Isotopy

[#]Polyakov V.B., Mineev S.D., Khramov D.A., Gurevich V.M., Ovanesyan N. Mőssbauer spectroscopy and calorimetry determination of equilibrium isotope constants of two-element minerals.

key words [Mőssbauer spectroscopy calorimetry isotope]

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 Mőssbauer 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 Mőssbauer 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):

$$\ln\beta = \left(\frac{K_s}{zRT} - 1.5\right)\frac{\Delta m}{m^*} \tag{1}$$

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 sand substituting isotopes; $\Delta m = m^* - m$; R is the universal gas constant; T is the absolute temperature.

For K_s one can write: $K_s = K - K_M$, where K and K_M are kinetic energies of the overall lattice and the sublattice of the element containing the "Mőssbauer" isotope. Substituting this expression into (1) yields:

$$\ln\beta = \left(\frac{K - K_M}{zRT} - 1.5\right)\frac{\Delta m}{m^*} \tag{2}$$

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

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

$$E_{vib} = 2K = 3nRT + \frac{B_1}{T} - 2\frac{B_2}{T^3} + \frac{B_3}{T^5} - \ldots(-1)^{i+1}(2i-1)\frac{B_i}{T^{2i-1}} \tag{4}$$

C_v is the thermal capacity at a constant volume, n is the number of atoms in a molecule, ν_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.

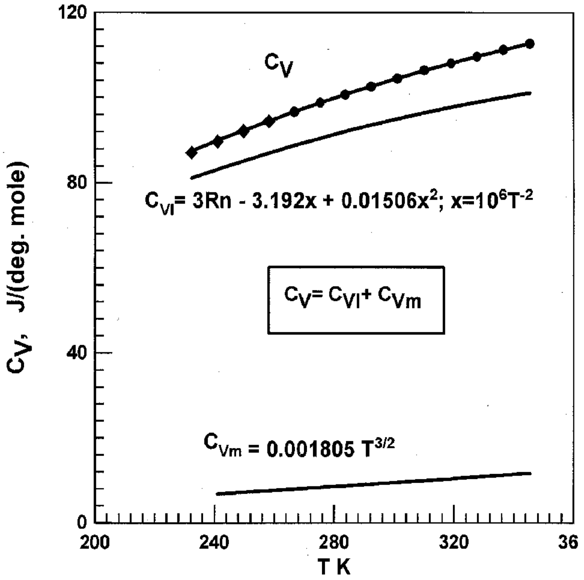

Fig.1.

Series (3) fairly describes the temperature dependence of the thermal capacity in the temperature range of $0.3\theta_D \div 0.6\theta_D$ (θ_D is the Debye temperature) with allowance for its several first terms (Naumov, 1997).

The kinetic vibration energy of the "Mőssbauer" element sublattice can be derived from the temperature (second order Doppler) shift in Mőssbauer spectra:

$$S = -K_m / m_{Fe}c \tag{5}$$

c is the light velocity; m_{Fe} is the mass of an iron atom.

Eqs (2)-(5) are used to determine the β^{34}S-factor of pyrite and the β^{18}O-factor of hematite.

The β^{34}S-factors of pyrite were defined from the thermal capacity data (Ogawa, 1976) and temperature shift of iron in pyrite (Nishihara, Ogawa, 1979). The temperature dependence of the β^{34}S-factors of pyrite can be expressed by the polynomial

$$10^3\ln\beta_{pyrite} = (1.5997 \pm 0.0419)\cdot x - (6.7744 \pm 0.4279)\cdot 10^{-2}x^2 + $$
$$+ (3.8254 \pm 0.5682)\cdot 10^{-5}x^3;\ x = 10^6/T^2$$

The table gives the $10^3\ln\beta$ value in comparison with the calculations of Sakai (1968)

T, K	375	400	475	500	575	600	675	700
I	11.05	9.74	6.97	6.29	4.78	4.40	3.48	3.35
II		10.9		7.0		4.8		3.6

I- Our data; II - H.Sakai (1968)

As seen from the given data, a good agreement exists between our data and the calculations of Sakai (1968). The shift between two data sets is 25K and does not exceed the usual geothermometric error.

In the case of hematite along with the contribution of lattice vibrations (lattice component) there is a contribution due to spontaneous magnetization in hematite (magnetic component). In order to allow for this circumstance, we have added into eq (3) the term proportional to $T^{3/2}$. The results of the approximation are given in fig.1. where the experimental data (Gronvold and Westrum, 1958) are used. The kinetic vibration energy of

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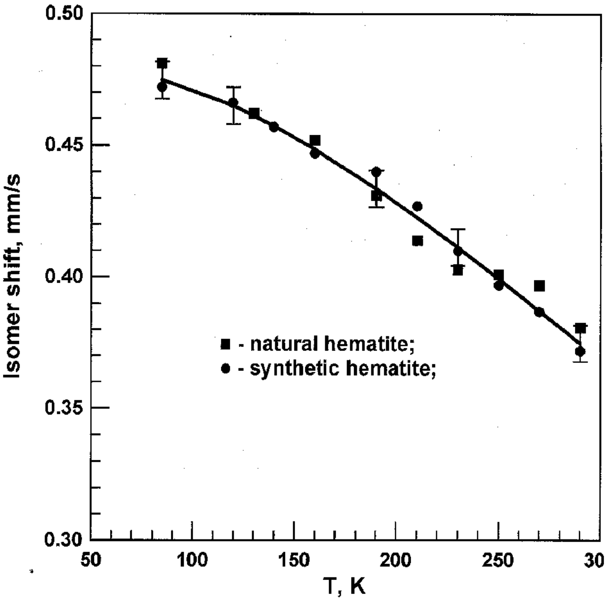
[#] The work has been sponsored by the RFBR (Grant N 98-05-64930) the iron sublattice are determined from the measurements of the temperature dependence of the isomer shift of the hematite Mőssbauer frequency (fig.2) in terms of the Debye model:

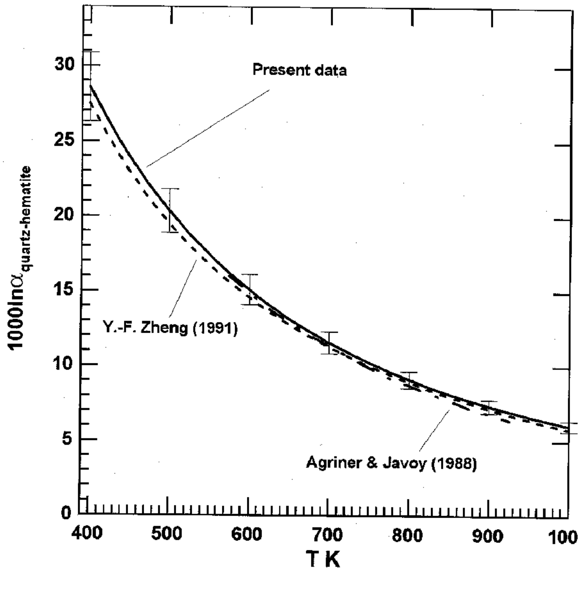


$$IS = A + \frac{9}{16}\frac{k\Theta_M}{Mc}\left[1 + 8\left(\frac{T}{\Theta_M}\right)^4 \int_0^{\Theta_M/T} \frac{x^3}{\exp(x) - 1}dx\right]$$

For synthetic hematite (a solid line):
θ_M=502.9±25.0 K, A= 0.06172±4.38·10^{-4} mm/s
For natural hematite :
θ_M=488.9±55.5 K, A= 0.06159±9.31·10^{-4} mm/s

The calculation of the β^{18}O-factor of hematite from Eqs (2), (4), and (5) yields the polynomial
$10^3 \ln\beta_{hematite} = (5.7215 \pm 0.3891)x - (0.02941 \pm 0.00449)x^2$, $x = 10^6/T^2$.

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 β^{18}O-factors of hematite.



Whenever the β-factors of minerals in "non-Mőssbauer " 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, Anbart 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):

$$\ln\beta = -\left(\frac{mSc}{RT} + \frac{3}{2}\right)\frac{\Delta m}{m}, \qquad (1)$$

β is the β-factor, m is the mass of the "Mőssbauer" isotope, e.g., Fe^{57}, 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 Fe^{3+} than Fe^{2+}. 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 intrastructural (intramolecular) isotope effect (diopside, celadonite, fig.2).

Fig.3 illustrates the results for a number of mineral 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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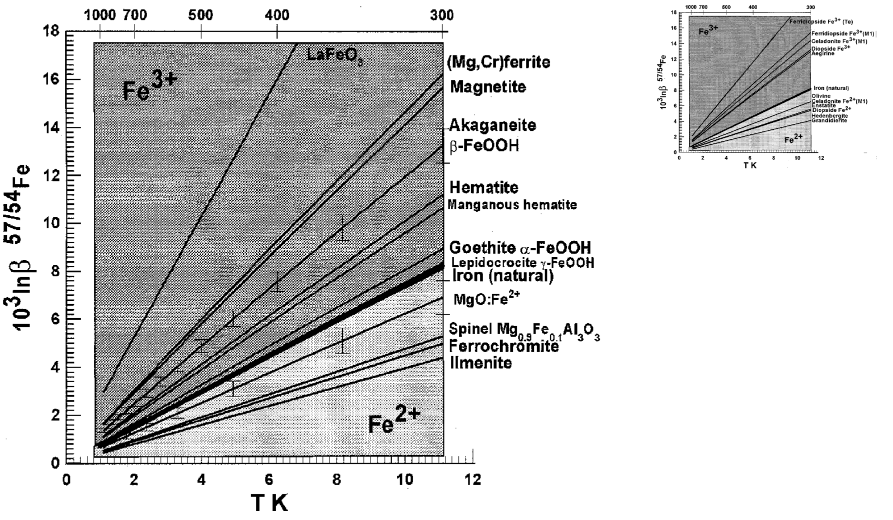

Figs.1,2.

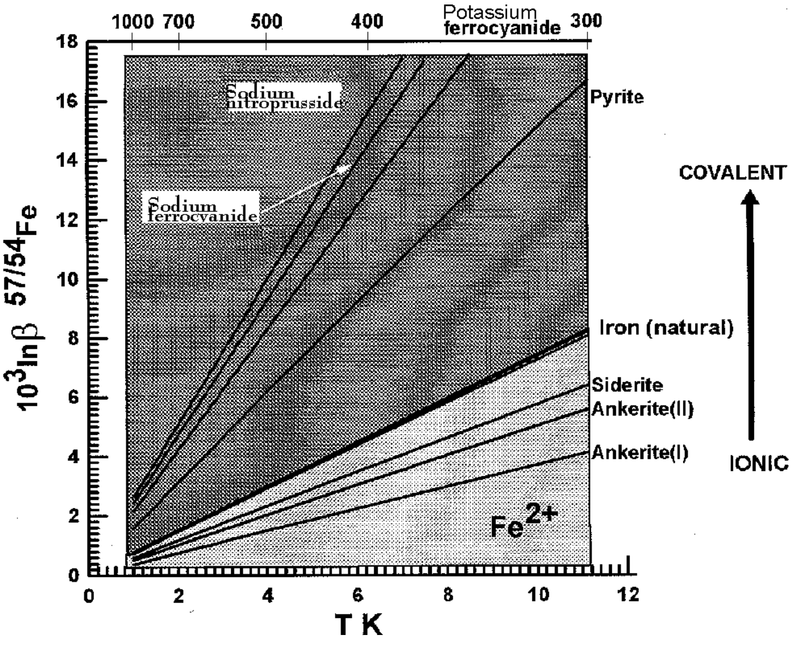

Fig.3.

So, despite the divalence of iron in pyrite and cyanides, the β-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 β-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).

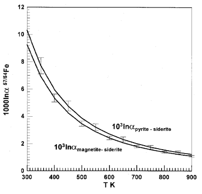

Fig.4.