Theory and Calculation of Nontraditional Stable Isotope Fractionation

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Abstract. This paper conducts processing on isotope anharmonic effect with molecular dynamics method and Monte Carlo method based on path integration. It introduces the theoretical calculation method of pressure effect, and finally the nuclear volume effect and its theoretical calculation method, stressing that the nuclear volume effect is an important part of isotopic studies of heavy metals in the future. This paper makes an analysis on the equilibrium fractionation theory based on simple harmonic approximation.

Keywords: non-traditional stable isotopes, fractionation theory and calculation

1. Introduction
With the breakthrough of mass spectrometer technology, isotope geochemistry has achieved rapid development for over 20 years; isotope method becomes one of the main research tools of the whole earth science beyond other analysis methods. Stable isotope method in the isotopic geochemistry also extends to the system of “non-traditional stable isotope”, which is widely applied in astrochemistry, petrology, environmental geochemistry, marine geochemistry, mineral deposits, and many other fields. Along with the gradual development in the research on increasing heavy metal isotope system (e.g., 5, 6 cycles of heavy metals), it is foreseeable that isotope geochemistry will get at least another two hundred and thirty years of the “active period”, and it will also exert more profoundly effect on the development and breakthrough of numerous branches. The theory of non-traditional stable isotopes has much in common with traditional stable isotopes (CHONS), as well as some differences.

Especially when non-traditional stable isotopes are expanding in some emerging directions, the original isotope theory system cannot cover these new directions, such as nuclear volume effect, some non-quality fractionation effect and non-equilibrium fractionation effect, etc.; it is necessary to create a new fractional theory. These new theories are an important part of the stable isotope geochemistry system. This paper introduces the current theoretical research status from the two aspects of equilibrium and non-equilibrium (dynamics) fractionation, trying to show a global picture and to emphasize some key problems. The main basic theory of balanced fractionation has been perfected, but the basic theory of non-equilibrium (dynamics) fractionation in some emerging directions either just appears or is still under construction. It is worth to point out that non-equilibrium process (dynamics) isotope
fractionation theory construction is the focus of competition in the international academic field; to be the first to establish the theory, not only can lead the international counterparts, but also can decide the future development depth and way of non-traditional stable isotope geochemistry.

2. Statistical Mechanics Basis of Isotope Fractionation

The essence of isotope fractionation is caused by the energy difference in isotope substitution.

For a single molecule, its energy usually includes translational energy for molecules moving in the space, rotational energy for turning around the center of mass, vibrational energy for different atoms attracting and rejecting each other, and the energy contained in the electron and the nucleus of each atom in the molecules.

We can express the energy of molecules as follows:

\[ E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} + \ldots \]

Among them, \( E_{\text{total}} \) is the total energy of molecules, and \( E_{\text{trans}} \), \( E_{\text{rot}} \), \( E_{\text{vib}} \), and \( E_{\text{elec}} \) represent the translational energy, rotational energy, vibration energy and electron energy of the molecules respectively. These energy terms also include their ground states and excited states. The omission is some minor, or minor energy terms.

Statistical mechanics suggests that a molecule may appear in any energy state; and the lower the energy, the greater the probability. In 1877, Boltzmann proposed the probability of the presence of a molecule with certain energy in space in the form of a partition function, and the expression of its mature definition is

\[ Q = \sum_{m} \exp \left( -\frac{E_{m}}{kT} \right) \]

In which, \( E_{m} \) is the energy of the m state, and \( k \) is the thermodynamic temperature of the Boltzmann constant.

In the approximation of simple harmonic vibration and rigid rotor, the partition function of the molecule’s translation, rotation and vibration can be expressed as the following:

\[ Q_{\text{trans}} = V \left( \frac{2\pi MkT}{h^2} \right)^{3/2} \]
\[ Q_{\text{rot}} = \frac{\pi^{1/2}(8\pi 2kT)^{3/2}}{sh^3} \left( I_A I_B I_C \right)^{1/2} \]
\[ Q_{\text{vib}} = \Pi \frac{\exp \left( -\hbar \omega_i / 2kT \right)}{1 - \exp \left( -\hbar \omega_i / kT \right)} \]

In which, \( M \) represents quality, \( v \) represents the volume, \( h \) is Planck’s constant, \( s \) is symmetry number, \( I_A, I_B, I_C \) are rotational inertia of molecules turning around A, B, C axle; \( \omega_i \) is the simple harmonic frequency of the molecular of \( i \)th vibration freedom degree, known as the wave number (\( \text{cm}^{-1} \)). The translational and rotational partition functions above are the classical forms of the partition function expression; and the vibrational partition function is the expression of the form of quantum mechanics. The contribution of translation and rotation in the molecular energy is small, which means that the classic expression can express the statistics law of the energy part well from normal temperature to high temperature; as for vibration energy, the research accuracy can only be satisfied with the partition function in the form of quantum mechanics.

3. Balanced Fractionation Theory Based On Simple Harmonic Approximation.

The cornerstone of stable isotope geochemistry. This model is taken to calculate the equilibrium fractionation coefficient \( K \) in the isotopic exchange reaction with the form of partition function under the condition of harmonic vibration and rigid rotation approximation.

The Urey model is described in detail in many geochemistry textbooks and reviews.
For an isotope exchange reaction:
AX+BX* ↔ AX*+BX

In the formula, X and X * represent the light and heavy isotopes of the same element; when the reaction reaches equilibrium, according to the Uibb, the relationship between free energy and its equilibrium constant K, K can be expressed as the ratio of partition function before and after the replacement of two isotopes of the molecular:

\[
K = \frac{Q_{2\text{trans}}, Q_{\text{vib}}, Q_{\text{elec}}}{Q_{1\text{trans}}, Q_{\text{vib}}, Q_{\text{elec}}} \frac{Q_{2\text{trans}}, Q_{\text{vib}}, Q_{\text{elec}}}{Q_{1\text{trans}}, Q_{\text{vib}}, Q_{\text{elec}}} \]

In the formula, the numerator or denominator represent the “Partition Function Ratio” before and after the isotope exchange reaction. We call it as the Partition Function Ratio, or PFR, and its expression is.

\[
PFR = \frac{Q^*}{Q} = \left(\frac{M^*}{M}\right)^{3/2} \frac{\left[I_A I_B I_C^*\right]^{1/2}}{\left[I_A I_B I_C\right]^{1/2}} \prod_i \frac{\exp(-u_i^*)/2 \left[1 - \exp(-u_i)\right]}{\exp(-u_i)/2 \left[1 - \exp(-u_i^*)\right]}
\]

In which:

\[
u_i = \frac{k c \sigma_i}{k T}
\]

The Born - Oppenheimer: under the approximation and other approximate situations, the electronic energy doesn’t change before and after isotope exchange reaction; therefore, electronic energy part is not taken into account at time of calculating the equilibrium constant (but it is not applicable for isotope system of heavy metal, which can be referred to this article “nuclear volume effect” section); and according to the principle that the force constants don’t change, the following relationships can be concluded:

\[
\left(\frac{I_A I_B I_C^*}{I_A I_B I_C}\right)^{1/2} \left(\frac{M^*}{M}\right)^{3/2} \left(\frac{m^*}{m}\right)^{3n/2} \prod_i \frac{u_i}{u_i^*} = 1
\]

The formula above is the Teller-Redlich principle. It describes the relationship between the rotational inertia and the vibration frequency before and after the isotope exchange reaction. Bring it into the PFR expression and get:

\[
\text{RPFR}(AX^* / AX) = \frac{S^*}{S} f = \prod_i \frac{3n - 6 u_j(AX^*) \exp[-u_j(AX^*)]}{u_j(AX) \exp[-u_j(AX) / 2]} \left[1 - \exp[-u_j(AX^*)]\right]^{-1}
\]

The formula above is the so-called Bigeleisen-Mayer Formula (or Urey model), which gives the calculation method of the C Reduced Function Ratio (RPFR). The formula looks complex at first, but only the frequency of vibration is unknown.

In other words, if you know the vibrational frequency of certain substance (including the vibrational frequency of its isotope replacement), you can obtain its RPFR value.

The equilibrium constant K of isotopic exchange between the two substances (AX and BX) is equal
to the ratio of the RPFR value of these two substances plus the change in the symmetry after the substitution of the isotope (usually available):

\[
K = \frac{\frac{S}{S^*}AX}{\frac{S}{S^*}BX} \times \frac{RPFR_{AX}}{RPFR_{BX}}
\]

In the study of stable isotope geochemistry, we are interested in the fractionation coefficient “\(a\)” rather than the equilibrium constant \(K\). However, in the equilibrium isotope exchange reaction, the fractionation coefficient \(a\) corresponds to the equilibrium constant \(K\). Consider an exchange of any of the following isotope:

\[a.AX^m + b.BX^n \leftrightarrow a.AX^m + b.BX^n\]

As for the two substances reaching equilibrium in isotopic exchange reaction, the fractionation coefficient can be simply expressed as the ratio of \(R\) factor of the two. If the molecular research elements occupy numerous different valences and the isotope replacement of different valences replace with each other, the situation will become more complex, and we need to make careful and detailed processing for a particular system to get the desired results.

Advanced correction for the calculation of equilibrium fractionation coefficient. The Bigeleisen-Mayer formula (or Urey model), which is based on a simple, harmonic and rigid rotation approximation, cannot give satisfactory results at the time of dealing with a system with a large non-harmonic effect. Through the analysis of high order molecular energy, several formulas, such as non-harmonic correction, rotation-vibration coupling correction and quantum mechanical rotation correction, are proposed, and the fractionation coefficient of multiple systems is predicted successfully. These formulas were further modified, and the effect of internal rotor and centrifugal deformation on isotope fractionation was first calculated. We will describe these corrections one by one.

1) Anharmonic correction of the partition function

In harmonic level, the energy difference between the vibration levels is equal; we can simply divide vibration partition function at simple harmonic level into two parts of zero-point energy (ZPE) and the excited state (EXC):

\[
Q_{hzpe} = \prod_i \exp(-u_i / 2)
\]

\[
Q_{hzpe} = \prod_i \frac{1}{1 - \exp(-u_i)}
\]

In the formula, \(h\) indicates that the formula is derived from the harmonic approximation.

The simple harmonic vibration does not fully represent the real vibration of the molecules. If we want to calculate vibration energy more accurately, we need to introduce more complex vibrational potential energy to describe the vibrational mode of the molecule. The eigenvalue of the vibrational energy is obtained by taking into account the three- and fourth-order non-harmonic potential curves and introducing it into the Schrödinger equation.

\[
E_n / \hbar c = G_0 + \sum_i \sigma_i (n_i + \frac{1}{2}) + \sum_{i \leq j} x_{ij} \left(n_i + \frac{1}{2}\right) \left(n_j + \frac{1}{2}\right)
\]

In the formula, both \(G_0\) and \(x_{ij}\) are constants (cm\(^{-1}\)). At the time of selecting potential energy, if choose the Morse and approximation, the \(G_0\) term will not appear in vibration expression, but \(G_0\) item exists in the real molecular vibration; as the \(G_0\) term is rather complex in form, and the formula derived from the different researchers are different. We selected the \(G_0\) term in the literature. When the vibration quantum number \(n\) is equal to 0, it is in the ground state of the vibration, and the zero energy expression with the non-harmonic effect is obtained:
\[ E_0 / h c = G_0 + \frac{1}{2} \sum_i \sigma_i + \frac{1}{4} \sum_{i \leq j} x_{i,j} \]

\( X_{ij} \) denotes the non-harmonic constants of the vibration coupling between the two vibration degrees of \( i \) and \( j \).

A theoretical model based on local thermodynamic equilibrium theory

Thermal diffusion is a non-equilibrium process, and the diffusion of silicate melt includes a series of bonding and bond-breaking. Therefore, the good method must conclude two points: the first is the quantum mechanism; the second is the non-equilibrium process based on strict statistical mechanics. This paper uses the local thermodynamic theory (LTE) to deal with the temperature gradient, and derives the isotopic fractionation formula of all kinetic energy components with the combination of the quantum mechanical calculation.

Local thermodynamic theory is a commonly used method to deal with non-equilibrium processes. This method divides the research system into many small-volume elements. On one hand, the volume element is very small from a macro point of view, and it can be believed as enough to use a fixed value to express thermal dynamic variable; on the other hand, from a microcosmic point of view, these volume elements are large enough that the number of particles is already high enough to satisfy the requirements of statistical mechanics, such as the requirement to use the Maxwell-Boltzmann distribution relationship.

Eastman uses LTE for the first time to deal with small but macroscopic motions in a temperature gradient. The motion of molecules in liquid under temperature gradient was treated with LTE. Finally, they obtained the relation between \( S_T \) and the system canonical transformation entropy.

\[ S_T = \frac{1}{k_b T} S \]

Consider each small volume element as a canonical ensemble in statistical mechanics, this relationship can be applied:

\[ S = \frac{U - F}{T} \]

\( U \) is internal energy, \( F \) Helmholtz free energy, and they can be represented by the canonical ensemble partition function (Q); therefore,

\[ S = k_b T \frac{\partial}{\partial T} \ln Q + k_b \ln Q \]

As long as we know the relation between the partition function ratio (i.e. the ratio of energy) of heavy and light isotopes in the system and the temperature, the isotopic fractionation size of a certain temperature gradient can be obtained by the integration.

When the temperature is higher than 800 degrees, high temperature approximation processing can be taken. The isotope fractionation under thermal gradient can be further expressed by the following formula:

\[ \Delta^x M = A \ln \frac{T}{T_0} + B \left( \frac{1}{T^2} - \frac{1}{T_0^2} \right) \]

### 4. Method of Purification and Separation of Mg Isotopes

#### 4.1 Isotope purification method.

Before adopting MC-ICPMS to conduct Mg isotope assay, it needs isotope purification first to remove the effect of nuclear isobar from other elements or matrix, so as to obtain the high precision analysis of Mg isotopic results. We use ion-exchange resin to purify Mg.

For carbonate rock, AGSOW-X12 is taken to build the method of the separation of Mg and Na, Ca.

In diluted HCl (0.2 to O.S M), Mg can be separated from Na; and when HCl concentration reaches
2M to 3M, Mg can be separated from Ca, S. She uses two ion exchange columns to separate the Mg in two steps. The first step is to separate Mg, Na from Ca with 2M HCl. The second step is to separate Mg and Na with 0.4M HCl (Figure 1).

Take 100 mm X 10 mm specification exchange column, to make 2. SmlAG50W - X12 resin; adopt HN03 to wash 104 m1 and collect 60m1 Mg receiving liquid; this method can effectively remove Al, but Fe, Mn and other elements still need to be removed through other chemical methods.

![Fig. 1 AGSOW-X12 cation exchange resin to separate Na, Mg.](image)

4.2 Mg isotope analysis of low-Mg geological samples.

With the wide application of more than multiple receiving induced coupled plasma mass spectrometry (MC - ICP - MS), the measurement of many metal stable isotope system reaches unprecedented accuracy, from which a new field of non-traditional stable isotope geochemistry appears. As a new kind of geological tracer, Mg isotope system is getting more and more attention, and has made important progress in various geological studies. As the research scope and problem become more extensive and deeper, it is necessary to conduct measurement and study on the isotopic composition of more geological samples. A special chemical separation process was designed for the measurement of Mg isotopes in low-Mg samples; studies are conducted on the process of Mg separation in the rhyolite samples. The accurate measurement of Mg isotopic composition requires that the measured elements should be separated from the sample in order to reduce the influence of the matrix element and the interference of isobaric element. Secondly, we should ensure full recovery to avoid possible isotopic fractionation during chemical separation. With Neptune Plus, a large number of long-term stability tests are carried out to ensure the optimum operation of the instrument. We accurately measure the composition of Mg isotope composition in lower Mg samples, and provide a basis for the establishment of a simple, efficient and widely used method for the analysis of Mg isotopes.
5. Conclusion

Non-traditional stable isotope geochemistry is in comparison with H, C, O, S and other traditional stable isotope geochemistry, which includes isotope systems of Fe, Cu, Zn, Se, Hg, Mg, and so on. As these elements have some special properties in geochemistry, Cosmo chemistry, biochemistry and other fields; with the revolutionary progress of isotope mass spectrometry testing technology at the turn of the century, especially the appearance of multiple receiving induced coupled plasma mass spectrometry (MC - ICP - MS), the development and utilization of the stable isotope system of these elements comes into a booming period; thus a new branch arises at the historic moment: non-traditional stable isotope geochemistry.

The first decade of the 21st century witnesses the birth and development of the non-traditional stable isotope geochemistry. The work of the past decade can be summarized into four basic aspects:

• Research and development of isotope test method;
• Study on the characteristics of isotopic distribution and variation range;
• Study on the process and mechanism of isotopic fractionation;
• Exploration of application potential and constraints on major scientific issues.

After ten years of foundation, the non-traditional stable isotope geochemistry has entered the stage of vigorous development. It is foreseeable that, compared with the first decade, the research focus of unconventional stable isotope geochemistry in the next decade will have some obvious trends:

• The research focus changes from technology to theory study;
• From the exploration of application potential to the direction of scientific problems;
• From the wide and ordinary research on the isotope system to the emphasized study on important isotope systems.

References

[1] Huang Fang, Nan Xiaoyun. Research progress of non-traditional stable isotopes in soil. [J]. Journal of University of Science and Technology of China, 2015, 45 (02):87-100.
[2] Li Shuguang. Chief Editor to the Reader [J]. Leading Edge of Earth Science, 2015, 22 (05):3.
[3] Liu Yun. Nontraditional Stable Isotope Fractionation Theory and Calculation [J]. Leading Edge of Earth Science, 2015, 22 (05):1-28.
[4] Gu Wen. Application of Non-traditional Stable Isotopes in the Field of Biological Archaeology [J]. Preservation of Cultural Relics and Archaeological Science, 2017, 29(06):135.
[5] Zhang Feiwu. The Study on the Fractionation and Diffusion of Stable Isotopes in Quantum Chemical Calculations -- A Case Study of the Diffusion of Li Isotopes in Olivine Stone [J]. Journal of Mineral Sciences, 2015, 35 (S1):1135.
[6] Niu Yaoling, Gong Hongmei, Wang Xiaohong, Xiao Yuan-yuan, Guo Pengyuan, Shao Fengli, Sun Pu, Chen Shuo, Duan Meng, Kong Juanjuan, Wang Gipdpmg, Xue Qiqi, Gao Yajie, Hong Di. Adopt Non-traditional Stable Isotopes to Explore Causes of Global Ocean Basalt, Deep Sea Peridotite and Several Important Problems of Geodynamics [J]. Journal of Earth Science, 2017, 32 (02): 111-127.