08.4-16   НЕОБЫЧНЫЙ СЕРПЕНТИН ИЗ КИМБЕРЛИТОВ.
Л.В.Никишова, Институт геологии Якутского филиала Сибирского отделения АН СССР, 677982, Якутск, СССР.

В электронном микроскопе изучены серпентиновые минералы из кимберлитовых пород Якутии. Обнаружен хризотил в виде коротких толстых трубок-рулонов с большими диаметрами волокон (600-1500Å). Отношение диаметров к длине порядка I:2-I:5. Период вдоль удлинения 5,38 Å. На картинах микродифракции рефлексы на слоевых сливаются в непрерывные линии, параллельные оси $c^{\times}$. Часто на фоне таких линий на чётных слоевых наблюдаются интенсивные дискретные отражения, расположение и интенсивность которых не позволяют отнести изученный материал к какому-либо определенному типу по существующим номенклатурам серпентиновых минералов (Звягин, Мищенко, Шитов, Кристаллография, (I965) 10, 635; Wicks, Whittaker, Can. Miner.(I975) 13, 227).Предполагается, что в данном случае встречен полигональный серпентин (Cressey, Zusseman, Can. Miner. (1976) 14, 307; Cressey, Can. Miner. (1979) 17, 741).

with 20 per cent replacement of calcium by strontium and similar replacement of silicon by germanium display a ring form at all temperatures, with either well ordered four- or six-layer polytypes, the latter being identical to the determined structure of strontium germanate (Hilmer, Soviet Physics, Crystallography, (1962) 6, 694). With further germanium substitution, the chain variety re-appears, existing in an ordered form when 80 per cent of the silicon has been replaced. At the annealing temperatures employed (1100 - 1350 °C), the maximum strontium replacement of calcium is limited to just over 20 per cent.

The observed results are in accordance with the structural principles established by Liebau (Handbook of Geochemistry, (1972) Vol. II, Chap. 14), namely that structure type is mainly dependent upon the radius ratio of tetrahedral and octahedral cations. Strontium replacement of calcium rapidly stabilises the ring structure, the chain variety only re-appearing if the larger germanium replaces silicon. With larger cations in both tetrahedral and octahedral sites, the anion framework is strained and structural distortions might be expected to be severe, resulting in a greater tendency to form regular stacking sequences. The experimental observation that severe disorder occurs only in calcium- and silicon-rich phases is in accordance with this hypothesis.

08.4-17   HIGH RESOLUTION ELECTRON MICRO-SCOPIC STUDIES OF THE SYSTEM $(Ca,Sr)(Si,Ge)O_3$
By Wen Shu-Lin and D.A.Jefferson, Dept. of Physical Chemistry, Lensfield Road, Cambridge, U.K.

The nature of phases and defect-structure phenomena, and the transformations in this system are clearly revealed by the lattice-imaging technique, using samples prepared by annealing the amorphous quench product from the appropriate oxide melts. In the calcium-silicon end member, conversion from chain- (wollastonite) to ring-structure (pseudowollastonite) is observed at 1150 °C. The transformation proceeds via an amorphous intermediate stage, which is directly observed. No evidence is found for a topotactic process. With 20 per cent germanium substituted for silicon, almost identical behaviour is noted, but at a higher (1250 °C) temperature. In both cases the ring form is a disordered four-layer polytype, and in the latter the chain variety also exhibits almost completely random stacking disorder. With germanium substitution of 40 per cent, the ring structure is not found, but severe stacking disorder persists in the chain form until more than 60 per cent substitution. Beyond this figure, only regular chain structures are found.

Replacement of calcium by strontium in the wollastonite structure has already been reported (Wen Shu-Lin, Jefferson and Thomas, Mat. Res. Bull. (1980) 15, 1643) where ring structures are observed at all compositions. With germanium substitution for silicon, this behaviour is modified. Compositions

08.4-18   THE NATURE OF COHESION ENERGY OF DICKITE LAYERS ON THE BASIS OF ITS STRUCTURE REFINEMENT. By A.S.
Bookin, V.A. Drits and I.V. Rozhdestvenskaya, Geological Institute of the Academy of Science, Moscow, USSR.

Refinement of the dickite structure with modern X-ray techniques did not produce appreciable deviations from the previous study (Newnham, Min. Mag. (1961) 32, 683). However, with more accurate data, the difference Fourier map contained peaks corresponding to the H atoms of the hydroxyls:

	x/a	y/b	z/c	O-H (Å)	Θ experimental	φ experimental	Θ calculated	φ calculated
H1	.425	.254	.144	.965	14	210	16	212
H2	.289	.917	.355	.805	83	143	70	138
H3	.282	.261	.361	.976	72	30	63	20
H4	.299	.588	.352	.898	72	266	66	255

where Θ is the angle between O-H and the ab plane, and ϕ is the angle between its projection and the a axis.

The orientations of the O-H bonds were also calculated by minimizing the electrostatic energy. The results of the two procedures showed good agreement for the 'inner' hydroxyl H1 but systematic discrepancies for the 'inner surface' ones, H2-H4, as shown in the Table. This led us to conclude that the approximation of formally-charged point ions is adequate in the first case but not in the last ones. This phenomenon is a good confirmation of the occurrence of hydrogen bonds between the 'inner surface' hydroxyls and the basal oxygen atoms of the next layer, namely the ones of donor-acceptor type but not those of electrostatic nature (Giese, Clays Clay Min. (1972) 21, 145).

The orientations of O-H bonds testify to their non-equivalence and throw doubt on the interpretation of the IR-spectra of kaolinite, based on the vibrations of the hydroxyls which are related by a 3-fold axis (Farmer,

Science (1964) 145, 1189) or a mirror plane (Rouxhet et al. Clay Min. (1977) 12, 171); as the interlayer space in kaolinite is more asymmetric than in dickite. This new evidence allowed us to take part in the discussion concerning the nature of cohesion of kaolinite layers (Cruz et al., Int. Clay Conf., Madrid (1972) 1, 59; Wieckowski & Wiewiora, Clays Clay Min. (1976) 24, 219). The shift of IR stretching bands of hydroxyls may be the result of interaction of the hydroxyls and the crystal field, and in this case cannot serve as a measure of the energy of a hydrogen bridge as mentioned in the references above. In our study, these energies are found to be 2.5, 1.5 and 2.5 Kcal for hydroxyls H2, H3 and H4 with the help of Brown's work (Acta Cryst. (1976) A32, 24). The calculations show that the crystal loses 2 Kcal/mole $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ after turning the OH vectors from the positions with minimum electrostatic energy to the experimental positions. Thus, the total gain by the appearance of hydrogen bridges is about 4.5 Kcal/mole. On the other hand, the dependence of electrostatic attraction on the expansion of interlayer space was obtained. In the simplest case of equally expanded interlayers, the electrostatic part is an order more compared to the hydrogen bridges if the increase of separation distance reaches 0.5 Å. More complex variants of the expansion will be also discussed.

08.4-19   THREE DIMENSIONAL MODULATED STRUCTURE OF DIGENITE, $Cu_{6.9}Fe_{0.1}S_4$. By A. Nakano*, Y. Hiratsuka*, K. Koto, M. Tokonami** and N. Morimoto***, (*) PERL of Hitachi Co., Yoshida-cho, Totsuka Yokohama 244, (**) ISIR, Osaka Univ., Suita Osaka 565, (***) Geol. and Miner. Inst., Fac. of Science, Kyoto Univ., Sakyo Kyoto 606, Japan.**

Digenite, $Cu_{6.9}Fe_{0.1}S_4$, is typical 5a-A type. The apparent space group is Fm3m and the cell edge, a, is 27.78(1) Å. The superstructure was analyzed using the intensity data collected by 4-circle diffractometer. A method for the analysis using modulation functions was developed and successfully applied to solve the structure of 5a-A type of digenite.
The apparent cubic symmetry was explained by the coherent twinning of four equivalent domains with rhombohedral symmetry. The face-centered unit cell contains 1000 tetrahedral sites among close packed sulfur atoms. Seven eighths of them are occupied by metal atoms but one eighth are left unoccupied. The vacancies concentrate around each lattice point in the cell. Metal atoms in the neighboring sites to vacancies slightly move toward vacancies. The vacancy concentration was first described by density modulation and the behavior of metal atoms by shift modulation and then the distribution of the vacant tetrahedra was determined. The final weighted and unweighted R values are 0.13 and 0.23, respectively, for 344 intensity data, within the range $\sin\theta/\lambda < 0.4$.

08.4-20   THE CRYSTAL STRUCTURE OF THE HOLLANDITE-TYPE PHASE OF SYNROC B BETWEEN $20°C$ AND $1060°C$. By T. M. Sabine, N.S.W. Institute of Technology, Sydney, Australia and A. W. Hewat, Institut Laue-Langevin, Grenoble, France.

Synroc B, a suggested repository for high level nuclear waste, has components which are synthetic hollandite, perovskite and zirconalite.

The crystal structure of the hollandite phase $BaAl_2Ti_6O_{16}$ has been determined by neutron-diffraction powder methods over a range of temperatures.

Over this temperature range:

1. Thermal expansion is linear with temperature and almost isotropic.
    $\alpha_a = 10.34 \pm 0.05 \times 10^{-6}$,
    $\alpha_c = 11.26 \pm 0.05 \times 10^{-6}$
2. There are no changes in the fractional atomic co-ordinates.
3. The temperature factors of all atoms are essentially isotropic.
4. The diffraction Debye temperature is 581 ± 16 K.
5. The amplitude of vibration of the barium atoms is anomalously high.

08.4-21   AN AUTOMATED X-RAY-DIFFRACTION METHOD FOR THE ROUTINE MINERALOGICAL ANALYSIS OF DRILLING CORES. By C.M.Shepperd and T.J.Laker, British Gas Corporation, London Research Station, London, England.

Phase analysis of minerals in the numbers required for geological surveys is laborious and time consuming whether carried out by X-ray diffraction or point-counting methods. Recent advances in the approach to quantitative X-ray analysis (F.H.Chung. J.Appl.Cryst. (1974) 7 519) have simplified calibration procedures and made this approach more attractive, especially as data acquisition and processing can be automated. We have developed a method for routine analysis of the main minerals in drilling cores which gives results comparable in accuracy and precision to point counting of thin sections, but which is far quicker.

Our method is based on the "matrix-flushing" approach of Chung. Reference intensity ratios for a dozen or so commonly encountered minerals were determined with respect to boehmite ($\alpha-Al_2O_3 \cdot H_2O$) as internal standard or "flushing agent". To allow for the possibility of unexpected and/or amorphous phases, 10% boehmite was added to the rock samples. Intensity data were collected on magnetic tape for subsequent computer processing. Smoothing of the data was found to be necessary for a satisfactory background fit; peaks are recognised and located by a flexible peak search routine in which certain parameters can be varied to suit the quality of the data. Concentrations are derived from measured peak areas by attributing them to the components of interest. Rather narrow d-value limits for the non-clay minerals are allowed (because of overlap problems) but wider limits were set for the clay minerals.

Results on synthetic mineral mixtures indicated an average relative error of up to 5%. For drilling cores it is slightly larger but comparable with point counting.