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CHANGE IN THE MOLECULAR STRUCTURE OF WATER IN CONSTANT CONTACT WITH COARSELY DISPERSED, NATURALLY OCCURRING MINERAL FLINT

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Based on NMR spectroscopic, diffractometric, and IR spectroscopic investigations of water and flint in constant contact, the effect of periodic accumulation of active molecular oxygen in the water has been established.

Experimental data and theoretical investigations associated with evaluation of the change in the molecular characteristics of water and ethyl alcohol in contact of these liquids with naturally occurring mineral flint have been presented in [1, 2]. The molecular characteristics include the values of the valence angles and bend angles of hydrogen bonds, the lengths of valence and hydrogen bonds, the distances between neighboring molecules, the force constants of the valence angle and the valence bond, and changes in the potential energy of molecular vibrations. It is also noted that the interaction of flint with adsorbed molecules of water and ethyl alcohol results in the deformation of the crystal lattice of flint and the transfer of charge from the flint surface along the chains of the hydrogen bonds to the oxygen molecules dissolved in the liquid. This charge is determined in [3] as the transverse charge of an oxygen atom of the lattice. Its capture by an oxygen molecule dissolved in the liquid determines the formation of active molecular oxygen. The procedure of calculation and the structural characteristic of the latter have also been presented in [1, 2].

Active molecular oxygen is intermediate in state between an oxygen molecule and a negative molecular oxygen ion.

As follows from [2], the bond energy of a molecule of "flint" water with active molecular oxygen is 10 to 20 times higher than the bond energy of a molecule of ordinary water with an oxygen molecule. Therefore, clusters of the $O_2^{-}\cdot(H_2O)_n$ type, forming the structure of "flint" water, are very stable.

The results (presented in [1, 2]) of evaluations of the molecular characteristics and accumulation of active molecular oxygen in liquids interacting with flint refer to water, ethyl alcohol, a water–alcohol mixture, cognac spirit, and cognac that have been filtered singly through dry flint.

Continuous contact between water and flint for at least six to twelve months is required for obtaining "flint" water under industrial conditions. Therefore, it has been proposed to study the dynamics of accumulation of active molecular oxygen in water in its long contact with flint.

Experimental investigations have been carried out in three different directions. The first direction included NMR spectroscopic investigations of water contacting flint over different periods of time, whereas the second and third directions included, respectively, diffractometric and IR spectroscopic investigations of flint impregnated with water over different periods of time as well.

The procedure of experimental NMR spectroscopic investigations has been presented in [1], and the results of calculations of the accumulation of active molecular oxygen and of evaluations of the change in the valence angle in a water molecule as a function of the time of its contact with flint are given in Figs. 1 and 2. We have been able to establish that the accumulation of active molecular oxygen and the change in the valence angle in a water molecule as a function of the time of contact of the water with flint obey the sine law. The accumulation maxima for the variant where water was only between flint particles corresponded to 2, 16, 28, 36, 44, and 70 days, whereas the minima (close to zero) corresponded to 9, 22, 34, and 56 days of contact (Fig. 1).

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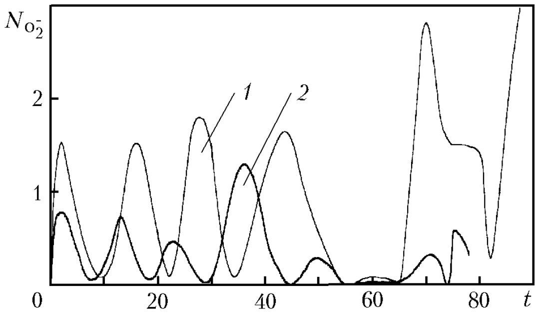

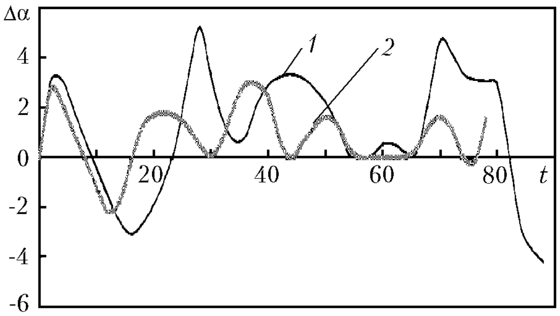

Fig. 1. Accumulation of active molecular oxygen in distilled water vs. time of its contact with flint in storage: 1) water is only between the flint particles; 2) water is between the particles and above the surface of the flint. *t*, days; $N_{O_2^-}$, mg/liter.

Fig. 2. Change in the valence angle in the molecule of distilled water vs. time of its contact with flint in storage: 1) water is only between the flint particles; 2) water is between the particles and above the surface of the flint. *t*, days; $\Delta\alpha$, deg.

The maxima of the change in the valence angle $\Delta\alpha$ in a water molecule are formed for the same times of contact as the maxima of accumulation of active molecular oxygen, whereas the values $\Delta\alpha = 0$ are formed for its minimum accumulations.

As follows from Fig. 2, the changes in $\Delta\alpha$ have both positive and negative values. "Flint" water I is formed for positive values of $\Delta\alpha$, and "flint" water II is formed for negative values.

In the case of drinking "flint" water I, radioactive cesium and strontium isotopes [4] and sugar are removed from the body, whereas selenium [5], iodine, and fluoride are accumulated.

According to our prediction evaluations, drinking "flint" water II will contribute to the accumulation of calcium, magnesium, zinc, and potassium in the body and to the removal of lead and radon and intense removal of sugar from the body.

The existence of sine dependences is explained as follows. In the naturally occurring mineral flint, just as in any mineral represented by a set of perfect and imperfect crystalline structures, there are internal pores (cracks). As follows from [6] and other works, the surface of the cracks consists of steps on which different atoms project outward.

In slow diffusion of water into the internal flint pores, water molecules interact with both the oxygen atoms of the lattice and the terminated bonds of the flint. In interaction of the water molecules with the oxygen atoms of the lattice, we have the transfer of electron charge to the adsorbed water molecules and next, by the chain of hydrogen bonds, to the oxygen molecules dissolved in water. Active molecular oxygen is formed in this case in water, and in interaction of the water molecules with the terminated bonds of flint, charge is transferred back to the flint atoms of the lattice and disappears.

The sine distributions of the content of active molecular oxygen and of the valence angle in a water molecule can be obtained for any form of naturally occurring flint, but, depending on the form, these distributions will differ in the height and period of attenuation of the peak.

It should be noted that the formation and transfer of electron charge from the surface of the crystal lattice of flint are associated with the deformation of the lattice in adsorption of water molecules. In [3], this charge is defined as a transverse macroscopic effective charge determined by local polarization occurring in relative displacement of the atoms in a deformed lattice.

Thus, the maxima on the curve of the distribution of the content of active molecular oxygen in water (see Fig. 1) must be associated with the maxima of distribution of the transverse charge (Fig. 3).

To assure ourselves that this is true we have carried out evaluations of the transverse surface charge of an oxygen atom in flint that previously contacted liquid water over different periods of time. These evaluations were based on experimental determinations of the volume of an elementary crystal lattice of flint as a function of the

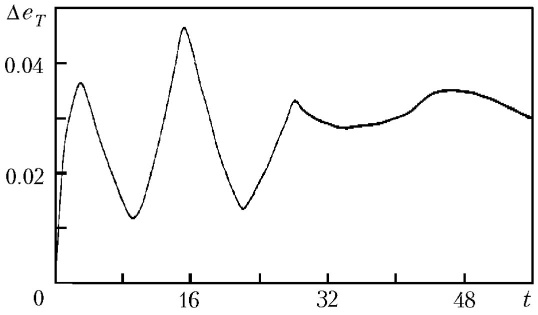

Fig. 3. Value of the transverse macroscopic effective charge of an oxygen atom of the lattice of flint vs. time of its contact with water. t, days; Δe_T in the units of electron charge.

amount of adsorbed water. For this purpose we used the diffractometry method. The procedure of experimental measurements has been presented in [7].

We found the maximum values of the deformations of the lattice for each of the flint samples differing in the time of contact with liquid water. These values were employed to calculate the transverse charge occurring due to the displacement of the atoms inside the lattice and characterizing the charge redistribution between the oxygen and flint atoms. We carried out this calculation, relying on the work of Harrison [3], where extensive use is made of the notion of transverse charge determining the relationship between the lateral vibrations of the lattice and the light waves and characterizing the local polarization of the atoms in their relative displacement in the lattice.

The general expression for transverse charge in any atom of the lattice and, in particular, in an oxygen atom is written as follows [3]:

$$e_T = \sqrt{e_x^2 + e_y^2 + e_z^2}\ . \tag{1}$$

According to [3], we have

$$e_x = Z^* + (3\sin^2\theta_0 - 1)\,\beta_{px}\,(1 - \beta_{px}^2) + 3\sin^2\theta_0\,(1 - \beta_{pz}^2)\beta_{pz}\ , \tag{2}$$

$$e_y = Z^*\ , \tag{3}$$

$$e_z = Z^* + 3\cos^2\theta_0\beta_{px}\,(1 - \beta_{px}^2) + (3\cos^2\theta_0 - 1)\,\beta_{px}\,(1 - \beta_{pz}^2)\ , \tag{4}$$

where

$$Z^* = \beta_{px} + \beta_{pz}\ ; \tag{5}$$

$$\beta_{px} = W_3\,(2W_2^2\sin^2\theta_0 + W_3^2)^{-0.5}\ ; \tag{6}$$

$$\beta_{pz} = W_3\,(2W_2^2\cos^2\theta_0 + W_3^2)^{-0.5}\ . \tag{7}$$

In deformation of the lattice, the angle θ_0 changes; its value is found from the formula

$$\Delta V/V = \Delta\theta_0\tan\theta_0\ , \tag{8}$$

where ΔV is the maximum change in the volume (maximum deformation) of the unit cell and V is the volume of the unit cell with a nearly zero content of the adsorbed water.

TABLE 1. Values of the Parameters Required for Calculation of the Electron Structure of SiO_2 (Flint) in Adsorption of Water on Flint Prestored over Different Periods of Time in Water

Time of presaturation of flint with water, days	$\Delta V/V$	d, Å	θ_0, deg	W_2, eV	W_3, eV	β_{px}	β_{pz}	Z^*	e_T	Δe_T
Flint without an adsorbate	0.00000	1.6100	18.000	10.9500	2.9300	0.5221	0.1951	0.7172	2.7510	–
0	0.00214	1.6070	17.613	10.9909	2.9300	0.5288	0.1940	0.7228	2.7810	+0.0300
3	0.00269	1.6056	17.511	11.0100	2.9300	0.5302	0.1935	0.7237	2.7875	+0.0365
9	0.00057	1.6090	17.900	10.9636	2.9300	0.5247	0.1949	0.7199	2.7621	+0.0112
15	0.00340	1.6045	17.380	11.0252	2.9300	0.5325	0.1932	0.7257	2.7978	+0.0458
22	0.00093	1.6085	17.830	10.9704	2.9300	0.5250	0.1946	0.7196	2.7640	+0.0131
28	0.00248	1.6060	17.550	11.0046	2.9300	0.5296	0.1937	0.7233	2.7848	+0.0339
34	0.00212	1.6066	17.618	10.9964	2.9300	0.5284	0.1939	0.7223	2.7795	+0.0285
44	0.00251	1.6060	17.545	11.0046	2.9300	0.5297	0.1937	0.7234	2.7853	+0.0343
56	0.00222	1.6064	17.600	10.9991	2.9300	0.5288	0.1939	0.7227	2.7813	+0.0303

Simultaneously with the change in the angle θ_0, we have a change in the length of the Si–O bond in the lattice, i.e.,

$$\Delta d = d\Delta\theta_0 \tan\theta_0 \,. \tag{9}$$

The energy of the covalent bond in the crystal depends on the bond length as follows:

$$W_2 = \frac{C}{d^2} \,, \tag{10}$$

where C is a constant.

We can determine the behavior of all the parameters appearing in formulas (2) and (7), knowing the change in the angle θ_0 and employing, in calculations, the values of these parameters obtained from the data of the "Generalized Periodic Table" [3] for $\Delta V/V \to 0$. The results of the calculations are presented in Table 1.

The dependence of the change in the transverse macroscopic effective charge of an oxygen atom of the lattice Δe_T on the time of preliminary storage of flint in water is also shown in Fig. 3.

As follows from Table 1 and Figs. 1 and 3, the maxima and minima of Δe_T coincide respectively with the maxima and minima of accumulation of active molecular oxygen in water. Such a coincidence is logical, since the mechanism of formation of this oxygen in water is associated with the occurrence and transfer of the transverse macroscopic effective charge of the lattice's oxygen atom.

In [3], it is stated that a strong interaction between electromagnetic vibrations and lattice vibrations exists for the crystal structures of SiO_2. This allows direct experimental study of the vibrational spectra in the crystal lattice from the IR-absorption spectra. In this work, it has also been established that each oxygen atom in the lattice corresponds to three frequencies of vibrations — ω_x, ω_y, and ω_z; the frequency ω_z has a maximum value, since it is associated with the largest extension of the bond. Next in value is the frequency ω_x, and the frequency ω_y has the lowest value.

The relationship between the frequency of vibration of the *i*th direction and the transverse macroscopic effective charge of an oxygen atom in the lattice in this direction is shown in [3]:

$$\omega_i = e e_{T(i)} \sqrt{\frac{N_0}{3\rho_i}} \,, \tag{11}$$

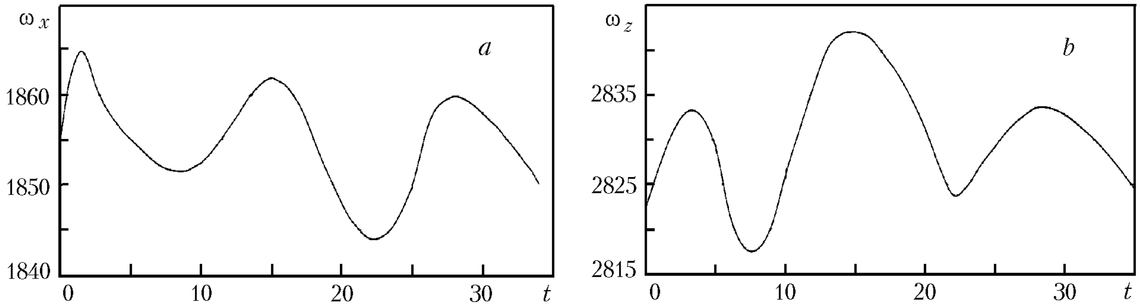

Fig. 4. Change in the frequency of vibrations of an oxygen atom along the x axis (a) and the z axis (b) in the SiO_2 structure in IR spectra vs. time of contact of water with flint. t, days; ω_x and ω_z, cm^{-1}.

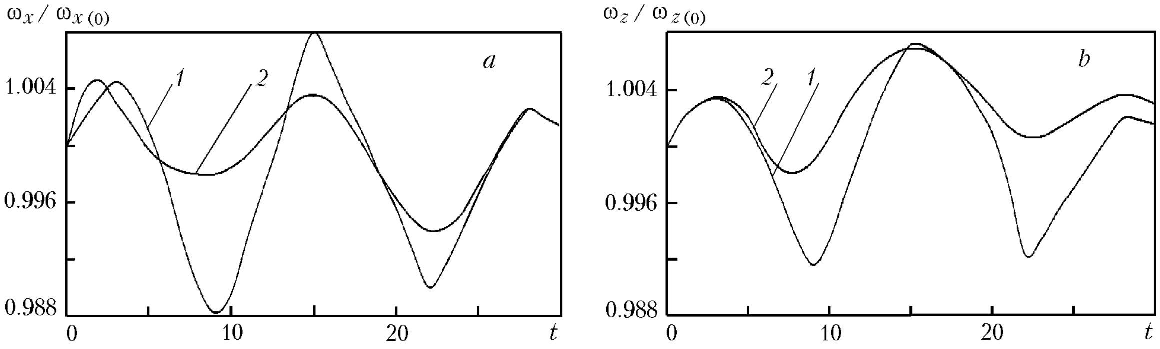

Fig. 5. Change in the relative value of vibration frequency of an oxygen atom along the x axis (a) and the z axis (b) in the SiO_2 structure vs. time of contact of water with flint: 1) in comparison of the frequencies in IR spectra; 2) from the data of calculation of the deformation of the crystal lattice of flint. t, days.

$$\rho_{i(x)} = \frac{N_0 e^2 d^2}{3W_3}\left[\beta_{pz}(1-\beta_{pz}^2) + \beta_{px}(1-\beta_{px}^2)\right]\frac{\sin^2\theta_0}{2}, \tag{12}$$

$$\rho_{i(z)} = \frac{N_0 e^2 d^2}{3W_3}\left[\frac{2\beta_{pz}\beta_{px}(1-\beta_{pz}\beta_{px})\cos^2\theta_0}{\beta_{pz}+\beta_{px}}\right]. \tag{13}$$

By substitution of the corresponding parameters from Table 1 into (11) and (12) we have determined the quantities $\omega_x/\omega_{x(0)}$ and $\omega_z/\ \omega_{z(0)}$, where $\omega_{x(0)}$ and $\omega_{z(0)}$ are the calculated frequencies obtained for flint without presaturation with water.

It is interest to obtain the experimental values of the frequencies of flint in the infrared spectrum as functions of the time of contact of the flint with water and to compare them to the experimental values of the frequencies obtained for flint without presaturation and to further compare the relative values of the frequencies, found from both the data on the deformation of the flint lattice and the experimental data on infrared spectra.

In the infrared spectrum of flint, we have obtained the following absorption bands: the first band with a frequency in the region of 800 cm^{-1}, corresponding to ω_y, the second band with a frequency of 1850 cm^{-1} (ω_x), and the third band with a frequency of 2820 cm^{-1} (ω_z). The frequency ω_y (800 cm^{-1}) is independent of the time of contact of the flint with water.

The experimental values of the frequencies ω_x and ω_z as functions of the time of contact of flint with water are presented in Fig. 4, whereas the changes in their relative values $\omega_x/\omega_{x(0)}$ and $\omega_z/\omega_{z(0)}$, obtained from the experimental data on their infrared spectra and from the data of calculation of the parameters of the electron structure of

SiO_2, are given in Fig. 5. These changes also obey the sine law; the positions of the extremum values of the frequencies and their relative values on the distribution curves coincide with the position of the extremum values of the transverse macroscopic effective charge of the crystal lattice and with the extremum values of the content of active molecular oxygen in water.

Thus, the results obtained establish the reasons why the molecular characteristics of water in constant contact with flint change.

These results yield a number of practical conclusions.

It has been established in the experiments that analogous sine dependences can be obtained not only in the storage cycle but in the filtration cycle as well. This brings up the question: Why is the mechanism of formation of the properties of "flint" water identical in the filtration cycle and the storage cycle? The answer is based on the following statement. As has already been noted, the formation of active molecular oxygen is associated with the capture of transverse charge by an oxygen molecule dissolved in water. This charge on an oxygen atom of the crystal lattice results from the deformation of the lattice in adsorption of water molecules. According to [8], the layer structure of the surface water in narrow pores with a regular distribution of hydrogen bonds between H_2O molecules enables us to single out the continuous filaments of Bernal and Fowler in these formations even at room temperature (or higher). Consequently, the surface water must serve as a good conductor for protons. It also follows from [8] that the limiting rate of transfer of a proton in water systems near the actual surfaces is $n \cdot 10^7$ cm/sec. The mobility of a proton does not attain its limiting value in the phase of water, since thermal motion destroys the stability of conductance filaments. Therefore, we can assume that the rate of transfer of charge (proton conductance) in the volume of water between flint particles will be 1 to 3 orders of magnitude lower than the rate in the thin pores of flint (this conclusion also follows from [8]). However, this rate of transfer in the volume will be 4 to 6 orders of magnitude higher than the rate of filtration of water. Consequently, the mechanism of accumulation of active molecular oxygen in "flint" water in both the filtration cycle and the storage cycle is identical. This is a very important conclusion which implies that in variation of the time of contact of flint with water one can obtain "flint" water with different degrees of charge in the molecular structure.

NOTATION

e_T, $e_{T(i)}$, and Δe_T, total value, value in the ith direction, and change in the total value of the transverse macroscopic effective charge of an oxygen atom in the crystal lattice; e_x, e_y, and e_z, components of this charge in the direction of the coordinate axes; e, electron charge; d, length of the Si–O bond in the crystal; N_0, number of oxygen atoms per unit volume of the lattice; $N_{O_2^-}$, concentration of active molecular oxygen, mg/liter; t, time, days; V, volume of the elementary crystal lattice; W_2 and W_3, energies of the covalent and ionic bonds in the crystal; Z^*, effective charge of an oxygen atom; n, number from 1 to 10; β_{px} and β_{pz}, fractions of the degree of ionization of the bonds in the crystal; $\Delta\alpha$, changes in the valence angle; θ_0, angle between the Si–Si and Si–O directions; ρ_i, dielectric susceptibility of the crystal along the ith direction; ω_i, frequency of vibrations of an oxygen atom in the lattice in the ith direction; ω_x, ω_y, and ω_z, vibration frequencies in the infrared spectrum of an oxygen atom in the crystal lattice along the x, y, and z axes; $\omega_{x(0)}$ and $\omega_{z(0)}$, calculated frequencies obtained for flint without presaturation with water. Subscripts: p, state of the electrons; x, y, and z, coordinates.

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