

UDC 548.736.6

CARCURMOLITE: NEW DATA ON CHEMICAL COMPOSITION AND CONSTITUTION THE MINERAL

Galina A. Sidorenko

All-Russian Scientific-Research Institute of Mineral Resources, Moscow, vims@df.ru

Natalia I. Chistyakova

All-Russian Scientific-Research Institute of Mineral Resources, Moscow, vims@df.ru

Nikita V. Chukanov

Institute of Problems of Chemical Physics RAS, Chernogolovka, chukanov@icp.ac.ru

Irina S. Naumova

All-Russian Scientific-Research Institute of Mineral Resources, Moscow, vims@df.ru

Victor A. Rassulov

All-Russian Scientific-Research Institute of Mineral Resources, Moscow, vims@df.ru

The revised crystallochemical formula of calcurmolite, $(Ca,Na)_2(UO_2)_3Mo_2(O,OH)_{11}nH_2O$, is given on the basis of electron microprobe analyses of the samples from Kazakhstan (Kyzyl-Sai) and Armenia (Kadjaran). Parameters of the monoclinic unit cell: $a = 16.30\ 0.03\ \text{\AA}$, $b = 25.49\ 0.05\ \text{\AA}$, $c = 19.50\ 0.06\ \text{\AA}$, $\beta = 90^\circ 07'$, are estimated by X-ray diffraction method. The IR spectra and spectra of laser luminescence of two mentioned findings of the mineral have been obtained for the first time; they show the identity, stability, and diagnostic value of both methods. Micro-textural and structural peculiarities of calcurmolite prevent from the research of a crystal structure of the mineral. Calcurmolite was formed as a pseudomorph after uranophane.

2 tables, 8 figures, 14 references.

Steady progress in methodology of mineralogical investigations makes it possible to obtain chemical and physical data, as well as structural characteristics with better reliability, precision and resolution. In some cases it can lead to revision of accepted notion about mineral species, varieties and series of solid solutions. Uranium minerals give bright examples of this tendency (Sidorenko *et al.*, 2003).

One of such examples is calcurmolite, which is considered either as a mineral with fixed chemical composition, or as an isomorphous series named «calcium-sodium uranyl molybdates» (Skvortsova *et al.*, 1969). Judging by previous publications, calcurmolites are morphologically extremely diverse and do not practically have even more or less reliable crystallochemical formula. Calcurmolite as a mineral species did not have the usual procedure of approbation in the IMA Commission on New Minerals and Mineral Names. The name **calcurmolite** was not suggested by discoverers of this mineral and has appeared in literature for the first time in the appendices on the group of calcium-sodium uranyl molybdates made by A.S. Povarennykh to the Russian version of the Mineralogical Tables of H. Strunz (1962).

For the first time, the considered mineral was described by L.S. Rudnitskaya in 1955 in the oxidized zone of the Kadjaran ore field (the Kafan region, Armenia) under the previous name **kadjaranite** (Pekov, 1998; Chernikov, 1971), however, so as not to disclose geography of the deposit, in the publication in Proceedings of the Geneva

Conference on Peace Use of Atomic Energy (1959, p. 161) the mineral has appeared as «**calcium molybdate of uranium**». According to the first data of microchemical analysis, L.S. Rudnitskaya characterised the chemical composition of this mineral by a formula $Ca(UO_2)_3(MoO_4)_3(OH)_2\ 8H_2O$.

The second finding of the calcium uranyl molybdate from the oxidized zone of the uranium deposit in Kazakhstan was briefly described by O.V. Fedorov in 1963, giving a formula $Ca(UO_2)_3(MoO_4)_3(OH)_2\ 11H_2O$, that differs from the formula of L.S. Rudnitskaya only by amount of the water molecules per formula unit.

The first full summary of data on calcurmolite under the name «calcium-sodium uranomolybdates» from deposits of the USSR was published in 1969 (Skvortsova *et al.*, 1969), after that the new data on these minerals did not appear for a long time. However, in the article about tengchongite (Chen Zhangru *et al.*, 1986), the close assemblage of the latter with calcurmolite was noted. In 1992, calcurmolite was found in Rabecac (France) and its «comparison with calcurmolite from the Soviet Union» was made (Deliens, 1992). However, it was concluded that a sample from France is a worse material for study.

K.V. Skvortsova and E.V. Kopchenova (Skvortsova *et al.*, 1969) have studied a series of calcium-sodium uranyl molybdates connected with oxidized zones of Kyzyl-Sai, adding to the summary the data of L.S. Rudnitskaya and O.V. Fedorov.

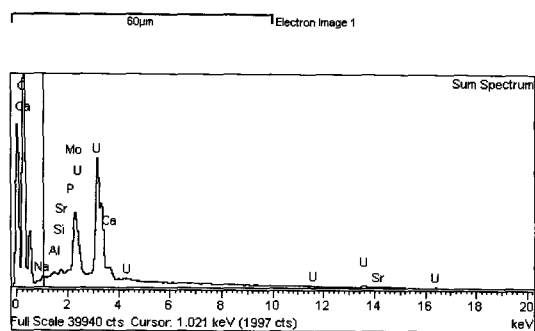


Fig. 1. Inner bunch-shaped texture of outwardly monocrystal (massive, compact) calcurmolite and its total spectrum of the element composition, revealing U and Mo as a dominative elements.

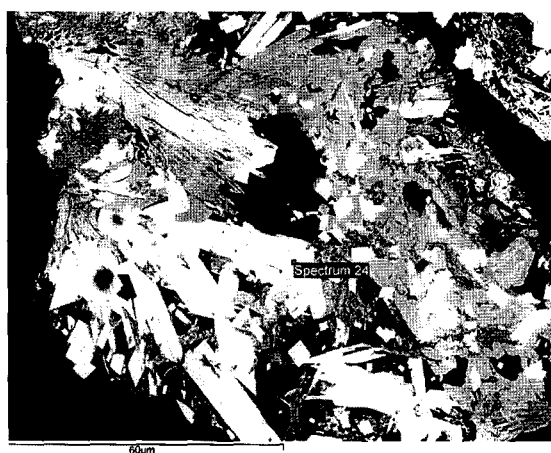


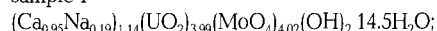
Fig. 2. Bunch-like form of segregation of calcurmolite, similar to one presented at Fig. 1, in closest assemblage with uranophane (white crystals) and phosphate of strontium (uranocircite).

Quite full description of genetic conditions, paragenetic assemblages, morphological diversity, chemical composition, optical properties, X-ray characteristics with adduction of results of methods of study, accessible at that time, is presented in the work of K. Skvortsova with co-authors (1969). At that, the authors noted the closest assemblage of uranyl molybdates with other minerals of uranyl and took that into account during calculation of data of the microchemical analysis of practically phase heterogeneous matter on crystallochemical formulae.

The formula suggested in the article are extremely diverse and not charge-balanced and can evoke neither satisfaction no the least certainty in their correspondence to the true chemical composition of calcurmolites.

Because of remoteness of the summary publication, it is expedient to remind the crystallochemical formulae calculated in the work (Skvortsova *et al.*, 1969) by data of microchemical analyses of calcurmolites (in authors' determination, «calcium-sodium uranomolybdates») with the regard of admixtures of uranophane or «-uranotil»; without a suggestion of the general crystallochemical formula for calcurmolite as a mineral species, as follows:

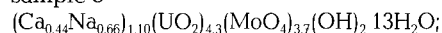
sample 1 –



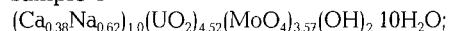
sample 2 –



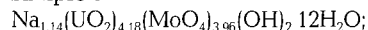
sample 3 –



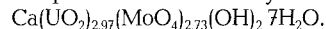
sample 4 –



sample 5 –



sample of L.S. Rudnitskaya –



It follows from these formulae that a value of the ratio U:Mo in them lays within the limits from 0.99 to 1.27 and an amount of sodium, calcium and water varies widely. Some inconstancy of the U:Mo value seems to be the most considerable, since just the ratios of $[\text{UO}_2]$ and anion-forming complex are determinative in the crystal structures of uranyl minerals formed by them (Sidorenko, 1978). Just this fact was a basis for revision of chemical composition and simultaneously carrying out of additional studies of calcurmolite both from Kadjaran and Kyzyl-Sai, with use of new methodical, technical, and apparatus means.

In the present work the samples from collections of minerals and rocks, containing

uranyl molybdates, which have been studied earlier by K.V. Skvortsova and E.V. Kopchenova and kept to one of the authors of this work, were studied. The study of chemical composition of sodium-calcium uranyl molybdates and ratios of the main mineral-forming elements (uranium, molybdenum, calcium, sodium) and also the research on crystal structure of calcurmolite were the main objective. Implementation of this goal was complicated by the absence of perfect crystals and synthetic analogues of uranyl molybdates of calcium and sodium. It is necessary to note that during study of the R-U-Mo system, where R is a cation (alkaline and alkaline-earth elements), one failed to synthesize the analogue of calcurmolite (Spitsyn *et al.*, 1981).

Methods of study

Study of element composition and morphological peculiarities of the mineral was made with the electron microprobe instrument JXA-8100 (JEON, Japan) equipped with the energy-dispersive system Inca Energy 400 (Oxford Instruments, Great Britain). Chemical composition was obtained by the crystal-diffraction method at accelerating voltage 20 kV and electron microprobe current 10 nA. The standards were as follows: UO_2 , MoO_3 , diopside (Ca), and albite (Na).

The X-ray powder patterns of the samples were performed with the ADP-1 diffractometer (monochromatic $\text{CuK}\alpha_1$ radiation).

The IR spectra of calcurmolite were registered by a standard method with use of pellets with KBr with the spectrophotometer Specord 75 in a range of frequencies $400\text{--}4000\text{ cm}^{-1}$. Polystyrene and gaseous ammonia were used as standards.

Measurement of luminescence properties was made with a complex assembled on a basis of microscope, single-beam spectrophotometer MSFU-312 equipped with a computer, a counter board for use of a method of photons counting and a module of control of step engine of diffraction lattice drive. The source of generation of luminescence was a laser on molecular nitrogen ($\lambda_{\text{rad}} = 337.1\text{ nm}$).

The complex is intended to registration of luminescence spectra of different microobjects approximately of $50\text{ }\mu\text{m}$ in size and also microparts of macroobjects in polarized and depolarised light in a spectral interval of $250\text{--}1200\text{ nm}$ at a room temperature and a temperature of liquid nitrogen.

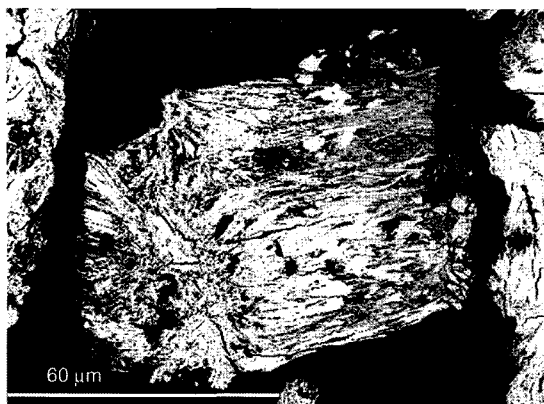


Fig. 3. «Crystallite» of calcurmolite, entirely composed by fibres and laths of the mineral, between which there are grains of uranophane (light).

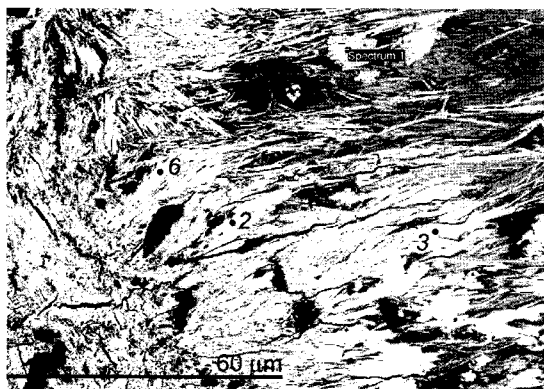


Fig. 4. A fragment of Fig. 3 with some more magnification, interfiber inclusions of uranophane are more clear and confirmed by element analysis.



Fig. 5. Heterogeneous structure of a grain of calcurmolite, in which the crystals of uranophane with different degree of alteration prevail (the most perfect are white (1), less perfect are light grey (2), and still more altered are grey (3)); at the periphery of a grain the fibrous calcurmolite grow.

Table 1. Results of electron microprobe analyses of calcurmolite (wt %) from Kazakhstan and Armenia and its calculation on ratios of main mineral-forming elements

Deposit-	No. of analysis	Na ₂ O	CaO	MoO ₃	UO ₃	Total	Atomic quantities				Formula coefficients*			
							Na	Ca	Mo	U	Na	Ca	Mo	U
Kazakhstan														
(Kyzyl-Sai)	1	0.6	6.1	20.9	64.4	92.0	0.0194	0.1088	0.1453	0.2252	0.13	0.75	1	1.55
	2	0.6	5.8	21.5	63.9	91.8	0.0194	0.1034	0.1493	0.2233	0.13	0.69	1	1.50
	3	0.9	5.6	20.9	64.1	91.5	0.0290	0.0999	0.1454	0.2240	0.20	0.69	1	1.54
Armenia														
(Kadjaran)	4	0.7	5.8	20.6	62.2	89.3	0.0225	0.1034	0.1430	0.2173	0.16	0.72	1	1.52
	5	0.5	5.4	20.4	61.3	87.6	0.0161	0.0962	0.1415	0.2144	0.11	0.68	1	1.52
	6	1.0	5.5	20.7	61.2	88.4	0.03223	0.0981	0.1438	0.2152	0.22	0.68	1	1.50
Average value		0.72	5.7	20.8	62.85	90.07	0.0231	0.1016	0.1447	0.2199	0.16	0.70	1	1.52

*Basis of calculation: Mo=1

Results of study of calcurmolite

Up to now calcurmolite was characterized by a set of interplanar distances obtained by the clear X-ray diffraction patterns and not quite convincing unit cell parameters, approximately monoclinic. The examination under binocular of the monomineral fractions of calcurmolite from Kazakhstan and Armenia revealed the transparent yellow crystals in a fractions of a millimetre in size, which looked as single crystals (though far from crystallographic perfection in comparison with the needle-shaped crystals of uranophane associated with them). However, all crystals of calcurmolite were not suitable for structural investigations: one failed to obtain a point diffraction pattern even at use of synchrotron radiation.

An explanation of this fact was given by studies in reflected electrons and in characteristic radiation, which have revealed a real constitution of the crystallites, being microheterogeneous system, in which there are bunches or laths tangled in ball and small crystals both needle-shaped, orthogonal and without crystallographic contours. For outwardly homogeneous transparent segregations, such textural-structural constitution is so unusual and diverse that it deserves a number of illustration. Figures 1-4 present the inner bunch-like texture of the outwardly monocrystal (massive, compact) calcurmolite and its total spectrum of element composition, revealing both dominating elements, U and Mo, and very low contents of admixture elements (As, Si, P, Sr). In the same crystallite of calcurmolite, in closest assemblage, there are uranophane and strontium phosphate (uranocircite). Some crystals of calcurmolite entirely consist of the tangled fibres and laths of the mineral, between which are uranophane grains. Possibly, this is a pseudomorph of calcurmolite after the uranium silicate.

In some grains of calcurmolite, the inclusions of uranophane crystals with different degree of alteration prevail; their difference by reflected ability is an evidence of that; fibrous calcurmolite grows at the periphery of the grain (Fig. 5). A process of substitution of uranophane by calcurmolite, above-mentioned as a suggestion, is clearly shown within the limits of a crystallite in reflected electrons and in characteristic radiation (Fig. 6).

Chemical composition of calcurmolite from Kyzyl-Sai and Kadjaran was studied by a method of the local X-ray spectral analysis. The results of quantitative analysis on mineral-forming elements with taking into account of uranophane inclusions are given in Table 1. In the same Table are the atomic quantities of contained elements calculated by the results of analysis and their ratios (at the calculation the quantity of Mo was accepted as a unit). The total of oxides was less than 90% that is connected with high hydration of the mineral, which (by difference from total 100) contains more than 10% of water, including the water in the form of hydroxide (see below).

From the data given in Table 1, it follows that in the chemical composition of calcurmolite:

- 1) the ratio $[\text{UO}_2]^{2+}:(\text{MoO}_4)^{2-}=3:2$, that creates the $[\text{U-Mo}]^{2+}$ complexes, for which binding together in a three-dimensional structure the additional ions are required;
- 2) the presence of additional ions of Ca and Na requires the compensation of valency, that can be achieved by the entry of hydroxyl ions in the mineral, their amount is determined by a sum of additional cations and their charge;
- 3) the additional cations are represented predominantly by Ca at constant presents of sodium, with relatively constant ratio, which is close (but not equal) to 3:1.

On the basis of data on chemical composition for the samples from Kyzyl-Sai and Kadjaran, the

