A new method has been proposed for the determination of equilibrium isotope geochemistry (S, O, C, etc.). The method employs experimental data on temperature (second order Doppler) shift in Mössbauer spectra and on mineral thermal capacity. The method is applicable to minerals consisting of two elements if one of the elements contains an isotope for which the Mössbauer effect is observable.

The method is based in the first order thermodynamic perturbation theory equation that expresses the β-factor via the isotopes mass difference and the kinetic energy of the atom having suffered the isotope substitution (Polyakov, 1989, 1994; Polyakov 1991):

$$\ln \beta = \frac{K - K_M}{zRT} - 1.5 \frac{\Delta m}{m}$$  \hspace{1cm} (1)

where β is the β-factor; K is the kinetic energy of the isotopically substituted atom, z is the multiplicity of the isotope substitution; m and m* are masses of substituted and substituting isotopes; \(\Delta m = m^* - m\); R is the universal gas constant; T is the absolute temperature.

For Ks one can write: \(K_s = K-K_M\), where K and K_M are equilibrium isotope constants of two-element minerals.

The total kinetic lattice energy can be derived from the thermal capacity data. In harmonic approximation at \(kT \geq h\nu / 2\pi\) the thermal capacity and the kinetic vibration energy can be represented as the series (see e.g. Polyakov and Kharlashina, 1995):

$$C_v = 3nR - \frac{B_1}{T^2} + \frac{3B_2}{T^4} - \frac{5B_3}{T^6} + \ldots - (-1)^i (2i - 1) \frac{B_{2i-1}}{T^{2i}}$$  \hspace{1cm} (3)

$$E_{vb} = 2K = 3nRT^2 + \frac{B_1}{T} - 2 \frac{B_2}{T^3} + \frac{B_3}{T^5} + \ldots - (-1)^i \frac{B_{2i-1}}{T^{2i-1}}$$  \hspace{1cm} (4)

C_v is the thermal capacity at a constant volume, n is the number of atoms in a molecule, \(v_m\) is the right -side boundary of the crystal vibration spectrum, E_vib is the lattice vibration energy, k, h, are Boltzmann and Plank constants, respectively.

**Isotopy**

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the iron sublattice are determined from the measurements of the temperature dependence of the isomer shift of the hematite Mössbauer frequency (fig.2) in terms of the Debye model:

\[
\text{IS} = A + \frac{9 k T_{\text{M}}}{16 M_c} \left[ 1 + 8 \left( \frac{T}{\Theta_{\text{M}}} \right) \frac{1}{\Theta_{\text{M}}} + \int_0^\Theta \frac{x^3}{\exp(x) - 1} \, dx \right]
\]

For synthetic hematite (a solid line):
\[\Theta_{\text{M}} = 502.9 \pm 25.0 \text{ K, } A = 0.061 \pm 0.001 \text{ mm/s}\]

For natural hematite:
\[\Theta_{\text{M}} = 488.9 \pm 55.5 \text{ K, } A = 0.06159 \pm 0.0011 \text{ mm/s}\]

The calculation of the β¹⁸O-factor of hematite from Eqs (2), (4), and (5) yields the polynomial

\[10^3 \ln \beta_{\text{hematite}} = (5.7215 \pm 0.3891) x - (0.02941 \pm 0.00449) x^2, \quad x = 10^6 / T^2\]

Fig.3 illustrates the temperature dependence of the equilibrium fractionation coefficient between hematite and α-quartz, the mineral used as standard. Good agreement between the results obtained by different methods evidence for the reliability of the found values of β¹⁸O-factors of hematite.

Whenever the β-factors of minerals in "non-Mössbauer" element are known, their combination with the data on nuclear gamma resonance frequency temperature shift enables one to determine the contribution of the lattice component to thermal capacity.

#Polyakov V.B., Mineev S.D. Regularities of an equilibrium fractionation of iron isotopes as suggested by the Mössbauer spectroscopy data.

key words [Fe Mössbauer spectroscopy isotope]

Now, due to the progress in mass-spectrometry technique and experimental methods, it becomes possible to measure the isotope composition of Cu, Zn, Mo, Ta, Fe, and other elements not used before in geochemical isotopic studies (O’Nions et al., 1998, Marechal et al., 1998, Anbatt et al., 1998, Dixons et al., 1991, Rehkämper et al., 1998). In the present work we consider the regularities of an equilibrium fractionation of iron isotopes using the Mössbauer spectroscopy data and the equation which binds the equilibrium fractionation constant (β-factor), and the temperature (second-order Doppler) shift of the resonance frequency in Mössbauer spectra (Polyakov, 1996, 1997):

\[\ln \beta = \left( \frac{m \text{Sc}}{RT} + \frac{3}{2} \Delta m \right) \frac{\Delta m}{m}\]

β is the β-factor, m is the mass of the "Mössbauer" isotope, e.g., Fe⁵⁷, S is the second order Doppler shift, T is the absolute temperature, R is the universal gas constant, c is the velocity of light, Δm is the isotope mass.

The results of the calculations of the β-factors of oxides, hydroxides, and silicates, performed using the experimentally measured S values, are illustrated in figs.1 and 2. As seen from figs.1 and 2, the β-factors are greater in the case of Fe³⁺ than Fe²⁺. Interestingly, that the boundary between the two regions is natural iron characterized by the metallic bond. Whenever iron atoms are present in the same mineral in non-equivalent positions, one can observe an infrastructural (intramolecular) isotope effect (diopside, celadonite, fig.2).

Fig.3 illustrates the results for a number of minerals which are neither silicates nor oxides (hydroxides). Ibid. is demonstrated the dependence of the β-factor value on the bond type: covalent or ionic. As the bond covalence grows, the β-factor value increases.

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So, despite the divalence of iron in pyrite and cyanides, the $\beta$-factor value in these compounds corresponds to (and even exceeds) those characteristic of Fe$^{3+}$ in the case of ionic bonds (compare with figs 1,2). The greater $\beta$-factor value, characteristic of covalent bonds as compared with ionic ones, was mentioned earlier (Humayun and Clayton, 1995).

The reported results enable one to propose a prospective isotope magnetite-pyrite-siderite geothermometer (fig.4). Said minerals coexist in a broad temperature range. A weak fractionation between magnetite and pyrite and a considerable isotopic effect between siderite and two other minerals have to be observed when in equilibrium. The observable fractionation exceeds greatly an error of iron isotope composition measurement equal with allowance for the sample preparation, to 0.5% (Wang, 1998).