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Isotope/element fractionation during surface adsorption

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The adsorption of ions onto mineral surfaces accompanies isotope/element fractionation in planets and asteroids. A model based on simple classical physics is presented to predict these fractionations. The agreement between the experimentally observed isotope/element ratios and their predicted values is found to be excellent. This fractionation can be demonstrated experimentally in advanced physics laboratories using macroscopic particles. The success of the model shows students that even a very complex naturally occurring process can be explained quantitatively with simple physics.

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I. INTRODUCTION

The various isotopes of an element have slightly different physical and chemical properties because of their mass differences. Such differences can manifest themselves as a mass-dependent isotope fractionation effect.[1] For elements of low atomic numbers, these mass differences are large enough to fractionate the relative proportions of different isotopes of the same elements in various compounds. As a result of the fractionation process, substances often develop unique isotopic compositions (ratios of heavy to light isotopes), which may indicate their source or the processes that formed them. In general, chemical reactions, phase changes, and diffusion bring about isotope/element fractionation. During adsorption of ions onto charged surfaces such as clay minerals, a mass-dependent fractionation has been observed[2] for molecules[3] and isotopes,[4,5] but the theoretical basis of it is understudied due to the complexity of the process.

We will derive a simple equation for the isotope/element fractionation due to the adsorption process in geological systems. This process can be demonstrated experimentally in advanced physics laboratories using macroscopic particles.

II. MODEL

In the liquid phase in natural systems such as soil solution, ground and ocean waters, and fluid inclusions of rocks, there are many dissolved ions which make the system electrolytic. Generally, these are colloidal solutions with dissolved organic matter and clay minerals that have surface charges. In these systems, the ions and polarized molecules are attracted and adsorbed by the charged solid surfaces, showing electrophoretic mobility due to their movement in electric fields. Electrophoresis is a process of separating ions and charged molecules from a similar mixture. In the laboratory, this separation is achieved by passing a current through a medium containing the mixture, and each kind of ion or molecule travels through the medium at a different rate, depending on its electrical charge and size. Electrophoresis also can occur in natural systems.

This process forms an electrical double layer on the adsorption surface. The force F on an ion of charge q exerted by an electric field of intensity E is given by $F=qE$. This force accelerates an ion until it is balanced by the frictional forces due to the viscosity of the medium. The frictional force for a spherical ion in a liquid is given by Stokes' law, $F=6\pi r\eta v$, where η is the viscosity of the medium and r and v are the radius and velocity of the ion, respectively.[6] If we equate the two forces, we obtain

$$v=\frac{Eq}{6\pi r\eta}. \tag{1}$$

Thus, for a particular liquid phase, $v\propto q/r$. In systems with adhesive contacts between the ions and molecules, the frictional force is proportional to the surface area of the ion, which is in turn proportional to r^2 (see the Appendix). Then the proportionality becomes

$$v\propto\frac{q}{r^2}. \tag{2}$$

In these systems, ion exchange reactions take place constantly on the charged surfaces. In order to absorb mobile phase ions onto the adsorption surface during the reactions, they should penetrate the electrical double layer and replace the immobilized ions on the surface. This process is determined by the kinetic energy of the mobile ions. Consider two ions with masses m_1 and m_2, radii r_1 and r_2, and electrical charges q_1 and q_2. Because the velocities in Eq. (2) are proportional to q/r^2, the kinetic energies of these ions, K_1 and K_2, are proportional to

$$\frac{1}{2}m_1\left(\frac{q_1}{r_1^2}\right)^2,\quad \frac{1}{2}m_2\left(\frac{q_2}{r_2^2}\right)^2,$$

respectively. A fractionation factor α (generally greater than unity) associated with the exchange reactions is defined as the ratio of the physical quantity that determines the fractionation.[1] In the present case it is the kinetic energy of the two isotopes. In other cases, this physical quantity could be the velocity or the diffusion rates. Without loss of generality, we assume that $K_1\geqslant K_2$. Because $\alpha>1$, α for the two ions on the adsorption surface is defined as $\alpha=K_1/K_2$. Therefore,

$$\alpha=\left(\frac{m_1}{m_2}\right)\left(\frac{q_1}{q_2}\right)^2\Bigg/\left(\frac{r_1}{r_2}\right)^4. \tag{3}$$

III. RESULTS AND DISCUSSION

Several observed isotope/element ratios found in the literature and their predicted ratios from Eq. (3) are given in

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Table I. Observed isotope ratios and their predicted ratios by Eq. (3).

Isotope ratio	Original ratio	Calculated fractionation factor[a] (α)	Predicted ratio	Observed ratio	Reference
^{87}Sr/^{86}Sr	0.7090	1.012	0.7170	0.7130	7
^{87}Sr/^{86}Sr	0.6995	1.012	0.7080	0.7050	8
^{87}Rb/^{86}Sr	0.0071	11.7	0.0831	0.0876	8
^{87}Sr/^{86}Sr	0.7088	1.012	0.7170	0.7142	9
^{87}Sr/^{86}Sr	0.7089	1.012	0.7171	0.7151	9
^{187}Os/^{188}Os	0.1178	1.005	0.1172	0.1173	14
^{187}Re/^{188}Os	0.0580	1.21	0.0700	0.0670	14
^{187}Re/^{188}Os	0.2200	1.21	0.266	0.264	15
^{187}Os/^{188}Os	0.1309	1.005	0.1302	0.1297	15
^{176}Lu/^{177}Hf	2.564	1.42	3.641	3.529	16

[a] According to Eq. (3). The original ratio refers to the isotope ratio before the system undergoes adsorptive fractionation, determined experimentally. The predicted ratio is the product of α times the original ratio. In calculating α, the ionic radii and ionic charges were taken from Ref. 17. The elements and their charges and ionic radii are Sr^{2+} (1.12 Å), Rb^{+} (1.47 Å), Os^{2+} (1.05 Å), Re^{2+} (1.00 Å), Lu^{2+} (1.20 Å), Hf^{2+} (1.10 Å).

Table I. Brannon *et al.*[7] found fractionated fluid inclusions and the solid fraction of sphalerite (the most important mineral of zinc ore) of the upper Mississippi valley zinc-lead deposit and analyzed the ^{87}Sr/^{86}Sr ratios of nine samples of each fraction. They found heavy-isotope enrichment in the solid fraction, indicating an adsorptive fractionation. Our predicted isotope ratio of the ^{87}Sr/^{86}Sr was 0.7170, which is consistent with the observed ratio of 0.7130 (see Table I). Enrichments of ^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr isotope/element ratios in a glass-pyroxene association of the Juvinas basaltic achondrite, a class of meteorites, have been measured,[8] and our calculation gave reasonably accurate predictions of the isotope ratios. Muller *et al.*[9] analyzed two large pyrite-fringe complexes of the Pyrenean shear zone of France for ^{87}Sr/^{86}Sr ratios of quartz plus chlorite and calcite. Most of the experimentally observed samples had isotope ratios close to the predicted value due to adsorptive fractionation of Sr isotopes in calcite on the charged surfaces of the quartz plus chlorite. The values of α for some other isotopes of Os, Re, Lu, and Hf in rock minerals are also given in Table I. The observed and predicted isotope/element ratios in Table I show very good agreement with a goodness-of-fit of 99% (Fig. 1). This agreement is evidence for an adsorptive fractionation of isotopes and elements in rocks and minerals on the earth as well as in planetary objects.

During the ion exchange reactions, some ions form stronger interactions with minerals, often termed as inner-sphere complexation.[10] This process is not completely reversible, and causes a permanent isotope/element fractionation in the medium. Hence, the measured isotope/element compositions in the fluid inclusions and solid fractions of rocks represent an apparent composition. Due to the natural decay of isotopes, these ratios change with age and can be used for age determination. However, isotope ratios also change due to fractionation. The changes in the isotope ratios due to fractionation need to be incorporated for accurate dating. Otherwise, incorrect estimates of the age of the solar system and other planetary objects would result. When adsorptive fractionation dominates in geological systems, their inclusion of the changes in isotope ratios due to fractionation will allow better interpretations of ratios.

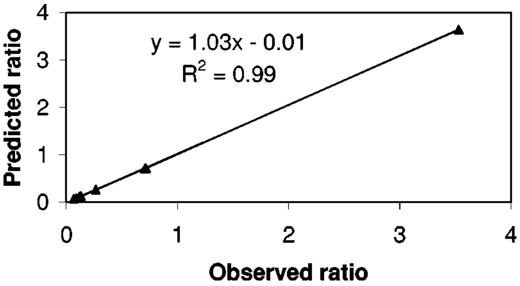

Fig. 1. The relationship between observed and predicted isotope ratios as of Table I.

The fractionation of different elements with the same atomic mass also can be explained by this model, which suggests that any difference in chemical forms or physicochemical properties does not affect the fractionation. In our calculations, we have assumed that all isotopic/elemental ions are atomic, but this assumption is not always true in natural systems. For example osmium (Os) may exist as OsO_3^-. In addition, the charge and radius of isotopic ions may change when they are on planetary surfaces and in the mantle and in magmas. These effects, which complicate the adsorption process, should be taken into account to predict α more accurately.

On the other hand, the simplicity of the present model enables even undergraduate students to simulate the fractionation process in their laboratories using charged macroscopic particles. Furthermore, the success of this model shows that even a very complex naturally occurring process such as isotope/element fractionation can be explained quantitatively with what they learned in elementary physics classes.

APPENDIX

van der Waal's forces adhere ions and molecules in a liquid medium. Bowden and Tabor[11] have extended the laws of friction to the case of adhesive contacts. Their model is simple and assumes that the frictional force F_i arises from the force required to shear the adhesive junction between an ion and a molecule. That is, $F_i = S_c A_i$, where S_c is the critical shear stress at the contacting interface, and A_i is the real ionic-molecular contact area. For a detailed description of this relation, see Ref. 12. The direct proportionality between F_i and A_i at the nanometer scale has been shown recently using an advanced microscopic technique.[13] The total friction F on an ion due to n adhesive contacts around an ion is

$$F = \sum_{i=1}^{n} F_i = S_c \sum_{i=1}^{n} A_i . \tag{4}$$

For a particular medium, $\Sigma_{i=1}^{n} A_i$ is proportional to the surface area of the ion, which is proportional to r^2. Thus, $F \propto r^2$.

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Faraday's Bag. Electric charge placed on a conducting body accumulates on the outside of the body. This can be demonstrated with a cloth bag mounted on an insulating stand. The cloth conducts well enough to allow the charge to travel from one surface of the bag to the other as it is turned inside out using the strings attached to both sides of the bag's vertex. This example is at the apparatus collection of Colby College. It is unmarked, but looks very much like an illustration in the 1860 catalogue of Edward S. Ritchie of Boston. The catalogue description is ''Faraday's Muslin Bag; sustained upon an insulated ring of wire, with silk strings,...$4.00.'' (Photograph and notes by Thomas B. Greenslade, Jr., Kenyon College)

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