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### STRUCTURAL INVESTIGATION OF ADELITE AND COBALTAUSTINITE, TWO MEMBERS OF THE ADELITE-DESCLOIZITE GROUP

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Compounds crystallizing in the adelite-descloizite structure type have the formula  $M1^{1+,2+}M2^{2+,3+}(OH)(X^{4+,5+,6+}O_4)$ , M1 = Na, Ca, Pb; M2 = Mg, Al, Mn, Fe, Co, Ni, Cu, Zn; X = Si, P, V, As, Mo. More than a dozen of minerals belong to this group, however, investigations on synthetic compounds are rare. Compounds with accurate structure refinements exhibit space-group symmetries Pnam or  $P2_12_12_1$ . The deviation from the centrosymmetric parental structure is moderate. Single-crystal X-ray structure investigations were performed for adelite,  $CaMg(OH)(AsO_4)$  (Palache et al., 1951) and cobaltaustinite,  $CaCo(OH)(AsO_4)$  (Nickel & Birch, 1988). The acentric space group  $P2_12_12_1$  was proved for both minerals:  $a = 7.468(1) / 7.475(1)$ ,  $b = 8.953(2) / 8.976(2)$ ,  $c = 5.941(1) / 5.916(1)$  Å; NONIUS four-circle diffractometer, CCD detector, capillary-optics collimator, Mo tube, graphite monochromator; program SHELXL (Sheldrick, 1996),  $R1 = 0.018 / 0.020$ ,  $wR2 = 0.038 / 0.048$ ; 1378 / 1364 reflections [1355 / 1342 with  $F_o > 4\sigma(F_o)$ ] up to  $2\theta = 65^\circ$ ; for non-hydrogen atoms anisotropic displacement parameters were refined; the H atom was found from a difference Fourier map and was refined isotropically. The type structure exhibits  $M2O_6$  octahedra (elongated tetragonal dipyramids in case of divalent Cu atoms due to Jahn-Teller distortion) edge linked to chains parallel to [001]. Each of the  $XO_4$  tetrahedra link two such chains to a three-dimensional network. Cavities house the M1 atoms. Their coordination varies from [7] to [8] depending on the space-group symmetry. In adelite / cobaltaustinite the average M2-O and As-O bond distances are 2.0754 / 2.0867 and 1.6924 / 1.6911 Å. The average M1-O bond distance is 2.5238 / 2.5187 Å; the coordination polyhedron is a slightly distorted tetragonal antiprism. O-H is 0.85 / 0.84 Å, O-H...O is 2.766 / 2.714 Å.

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### ISOMORPHISM PECULIARITIES OF THE SYSTEM CHATKALITE - MAWSONITE, $Cu_6FeSn_2S_8$ - $Cu_6Fe_2SnS_8$

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Mawsonite,  $Cu_6Fe_2SnS_8$  is the mineral related to stannite group with the structure derivative of sphalerite type (Szymanski, 1976). Based on the formula and x-ray data similarity the rare mineral chatkalite,  $Cu_6FeSn_2S_8$ , found in 1981, has been assigned to the same structure type (Kovalenker et al., 1981). The chatkalite structure is not carried out till now because of its rarity and of the absence of available crystals. The element composition and the "Metals:S" ratio of these two minerals are identical, and lead to the conclusion about the isomorphous replacement Fe-Sn. For prove this idea the experimental study of the series  $Cu_6FeSn_2S_8$  -  $Cu_6Fe_2SnS_8$  has been carried out for the first time. Compounds  $Cu_6Fe_{2-x}Sn_{1+x}S_8$ , synthesized by melting the elements in necessary proportions under condensed system, have been studied using ore microscopy, x-ray, microprobe, and moessbauer spectroscopy. Although the whole isomorphous series chatkalite-mawsonite was not obtained, but end members as well as some intermediate ones have been studied. In connection with the recent results on the complex type of isomorphism in stannite type compounds, i.e. kesterite (Rusakov et al., 2001), and kuramite-stannite series (Evstigneeva et al., 2001) the valence state and the co-ordination of  $^{57}Fe$  and  $^{119}Sn$  in these compounds are have been studied. Moessbauer spectra of  $^{57}Fe$  under the room temperature have the ultrafine structure of paramagnetic type. Iron in chatkalite corresponds to  $Fe^{2+}$ . Mawsonite contains  $Fe^{3+}$ . Spectra of other members of the series present the superposition of two well-resolved partial spectra ( $Fe^{2+}$  and  $Fe^{3+}$ ). The number of  $Fe^{3+}$  increases but of  $Fe^{2+}$  decreased as the total Fe contents increases. Moessbauer spectra of  $^{119}Sn$  are of paramagnetic type, and present two type of  $Sn^{4+}$ : a) with strong ionic bond  $Sn^{4+}-S$ , and strong covalent bond  $Sn^{4+}-S$ . The covalence of bond  $Sn^{4+}-S$  increases, but of  $Fe^{2+}-S$  decreases as the Fe content increases. Authors thank the Russian Foundation of Basic Researches for financial support (Project\_00-05-64609).

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