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SECOND OCCURRENCE OF CARLETONITE, MURUN MASSIF (RUSSIA): SCXRD, POWDER XRD, EPMA, FTIR AND TG-DSC STUDY

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Carletonite, $KNa_2Ca_4Si_8O_{18}(CO_3)_4(OH,F)\cdot H_2O$, a rare mineral, belonging to apophyllite group of phyllosilicates, was discovered in 1971 by Chao and named after Carleton University [1]. Before now the only known world occurrence of carletonite was the Poudrette Quarry, Mount Saint-Hilaire, Canada. The SCXRD investigation on this mineral dates back to 1972 [2]; it has a complex layer structure. Carletonite structure contains infinite branched sechser double silicate layers [3], composed of interconnected four and eight-member rings of Si-tetrahedra and connected through walls of K-, Na- and Ca-polyhedra and CO_3-triangles.

In this work the first description of the crystal chemical features of carletonite from the Murun massif (the second finding in the world), obtained by means of SCXRD, powder XRD, EPMA and, in addition, TG-DSC and FTIR methods, is reported.

The investigated sample was found in the unique charoititic rocks of the Murun potassium alkaline complex, located in the northwestern part of the Aldan Shield, Siberia, Russia. It associates with charoite, apophyllite-(KF), pectolite, fluorapatite, aegirine, agrellite, microcline, quartz, chalcocite, digenite, galena, covellite and copper, whereas carletonite from nepheline syeniyes of Mount Saint-Hilaire coexists with pectolite, arfvedsonite, quartz, microcline, albite, apophyllite-(KF), fluorite, ancelite-(Ce), and leifite [1].

The XRD pattern is similar to that obtained by [1]. SCXRD analyses confirm that carletonite is tetragonal, it crystallizes in sp. gr. P4/mbm and has following unit cell parameters: a = 13.216(2) Å, c = 16.722(2) Å, V = 2920.8(9) Å3 (Crl-1 sample, at room temperature), a = 13.1808(5) Å, c = 16.6980(8) Å, V = 2901.0(3) Å3 (Crl-2 sample, at 100 K). The analyzed crystals were refined up to R = 5.0% (Rw = 5.6%) and R = 1.7 (Rw = 1.9%), for Crl-1 and Crl-2, respectively. The EPMA (an average of 15 analyses) gave the following component contents (wt. %): SiO_2 43.9(6), CaO 20.0(3), Na_2O 11.0(3), K_2O 4.4(2), F 0.9(5), TiO_2 0.1(1), Al_2O_3 0.03(3), the sum is 80.33. The mass spectra (TG-DSC) exhibited the presence of H_2O and CO_2: the endothermic effects at 45 – 127 ºC and 127 – 315 ºC are accompanied by a weight loss of 0.15% and 1.02% related to the release of water; the endothermic effect at 630 – 1134 ºC accompanied by a weight loss of 14.9% results from the release of CO_2.

FTIR spectrum was acquired from 4000 to 400 cm-1 range. The bands observed at 1396, 1451, 1479 and 1526 cm-1 are assigned to CO_3 stretching vibration, whereas the bands founded at 660, 691, 728, 783, 874 cm-1 are attributed to bending vibration of CO_3. Water stretching band is observed at 3434 cm-1 and a line at 1624 cm-1 is assigned to the bending vibration of H_2O. Finally, a peak at 3554 cm-1 is attributed to the stretching vibration of the hydroxyl units.

An empirical formula of the studied carletonite, calculated on the basis of (Al+Si)=8, is $K_{1.04}Na_{3.95}Ca_{3.97}Ti_{0.02}Si_{7.99}Al_{0.01}O_{18}(CO_3)_{3.98}(F_{0.5}OH_{0.5})*1.05H_2O$. The H_2O and CO_3 contents were defined by structural refinement of the occupancy of the Ow11, Ow12, C1 and C2 sites.

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