

Hydroxylchondrodite $\text{Mg}_5(\text{SiO}_4)_2(\text{OH})_2$: A New Mineral of the Humite Group and Its Crystal Structure

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The humite group comprises monoclinic and rhombic orthosilicates with additional anionic positions and a general formula $nA_2\text{SiO}_4 \cdot AR_2$, where the specie-forming components are $A = \text{Mg}, \text{Mn}^{2+}, \text{Ca}$; $R = \text{F}, \text{OH}$. The most abundant in nature are magnesium members of the group, which are accessory, but often rock-forming minerals of Mg-rich metamorphic rocks, skarn, alkaline–ultrabasic, and some other rocks. Four representatives of the magnesium subgroup with fluorine as a prevailing additional anion have been known for a long time. These are norbergite $\text{Mg}_3[\text{SiO}_4]\text{F}_2$, chondrodite $\text{Mg}_5[\text{SiO}_4]_2\text{F}_2$, humite $\text{Mg}_7[\text{SiO}_4]_3\text{F}_2$, and clinohumite $\text{Mg}_9[\text{SiO}_4]_4\text{F}_2$ [1]. Hydroxylclinohumite $\text{Mg}_9[\text{SiO}_4]_4(\text{OH})_2$ was described in 1999 as an individual mineral [2]. This paper concerns hydroxylchondrodite, an OH-dominant analog of chondrodite with the idealized formula $\text{Mg}_5[\text{SiO}_4]_2(\text{OH})_2$. It was approved as a new mineral specie by the IMA Commission on New Minerals, Nomenclature, and Classification July 5, 2010 (IMA No. 2010-019). The standard sample was sent to the Fersman Mineralogical Museum, Russian Academy of Sciences (registration no. 3986/1).

Hydroxylchondrodite was found in the Perovskitovaya Kop' on the western slope of the Chuvashskie Mountains in the Zlatoust region of the Southern Urals (Russia). It is located in the contact zone between magnesium skarn and host marble being intergrown in aggregates composed of calcite and clinocllore with dependent amounts of dolomite and tremolite. Among the other minerals are diopside, garnet of the andradite–grossular row, magnetite, perovskite, hydroxylclinohumite, and titanite. Hydroxyl-

chondrodite occurs as coarsely formed tabular or lens-like individuals with sizes up to $0.5 \times 1.5 \times 1.5$ cm and their intergrowths up to 2 cm. Thin polysynthetic twinning by {001} is observed under the microscope; the thickness of twin lamellas is usually ~ 1 μm , rarely up to 5 μm . The mineral is semitransparent, reddish brown, up to brownish red, the streak is pale-yellow, and the luster is vitreous. Mohs' hardness is 6. Hydroxylchondrodite is brittle, cleavage is not observed, fracture is uneven; sometimes parting by {001} is observed most likely resulting from the fact that grains are crushed along the boundaries between twin subindividuals. The density measured by balancing in the Klerichi solution is $3.21(1)$ g/cm^3 ; the calculated density is 3.183 g/cm^3 .

Hydroxylchondrodite is optically biaxial, positive, $n_p = 1.662(3)$, $n_m = 1.669(2)$, $n_g = 1.688(2)$, $2V_{\text{meas}} = 80(10)^\circ$, $2V_{\text{calc}} = 63^\circ$. The mineral has a strong pleochroism: X , brown; Y , light brown with grayish green tint; Z , very pale, grayish greenish brown; the scheme of absorption is $X > Y > Z$. The optical orientation is $Z = b$.

The chemical composition of the new mineral was determined on a scanning electron microscope Jeol JSM-6480LV with a combined system for X-ray spectral analysis. The analysis was performed in a combined regime: the concentrations of Mg, Fe, Ti, Si, and P were measured by the energy-dispersive spectrometer INCA-Energy 350 (ATW-2 window); F, by the wavelength spectrometer INCA-Wave 500. The conditions of the analysis were the following: accelerating voltage 15 kV, current 30 nA, beam diameter 3 μm . The following standards were applied: olivine, for Mg, Fe, and Si; lorenzenite, for Ti; fluorapatite, for P; MgF_2 , for F. The concentrations of other elements with atomic numbers exceeding that of O were below the detection limits. The absence of B, C, and N was confirmed by the X-ray structural analysis and IR-spectrum. The concentration of H_2O was determined by the method of Alimarin: selective sorption from gaseous products of ignition of the mineral at 1080°C

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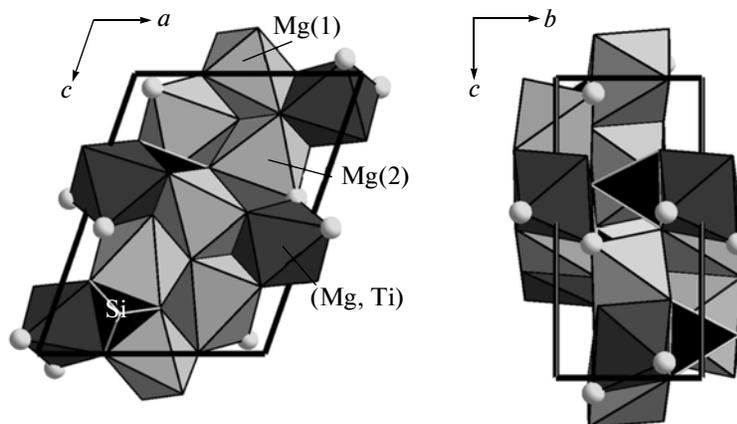


Fig. 1. Crystal structure of hydroxylchondrodite from the Perovskitovaya Kop', Southern Urals (*ac* and *bc* projections). Circles denote O(5) = (OH, O, F) positions; the solid line indicates the elementary cell.

and 1 atm in oxygen flow; absorption tubes filled with $\text{Mg}(\text{ClO}_4)_2$ were applied. The chemical composition of hydroxylchondrodite (wt %, dispersal of the values for 11 local analyses is given in parentheses) is the following: MgO 52.74 (52.2–54.3); FeO 1.51 (1.3–1.7); TiO_2 7.08 (6.8–7.2), SiO_2 34.38 (34.2–35.2), P_2O_5 0.47 (0.4–0.6); F 1.29 (1.1–1.5); H_2O 3.48; $-\text{O}=\text{F}_2 - 0.54$; total 100.41. The empirical formula calculated for the total of anions O + OH + F = 10 is $(\text{Mg}_{4.52}\text{Ti}_{0.31}\text{Fe}_{0.07})_{\Sigma 4.90}(\text{Si}_{1.98}\text{P}_{0.02})_{\Sigma 2.00}\text{O}_8[(\text{OH})_{1.33}\text{O}_{0.44}\text{F}_{0.23}]$. As is evident, OH in the new mineral significantly predominates over F. We should mention the high concentration of titanium in the hydroxylchondrodite and phosphorus admixture that is rarely observed for the members of the humite group.

Monocrystalline X-ray investigation of hydroxylchondrodite was performed for a polysynthetic twin on a diffractometer Xcalibur S CCD (MoK α radiation). The obtained parameters of the monoclinic cell [$a = 7.880(1)$ Å, $b = 4.726(1)$ Å, $c = 10.290(1)$ Å, $\beta = 109.04(2)^\circ$, $V = 362.2(5)$ Å³] and the structural model are typical for chondrodite [3, 4] and the synthetic analog of hydroxylchondrodite [5, 6]. However, twinning and the block character of crystals did not allow us to perform a study of the crystalline structure for the new mineral from the monocrystalline data up to a satisfactory value of the *R*-factor. The structure of hydroxylchondrodite was confirmed by the Rietveld method for a powder sample; the model of the structure of synthetic analog of the mineral reported by K. Yamamoto [5] was applied as the base.

Powder X-ray data were obtained on a diffractometer STOE STADI MP with linear position-sensitive detector (CuK α_1 radiation, $\lambda = 1.54056$ Å, scanning range $10.0^\circ \leq 2\theta \leq 97.8^\circ$) for the sample in a rotating capillary with a diameter of 0.5 mm. The powder diffraction data of the mineral is given in Table 1. The calculated parameters of the monoclinic cell are the following: $a = 7.8847(12)$ Å, $b = 4.7235(8)$ Å, $c =$

$10.2869(15)$ Å, $\beta = 109.19(1)^\circ$, $V = 361.83(16)$ Å³. The space group is $P2_1/c$, $Z = 2$.

Development of the powder data and structural analysis were performed using the software Wyriet 3.3 [7] and WinXPOW [8]. The Pearson-VII function was used for the modeling of the X-ray pattern profile. The final values of divergence factors are $R_p = 0.0335$, $R_{wp} = 0.0524$, $R_{\text{Bragg}} = 0.0340$, and $R_F = 0.0365$. The coordinates and parameters of heat mixing of atoms are given in Table 2.

As a whole, the crystal structure of hydroxylchondrodite from the Perovskitovaya Kop' is analogous to the chondrodite structure [3, 4], except for OH prevalence in the F position. Mg cations occupy the octahedral positions of three types. Admixtures of elements with atomic numbers exceeding that of Mg (Ti and Fe) are mainly accumulated in the positions Mg(3) = (Mg,Ti) (Table 2, Fig. 1). Additional anions with a strong prevalence of $(\text{OH})^-$ – occupy the O(5) positions located in two apexes of the octahedron connected by joint edge Mg(3) = (Mg,Ti) (Fig. 1).

H atoms were not localized during the structure refinement because of the low crystal quality. The previously published data demonstrate that in synthetic fluorine-free analogs of hydroxylchondrodite, H or D atoms (forming (OH) or (OD) groups with O atoms corresponding to O(5) in our model) are located in two positions; each of them is occupied by ~50% (H-disordered model [5, 6]). At the same time, only one H position was registered in chondrodite with $F \geq \text{OH}$ [4]. D atoms were in both positions for two H-bonds each in deuterium-replaced synthetic analog of hydroxylchondrodite [6]. Similarly to synthetic phases [5, 6] and according to the IR-spectroscopic data for our sample (see below), we suggest that H atoms occupy two positions and probably form bifurcated hydrogen bonds in hydroxylchondrodite from the Perovskitovaya Kop'. The distance O(5)–O(5) between neighboring octahedra is 2.88(1) Å, which is favorable

Table 1. Results of the calculation of the powder X-ray pattern of hydroxylchondrodite from the Perovskitovaya Kop', Southern Urals

I_{meas}	$d_{\text{meas}}, \text{\AA}$	I_{calc}^*	$d_{\text{calc}}, \text{\AA}$	hkl
24	4.869	38	4.8657	10-2
3	4.259	1.5	4.2480	011
10	3.9925	13	3.9887	110
4	3.9438	4.5	3.9417	11-1
6	3.7194	10	3.7233	200
26	3.5677	11, 21	3.5768, 3.5672	20-2, 102
26	3.4794	25	3.4808	111
16	3.3854	3, 15	3.3892, 3.3865	11-2, 012
36	3.0225	42	3.0237	21-1
2	2.9226	2.5	2.9241	210
6	2.8508	8	2.8515	21-2
37	2.7631	32	2.7635	11-3
37	2.6731	37	2.6710	013
44	2.6209	45	2.6196	211
3	2.5767	1.5, 1	2.5806, 2.5746	30-2, 202
59	2.5175	50	2.5175	21-3
7	2.4816	7.5	2.4822	300
10	2.4278	2.5, 6.5	2.4329, 2.4288	20-4, 004
18	2.3216	19	2.3220	113
35	2.2928	14, 23	2.2949, 2.2914	021, 31-1
74	2.2602	31, 27, 29	2.2647, 2.2606, 2.2586	31-2, 212, 11-4
3	2.2427	2	2.2427	12-1
9	2.1464	5.5	2.1467	121
2	2.1278	1.5	2.1287	31-3
6	2.1178	6	2.1187	30-4
5	2.0238	5	2.0251	22-1
3	2.0195	3	2.0204	311
2	1.9678	0.5	1.9709	22-2
4	1.9397	2.5	1.9411	12-3
7	1.8813	4	1.8822	11-5
2	1.8528	2.5	1.8539	21-5
4	1.8131	3.5	1.8136	312
5	1.8025	4	1.8030	41-1
6	1.7964	4.5	1.7970	015
2	1.7878	1.5	1.7884	40-4
2	1.7676	2	1.7687	41-3
100	1.7402	31, 37, 32	1.7423, 1.7404, 1.7395	32-2, 222, 12-4
2	1.7257	1	1.7260	31-5
4	1.7108	3	1.7110	320
3	1.7027	2	1.7037	20-6
11	1.6928	2.5, 8	1.6946, 1.6932	22-4, 024
2	1.6780	1.5	1.6780	32-3
3	1.6360	3	1.6370	115

Table 1. (Contd.)

I_{meas}	$d_{\text{meas}}, \text{Å}$	I_{calc}^*	$d_{\text{calc}}, \text{Å}$	hkl
8	1.6219	1.5, 5, 1	1.6234, 1.6219, 1.6216	321, 30-6, 411
8	1.6196	5.5	1.6192	006
12	1.6129	11	1.6132	313
2	1.6019	0.5, 1	1.6027, 1.6018	21-6, 11-6
11	1.5769	1, 5.5, 2	1.5786, 1.5771, 1.5765	223, 32-4, 50-2
3	1.5543	2	1.5542	031
2	1.5500	2	1.5495	41-5
3	1.5380	2.5	1.5377	13-1
2	1.5326	1	1.5332	22-5
4	1.5100	2	1.5099	50-4
9	1.5057	3, 4	1.5061, 1.5057	304, 131
5	1.4993	2, 2	1.5005, 1.4978	025, 032
46	1.4889	26, 21	1.4893, 1.4876	500, 40-6
31	1.4845	26, 9	1.4842, 1.4830	106, 51-3
3	1.4616	0.5, 1	1.4620, 1.4619	420, 23-1
1	1.4576	1	1.4584	32-5
2	1.4414	1	1.4411	23-2
1	1.4392	0.5	1.4382	51-4
3	1.4296	2	1.4293	13-3
1	1.4235	0.5	1.4233	224
3	1.4163	2	1.4160	033
4	1.4084	3	1.4082	231
15	1.4020	1, 11	1.4036, 1.4018	125, 21-7
6	1.3920	4	1.3916	23-3
3	1.3635	2.5	1.3637	413
2	1.3563	1.5	1.3558	133
3	1.3498	2.5	1.3496	33-1
27	1.3439	9, 9, 6	1.3441, 1.3432, 1.3428	33-2, 232, 13-4
3	1.3366	1.5	1.3367	50-6
3	1.3328	2, 0.5	1.3332, 1.3316	206, 017
4	1.3219	2.5, 1.5	1.3218, 1.3212	23-4, 034
2	1.3093	0.5, 1	1.3098, 1.3085	422, 502
1	1.2961	1	1.2961	52-1
4	1.2823	0.5, 0.5, 2.5, 1	1.2834, 1.2831, 1.2822, 1.2722	225, 216, 315, 52-4
2	1.2415	1.5, 1	1.2420, 1.2407	414, 21-8

* For better comparison of experimental and calculated data by intensities, the values I_{calc} were recalculated onto $I_{32-2} + I_{222} + I_{12-4} = 100$, since they are overprinted on the experimental powder pattern and combined give the most intense reflex. Primarily the values of I_{calc} for reflections 32-2, 222, and 12-4 were 63, 74, and 63, respectively, whereas the 213 reflection had $I_{\text{calc}} = 100$.

for the formation of an H-bond with participation of the hydrogen atom indicated as H(1) in [5]. The distances between O(5) and O(1) are 2.96(1), 2.87(1), and 3.03(1) Å; the latter does not contradict the formation of the hydrogen bond with the H(2) atom, and the first two, with the H(1) atom. The distance O(5)–

O(2) of 2.86(1) Å is favorable for the formation of the H-bond with participation of H(2) (all interatomic distances are given for the studied structure of the sample from Perovskitovaya Kop').

The absorption bands in the IR-spectra of hydroxylchondrodite (Fig. 2a) and their attributions are the

Table 2. Coordinates (x, y, z) and parameters of heat mixings ($B, \text{\AA}^2$) of atoms, frequency rate (Q), and occupation (s.o.f.) of positions in the structure of hydroxylchondrodite from the Perovskitovaya Kop', Southern Urals

Site	x	y	z	B	Q	s.o.f.
Mg(1)	0.5	0.5	0	1.4(4)	1	1
Mg(2)	0.3073(11)	0.016(2)	0.1753(9)	1.0(3)	2	1
Mg(3) = (Mg,Ti)*	0.0780(11)	0.498(2)	0.8915(9)	0.8(3)	2	1
Si	0.7029(13)	0.0800(15)	0.1429(8)	1.2(2)	2	1
O(1)	0.294(3)	0.777(3)	0.003(2)	1.0(6)	2	1
O(2)	0.119(3)	0.712(3)	0.240(3)	1.0(6)	2	1
O(3)	0.530(3)	0.226(3)	0.163(3)	1.2(6)	2	1
O(4)	0.300(3)	0.262(3)	0.856(3)	0.8(5)	2	1
O(5) = (OH,O,F)	0.098(3)	0.256(3)	0.051(3)	0.8(7)	2	1

* Specified as $(\text{Mg}_{0.85}\text{Ti}_{0.15})$.

following (cm^{-1} ; f, faint band; s, shoulder): 3555f, 3512f, 3377 (stretching vibrations O–H); 1080s, 1020s, 993, 901, 853, 830s (stretching vibrations Si–O); 779f, 738 (bending vibrations Si–O and stretching vibrations $\text{Mg}\cdots\text{O}-\text{H}$); 614, 541, 476, 445s, 416 (bending vibrations Si–O, and stretching Mg–O). The most intense band of stretching vibrations O–H at 3377 cm^{-1} corresponds to strong hydrogen bonds $\text{OH}\cdots\text{O}$, which are formed between OH-groups being a relatively short distance from each other: $\langle \text{O}(5)-\text{O}(5) \rangle = 2.88 \text{ \AA}$. The faint band at 3555 cm^{-1} corresponds to the local situation, when the O(5) position being an acceptor of the hydrogen bond is occupied by F. Such a conclusion follows from comparison with chondrodite, in which $\text{F} > \text{OH}$ and most of the hydroxyl groups neighbor with F, but not with other OH-groups [6, 9]: this band with a maximum at 3549 cm^{-1} in the chondrodite spectrum (Fig. 2b) is the strongest in the considered area. Another faint hydrogen bond in hydroxylchondrodite is evident from a low-intensity band at 3512 cm^{-1} . It is most likely that this H-bond appears between the O(5)–H group and the O atom that is a bridge between neighboring Mg atoms, similarly to the synthetic analog of hydroxylchondrodite [5], in which H atoms bonded with O(5) occupy two positions and form hydrogen bonds of two types. The formation of relatively strong H-bonds $\text{OH}\cdots\text{O}$ in hydroxylchondrodite (instead of $\text{OH}\cdots\text{F}$ in quite high-fluorine chondrodite) results in the low-frequency shift of the band of bending vibrations of $\text{Mg}\cdots\text{O}-\text{H}$ groups from 763 to 738 cm^{-1} .

The IR spectrum of the most high-fluorine chondrodite from the burnt bank of the coal mine in Kopeisk (Southern Urals) does not contain bands related to O–H vibrations (Fig. 2c). We should also mention that none of the spectra of chondrodite and hydroxylchondrodite contain the bands of bending

vibrations H–O–H; i.e., the total hydrogen in these minerals belongs to OH-groups, and H_2O molecules are absent.

As is evident from Fig. 2, hydroxylchondrodite is clearly different from chondrodite by the IR-spectrum. The index of refraction significantly exceeding that of chondrodite is another diagnostic feature of the new mineral; this undoubtedly results from F replacement by OH. The influence of this factor is much stronger than Mg replacement by Ti or Fe. Thus, indices of refraction of chondrodite varieties even enriched in Ti and/or Fe range in the following limits: $n_p = 1.592-1.643$, $n_m = 1.602-1.655$, $n_g = 1.621-1.676$ [10], this is remarkably lower than those for hydroxylchondrodite.

Members of the chondrodite series with a low concentration of fluorine up to its complete absence were already reported in publications. They are usually enriched in Ti. Thus, the full chemical analysis of fluorine-free “titanochondrodite” containing 8.46 wt % TiO_2 and 2.67% H_2O^+ , from the Bol'shaya Shishimskaya Kop' in the same Zlatoust region of the Southern Urals as the Perovskitovaya Kop' (and related to the same elongated zone of skarns located at the contact between granite–gneiss and dolomitic marbles) was reported by I.D. Borneman-Starynkevich in 1964 [11]. Fluorine-free “titanium chondrodite” from kimberlite of the Buell Park in Arizona (United States) was studied in [12, 13]. “Ti-chondrodite” with 0.33 F atoms per formula unit was established in garnet pyroxenite from Dabie Shan (China) [14]. Although H_2O was not analyzed in the samples from Buell Park and Dabie Shan, according to the calculation of their empirical formulas, we may assume with a high probability that they are related to hydroxylchondrodite. Thus, this mineral is most likely not so rare in nature, being observed in the formations of various geological

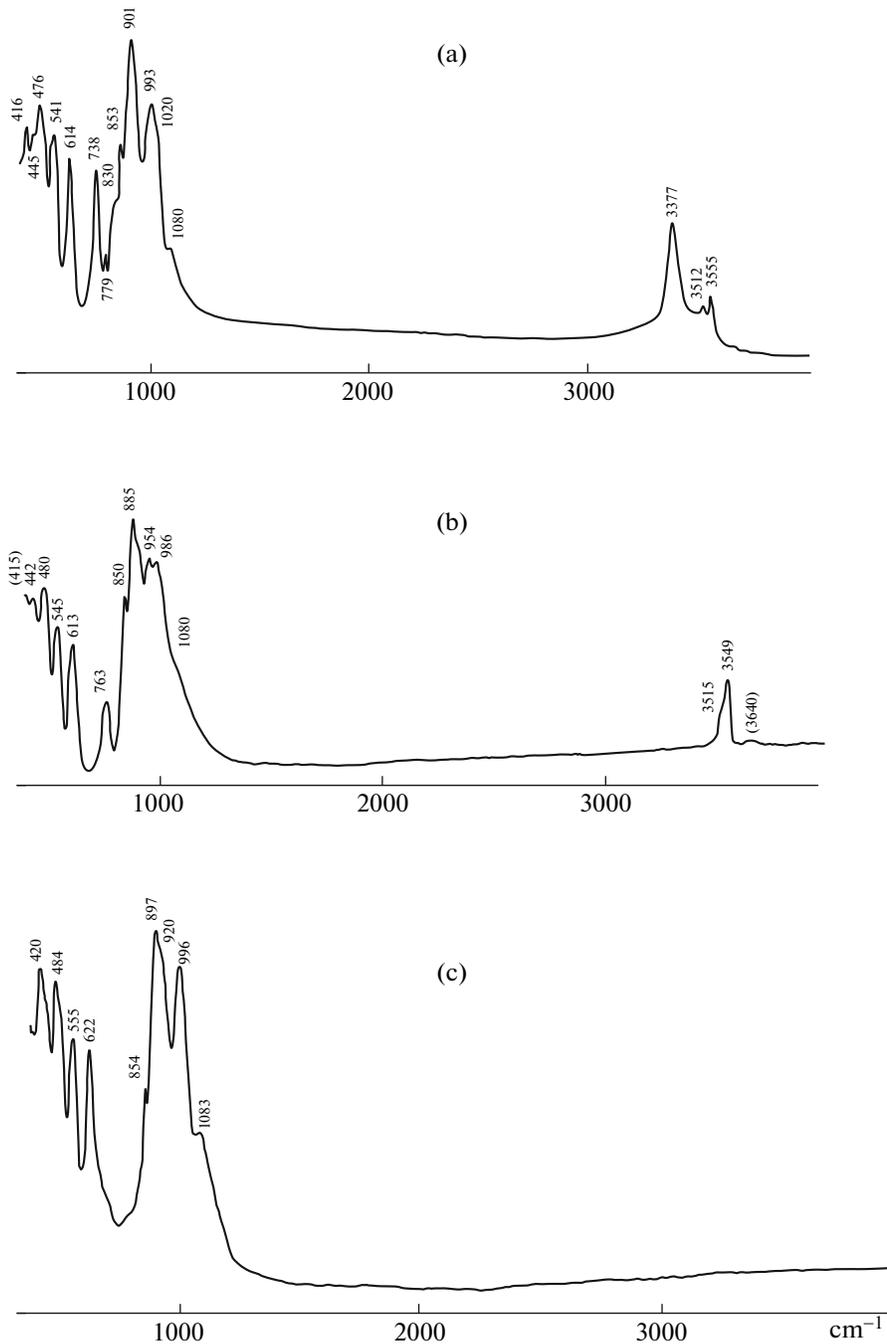


Fig. 2. IR-spectra: (a) hydroxylchondrodite from the Perovskitovaya Kop', Southern Urals; (b) typical chondrodite from Franklin, New Jersey, United States, with the composition $Mg_{4.59}Mn_{0.31}Zn_{0.16}Si_{1.97}O_{8.00}F_{1.10}(OH)_{0.90}$ (OH concentration is calculated); (c) hydroxyl-free chondrodite practically corresponding to the composition of $Mg_5(SiO_4)_2F_2$ end-member, from burnt bank of the coal mine in Kopeisk, Southern Urals.

and genetic types, under conditions of fluorine deficiency.

In conclusion, we should mention that the minerals of the humite group and OH-bearing magnesium silicates structurally similar to them are considered as important water accumulators in the Earth's mantle [15]. In this aspect, hydroxylchondrodite is interesting

not only from the geochemical position, but undoubtedly the geophysical point as well.

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