [4]. Combining all the fractions from the two studies yields a slope of 0.08855±0.00072, similar but more precise than obtained with each data set separately. Richardton phosphates show an extreme variation of the ^{176}Lu/^{177}Hf ratios from 0.8 to 143 [4]. This large variation range, compared to the range obtained in the present study, identifies the phosphates as a major host of Lu, and hence their key role in the Lu-Hf isotope systematics of chondrites and other meteorites.

Calcium phosphate minerals are common accessory minerals in both chondrites and achondrites that concentrate parent elements of several isotopic chronometers: Lu, Sm, U and Th. An important difference between the role of phosphates in the Sm-Nd systematics, on one hand, and Lu-Hf and U-Th-Pb, on the other, is that the phosphates effectively exclude Hf and Pb during crystal growth, and are similar in these sense to the "classical" geochronometer mineral systems such as U-Pb in zircon, and Rb-Sr and K-Ar in mica. Sm and Nd in phosphates are, however, only moderately fractionated from the silicate minerals [13,17,18].

Extreme fractionation between parent and daughter elements by phosphates in the Lu-Hf and U-Pb systems can be either beneficial or detrimental for isotopic dating, depending on whether the phosphates remained closed to diffusion. By increasing spread of the Lu/Hf ratios, this fractionation helps to obtain precise ages using the isochrons that contain phosphate minerals with very high Lu/Hf ratios, silicate minerals with moderate to low Lu/Hf ratios, and possibly oxide minerals (ilmenite and spinels) with very low Lu/Hf ratios. But it was also suggested that the presence of phosphates can induce poor reproducibility between duplicates for in Lu-Hf measurements [5,7,14].

Apatite has substantially higher diffusion rates of elements such as REE [19] and Pb [20] than most silicate minerals that comprise meteorites. It can, therefore, become open to diffusion under metamorphic conditions and lose accumulated radiogenic Hf and Pb. As a result, the phosphate Lu-Hf age would be decreased, and the radiogenic Hf would be captured by another mineral, or remain in the fine-grained interstitial material. Isotopic systems of the minerals with low Lu and Hf concentrations, such as plagioclase and olivine, should be more susceptible to gain of radiogenic Hf than relatively Hf-rich pyroxene and oxide minerals. This is consistent with interpretation of Sm-Nd isotopic exchange between phosphates and silicate minerals in achondrites [21] that indicated that the ^{143}Nd/^{144}Nd ratios in plagioclase can be elevated due to such exchange, while the mafic minerals are unaffected.

The magnitude of the Hf isotopic disturbance due to loss of radiogenic Hf depends on Lu concentration in the phosphates, Hf concentration in the potential acceptor minerals, time gap between phosphate crystallization and closure of Lu and Hf diffusion, conditions of metamorphism, crystal sizes of phosphate and the acceptor mineral, and spatial relations between the latter. A meteorite containing small phosphate grains closely intergrown with plagioclase and olivine would yield younger apparent phosphate Lu-Hf ages and show larger complementary excesses of ^{176}Hf in plagioclase and olivine. Analysis of phosphate crystals separated from coarser-grained meteorites will yield more reliable ages than an attempt to extract tiny phosphate grains closely intergrown with silicate minerals by selective acid dissolution. On the other hand, small grain size of phosphates in chondrites of low metamorphic grade is beneficial for determinations of the composition of CHUR, because it reduces the spread of Lu/Hf between the specimens caused by uneven occurrence of phosphate grains [11, 13].

Combined Lu-Hf and U-Pb study of the same phosphate minerals is an effective tool for diagnostics of complicated Lu-Hf isotopic systematics. Loss of radiogenic Hf is likely to be accompanied by loss of radiogenic Pb, which would be expressed in lowering of the ^{207}Pb/^{206}Pb (if it was an ancient event), and in discordance of the U-Pb system. Combined U-Pb and Lu-Hf dating is most straightforward for the mineralogically pure hand-picked phosphates, but may be attempted by selective acid leaching of meteorites containing dispersed fine-grained phosphates, if other acid-soluble minerals can be removed by some other treatment that does not break down the phosphates.

Two additional pieces of information are required for accurate interpretation on the role of phosphates in Lu-Hf systematics of meteorites:

1) Experimental data for diffusion Hf (or Zr) in apatite apparently do not exist. There are also no experimental diffusion data at all for merrillite and silico-apatite. It is commonly assumed that the diffusion rates of various elements in these minerals are similar to those in apatite, but this is not necessarily so considering compositional and structural differences.

2) Detailed mineral inventory of Lu and Hf, including fine-grained interstitial minerals if present, has to be determined in every chronological study. The sum of the element contents determined from concentrations in the minerals and abundance of the minerals in the rock must match the directly measured whole rock concentration (the mass balance check).

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