08.1.05 CRYSTAL CHEMISTRY OF Ca, R.E., AND Zr SILICATES, AS DERIVATIVES OF WOLLASTONITE CHAINS. By M. J. Chiragov, Department of Geology, The Azerbaijan State University, 370122 Baku, USSR.

Holmium silicate, $\text{K}_2\text{HoSi}_2\text{O}_7$ (Chiragov 1979), Azerb. Univ. Geol. Bull.), is isostructural with $\text{K}_2\text{Si}_2\text{O}_7(\text{OH})_2$ (Ilyukin 1968, Dokl. Acad. Nauk USSR). Both are insilicates and the $\text{Si}_2\text{O}_7$ groups that are part of their structures can be considered analogous to corresponding groups in the wollastonite chain, from the points of view of symmetry elements, bond angles and oxygen sharing with the cationic octahedron. Similar analogies exist in the arrangement of chains and distribution of cations in the structures of rhodonite (Ilyukin 1958), Dokl. Acad. Nauk Azerb.SSR), babingtonite Fe$^{2+}$Fe$^{3+}\text{Ca}_2\text{Si}_2\text{O}_7$(OH), inosite $\text{Mn}_2\text{Si}_2\text{O}_7$(OH)$_2\cdot\text{SH}_2\text{O}$, and pyroxmangite $\text{Mn}_2\text{Fe}_2\text{CaSi}_2\text{O}_7$. In these silicates the insilicate groups bond themselves only to the octahedron of the Ca atom. Taking this peculiarity into account, the formation of chain types can be presented as follows:

in rhodonite, $\leq$ equals

$\text{Si}_3\text{O}_10 + \text{SL}_2\text{O}_7 = (\text{SL}_3\text{O}_2\text{O}_3) + 2 \text{ O}$

12.2 $\tilde{A}$; $7.2 + 3.2 = 12.4$;

in pyroxmangite, $\geq$ equals

$\text{Si}_2\text{O}_7 + 2\text{SL}_2\text{O}_7 = (\text{SL}_3\text{O}_2\text{O}_3) + 3 \text{ O}$

17.4 $\tilde{A}$; $7.2 + 2x5.2 = 17.6$.

Our conclusion is that, in silicate structures characterized by derivatives of the wollastonite chain, the basic motifs are the insilicate groups $\text{SL}_2\text{O}_7$ polymerized with octahedrons of large cations. We consider the scheme of formation of different structural types from simple structural units from this point of view.

08.1.06 CRYSTAL STRUCTURE PREDICTION BY ENERGY MINIMIZATION. By N. K. Cullum, A.N. Cormack, University College London, and F. Theobald, Laboratoire de Chimie Physique, Besançon, France.

This paper will show that calculations of crystal energetics for ionic solids coupled with efficient minimization routines are capable of predicting the structure of complex inorganic solids, thereby promising to provide a valuable guide in structure refinements. The calculations we discuss are based on exact summations of both Coulomb and short-range components of the lattice energy. Energy minimisation may be performed with respect to all structural parameters. We illustrate the power of our method with two examples. The first concerns the recently discovered W phases of VO$_2$ and TiO$_2$ (Marchand et al., Mat. Res. Bull. 15, 1129 (1980)). Energy minimisations were performed starting from an ideal model based on regular octahedra. The minimised structure shows distortions close to those observed in the X-ray refined model for VO$_2$.

The predicted structure for the analogous "Ca" phase of TiO$_2$ is also presented; no experimental structure is yet available for this phase. Our second example is the mineral fetscherite (Na$_2$Si$_2$O$_7$) where again we show that distortions from idealised models are correctly predicted. We conclude with a discussion of potential future application of the technique to complex transition metal compounds and to minerals.

08.1.07 STRUCTURE BUILDING PRINCIPLES IN THE Pb-Bi-(Ag,Cu) SULPHOSALTS AND RELATED COMPOUNDS. By Emil Hakovicky, Mineralog. Inst., Copenhagen, Denmark.

In comparison with As and Sb, (1) bismuth displays the smallest differences in the lengths of distinct categories of Bi-S bonds (resp. distances) and sometimes forms regular coordination octahedra; (2) the S-S dimensions of the full Bi-S coordination polyhedra differ least from those of the Pb-S polyhedra. In some sulphosalts differences between Pb and Bi are important and they are ordered (cosalite) whereas some are based on, or tolerate extensive mutual Pb-Bi substitution (lillianite, heyrovskyite, PbS$_8$Bi$_5$, cannizarite). Introduction of Sb for part of S augments the geometrical tolerance for Pb-Mi variations over structural sites and the gamut of structural types. Structurally related compounds will also be quoted.

The structures of the Pb-Bi sulphosalts can be represented as modulated structures, usually based on somewhat deformed "galena-like" structure sliced in different crystallographic directions (slices parallel to (100) of PbS will be called T layers, those parallel to (111) of PbS will be called H layers). The combinations of several modulatory operators create distinct structural types; the homologues in each series differ in the H/T match and/or layer thickness: (1) The cannizarite, galena-like - regular octahedra.

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