Causes of Extraterrestrial Non-Mass-Dependent Isotope Fractionations

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Isotope fractionation refers to any physical or chemical process that results in differing abundances of isotopes. In most natural environments, isotope abundances can be explained by kinetic processes, which are unidirectional in reactions, or isotopic exchange reactions which are a result of differences in the zero-point energies of different isotopes. Both are referred to as mass-dependent fractionation because the relative differences in isotopic abundances scale with the differences in the mass of the isotopes. While Urey[1] and Bigeleisen and Mayer[2] provided a quantitative description for the mass dependence of isotope effects associated with equilibrium isotope effects, there are certainly cases that do not follow the regularities of mass-dependent fractionation. In one of the most prominent examples, Fujii et al[3] found that the fractionation of uranium in different oxidation states during isotope exchange reactions went far beyond what was expected based on mass differences. Bigeleisen[4] found that for U isotope fractionation, the size and shape of the nucleus on the electrostatic potential were similar in magnitude to the observed U isotope fractionation. This anomalous behavior was also observed in other heavy elements such as molybdenum[5]. Processes that exhibit isotope fractionation that is anomalous with the results expected from the previously described mass-dependent effects are referred to as non-mass-dependent or mass-independent fractionation.

These processes are overwhelmingly rare, and as such, are not well understood or documented. In fact, while mass-independent processes have been observed in stratospheric ozone[6] and by bacteria[7], the first nonnoble gas observation of a mass-independent isotopic ratio was seen in the oxygen isotopes found in a meteorite known as the Allende meteor. This led to a burst of research into the isotopic compositions of various meteorites and for other elements. Except for a few exceptions, bulk isotopic fractionations were generally attributed to nucleosynthetic origins[8]; these variations were hypothesized to arise from incomplete homogenization of isotopes after nucleosynthetic processes in the early universe.

Some isotopic anomalies could not be accounted for with nucleosynthetic processes[9]. Thiemens and Heindrick[10] discovered non-mass-dependent isotopic fractionation of oxygen, indicating that isotopic anomalies could have chemical origins instead of nucleosynthetic. Furthermore, it has been suggested that parts of the anomalies observed for heavy elements may have origins arising from nuclear field shift effect[11].

Nuclear field shift (NFS) effects arise from the differences in nuclear sizes and shapes of isotopes. The nuclear size and shape affect the minimum point of the vibrational frequency, which varies between isotopes and therefore results in an isotopic effect; as such, it is also called the nuclear volume effect or nuclear size and shape effect in literature. While it is sometimes

convenient in equilibrium isotope fractionation theory to imagine the positive charge on an atomic nucleus as an infinitesimal point, it is actually spread over a finite volume of space, with a radius ranging that electrons interact with. As such, the electron is not bound as strongly to a true, finite-volume nucleus as is predicted when assuming a point-charge nucleus. In other words, the electrostatic potential binding an electron to a nucleus is higher (weaker) for a larger nucleus than for a smaller nucleus. This is illustrated in Figure 1.
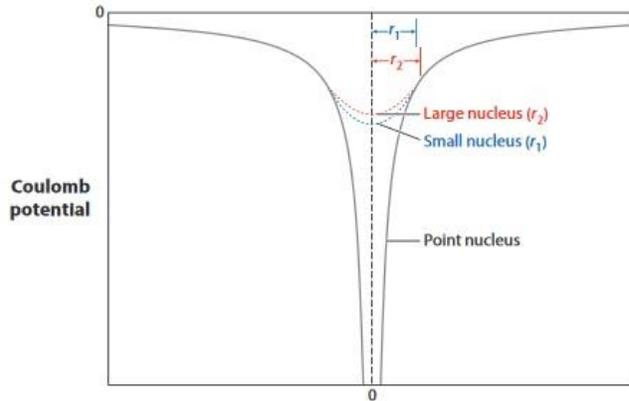

Figure 1. Electrostatic po tential binding of an electron to a nucleus. It is higher for a larger nucleus than a smaller one[6].

The total equilibrium isotope fractionation equation, which describes both conventional mass-dependent and NFS, can be simplified using standard epsilon notation.

$$\varepsilon = \left(\frac{hc}{kT}\right) \times \delta\left(r^2\right) \times A + \frac{1}{24}\left(\frac{h}{2\pi kT}\right)^2 \times \left(\frac{1}{m_1} - \frac{1}{m_2}\right) \times B$$

Where m_1 = light isotope, m_2 = heavy isotope, T = temperature, k = Boltzmann constant, h = Planck constant, c = velocity of light. A and B are constants that describe NFS effect and conventional mass dependent effects. $\delta\langle r^2 \rangle$ is the difference in the mean-square charge radius between the two isotopes.

The introduction of NFS theory, combined with the almost simultaneous advent of higher precision isotopic analytical techniques, fueled several observations and ab initio calculations of non-mass-dependent isotopic fractionations in laboratory settings. NFS effect isotopic fractionations of lighter elements has also been found in natural settings. The NFS effect becomes a major source of fractionation for heavy elements in nature (Z>80) and so they are of special interest in meteorites, for which understanding the causes of isotopic anomalies may reveal something about planetary or nebula chemistry.

Because nucleosynthesis alone could not account for the isotopic fractionation of all elements on meteorites such as tellurium on the Allende meteor, scientists turned to NFS to explain the anomalies in heavy elements seen. For example, Moynier et al.[12] fit isotopic variations of tellurium in Allende CAIs to the NFS effect as opposed to the prevailing nucleosynthetic models and found a better normalization. They hypothesized that this meant isotopic anomalies may have come from NFS effects during accretion of sulfides from the solar nebula as opposed to a record of nucleosynthetic origins.

Additionally, more recent work has applied NFS effects to troilite (FeS) inclusions in meteorites and were the first reported non-mass-dependent variations in Fe for material formed in the early solar system outside of some Ca-Al-rich inclusions in primitive meteorites. While they found that NFS provided a slight better trend to the data for the $^{58}Fe/^{56}Fe$, the resolving abilities for these two proved impossible to differentiate[13]. Further calculations by Fujii and Albarede[14]

also indicated that NFS effects associated with redox processes are significant for silver isotopes and that the reliability of literature values on meteorites should be questioned and reexamined.

While there have been promising results in identifying causes of extraterrestrial isotopic anomalies, many of the current research is limited. Many results could be a combination of both nucleosynthetic origins and the NFS effect. There remains more to be done in identifying the causes of unusual isotope fractionation in both cosmological sources and in terrestrial—do anomalies originate chemically on meteorite parent bodies or were they from materials in the protoplanetary disks? Future research dedicated to enhancing our understanding of the physical chemistry of field shift theory would also allow us to better understand the origins of the meteoric anomalies.

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