Zelensky M.E.[1], Kaz'min L.A.[2] Mineral associations and modeling of mineral formation processes in the high temperature fumarole zone of the Mutnovsky volcano (Kamchatka)

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key words [fumarole, mineral, incrustation, sublimates, modelling]

Geochemical and mineralogical studies of the most high-temperature fumaroles from the Mutnovsky volcano (Kamchatka) were carried out. The temperature of the fumarole gases was as high as 400-524°C (in 1999-2000) and 350-490°C (in 2001). The 26 minerals including 10 ore minerals among the fumarole incrustations were described. Dispersed $CaSO_4$ anhydrate, $(Na,K)Al_3(OH)_6(SO_4)_2$ natroalunite and cristobalite SiO_2 are the major incrustation components. Substantial ore mineralization consisting of pyrite FeS_2, magnetite Fe_3O_4, lead-bismuth sulfo salts, greenockite CdS, bismutite Bi_2S_3, and also anglesite $PbSO_4$ is deposited on that matrix. The $Cd_4PbBi_{12}(S, Se)_{23}$ and $CdPb_4Bi_6(S,Se)_{14}$ sulfo salts are the new minerals. The Na-Ti-Fe-(SO_4) and $Na_{1.86}(Ca, Fe, Mg)_{0.07}SO_4$ phases occurred among the incrustations and also X-ray amorphous arsenic sulfur (As up to 40 %) require further investigation, and can probably be referred to as new minerals.

The quartz tubes of 15-30 mm in diameter and 500-1000 mm in length were inserted in the fumarole mouths for up to 120 days to model mineral formation processes. The sublimates as inside the tubes as on their surface formed. Micromorphology and the sublimate qualitative compositions were examined by scanning electron microscope with the energy dispersion detector. The quantitative analysis of individual phases was conducted by SX-50 electron microprobe with three wave spectrometers. Some of the soluble phases were analyzed by "wet" chemistry. The sublimate composition was examined by ICP-MS and ICP-AES. Detection of the most common phases was confirmed by X-ray phase analysis.

The 25 different phases were fixed in the "inner" sublimates. Fig. 1. The zones of oxides, simple sulfides, complex sulfides, and arsenic sulfur were distinguished within the temperature interval of 490-150°C. The sublimates from the last two zones make up more than 95 % by weight. Cristobalite accompanied by titanomagnetite $(Fe,Ti)_3O_4$ and hematite Fe_2O_3 is the main mineral of the zone. Rutile TiO_2 and $CaFeSiO_4$ phase are in less quantities. Pyrite occurs in the zone of simple sulfides in relatively wide range of temperatures, whereas greenockite and bismutite are located within the narrow field with sharp borders. The thin colorless cadmium chloride needles are also present in that field. The zone of complex sulfides is composed mostly of Cd-Pb-Bi sulfo salts of variable composition with subordinate chlorides, oxides, sulfates and silicates. Fig. 2. The X-ray amorphous arsenic sulfur is the predominant phase in the most high-temperature area. Sulfur forms orange dendrites with a thin texture or drops of solidified melt. Formation of such drops can be explained by temporary temperature increase or by change of the tube cooling conditions due to change in weather conditions. Such a melt can be a unique environment for mineral formation – it contains parts enriched in iodine and also the crystals of lead and bismuth iodides. Fig.3. The thallium compounds were found in the same zone – the colorless needles composed of Pb_2TlCl_5 up to $PbTlCl_3$ and orange Tl cubic crystals. Fig. 4.

The sublimates formed on the tube surface under conditions of high partial oxygen pressure are similar to the natural incrustations by composition and composed mostly of sulfates and oxides – tschermigite $NH_4Al(SO_4)_2x12H_2O$, natroalunite, cristobalite, hematite, Fe_2O_3 and maghemite Fe_3O_4. Anglesite and bismutite are also present in smaller quantities.

The fumarole gas probes were taken to vacuumed capsules with alkaline charge. The probes of condensate were simultaneously taken for gas microcomponent analysis. The selected gas probes were analyzed by classical gas chromatography and "wet" chemistry methods. The condensate composition was determined by ICP methods. The gas is composed of: H_2O – 94-96%, CO_2 – 2-3%, SO_2 – 0.8-1.2%, H_2S – 0.35%, HCl – 0.17%, HF – 0.02%, H_2 – 0.25%, N_2 – 0.75%, O_2 – 0.003%, Ar – 0.0003% and some other gases. The major microcomponents are (mkg/kg): B – 27000, Na – 2300, Al – 4800, Si – 15000, Ca – 2700, Fe – 2100, Zn – 72, As – 3700, Se – 388, Br – 3800, Cd – 117, Te – 120, I – 350, Hg – 47, Tl – 87, Pb – 115, Bi – 46. Based on the resulted data the thermodynamic modeling of the equilibrium conditions for precipitation of solid phases from gases at different oxygen fugacity was performed with the "Selector" programming complex. A good convergence of the observed mineral zonality with the theoretical one is noticed. Chlorides and fluorides are the major ore element forms in gases. At the same time sulfates, sulfides and oxides are predominant among the calculation solid phases. Fig.5, Fig.6.

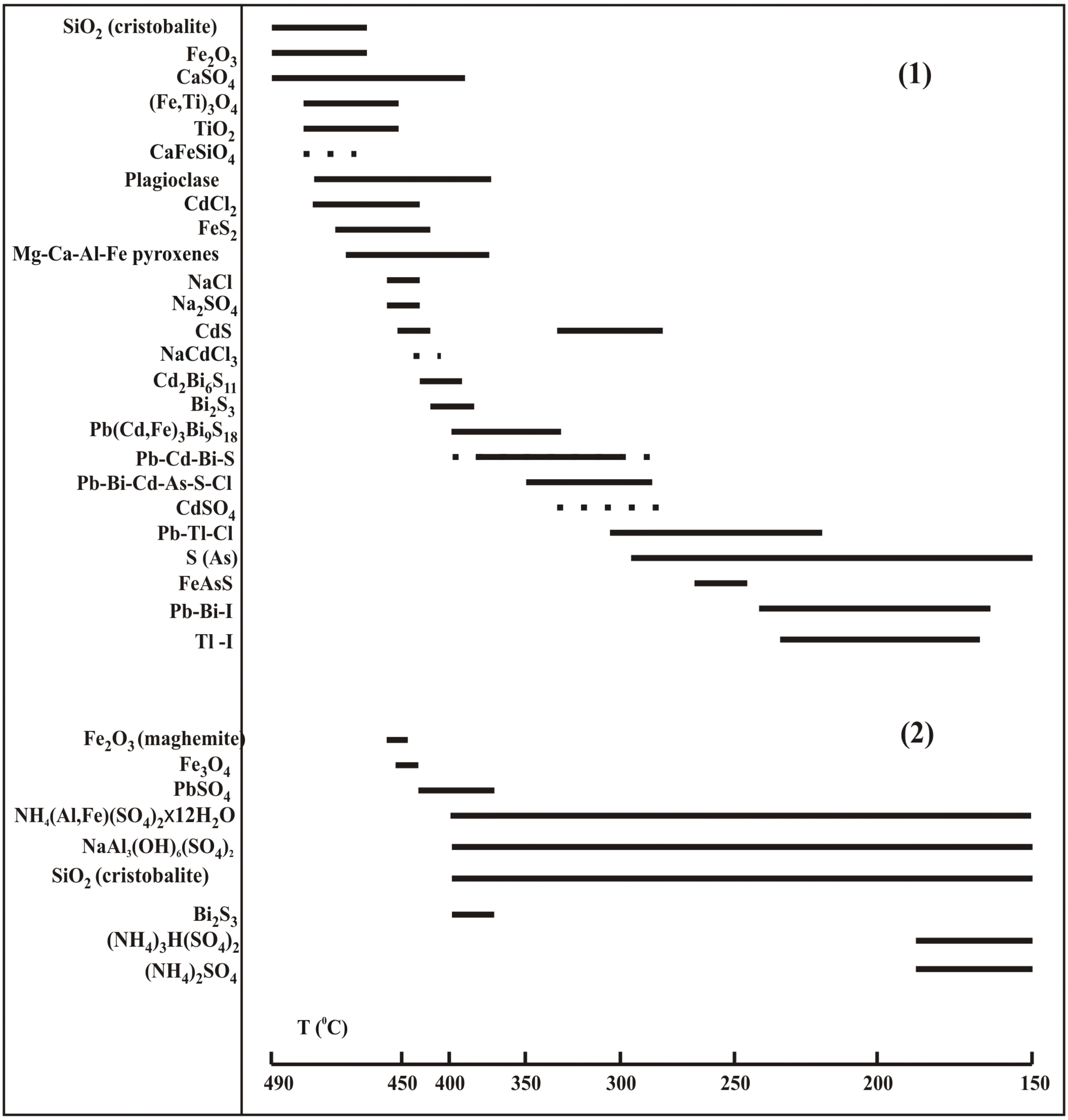


Fig. 1. Generalized temperature sequence of sublimate precipitation in tubes: (1) sublimates within the tubes, (2) sublimates on the surface of the tubes. Not enough precisely detected phases are marked with dash.

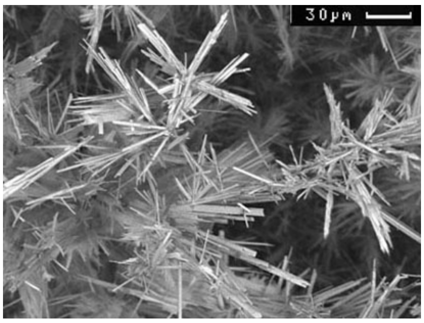


Fig. 2. Sulfo salt dendrites of composition $Cd_3PbFe_{0.5}Bi_9(S,Se)_{18}$.

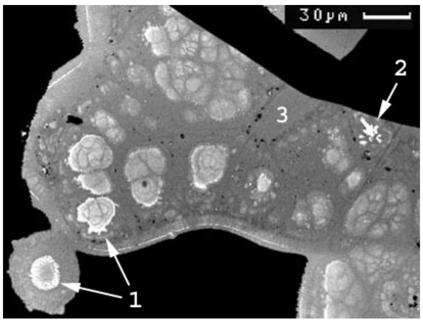


Fig. 3. The iodine enriched parts (1) and lead and bismuth iodide forms (2) in the solidified arsenic sulfur melt (3).

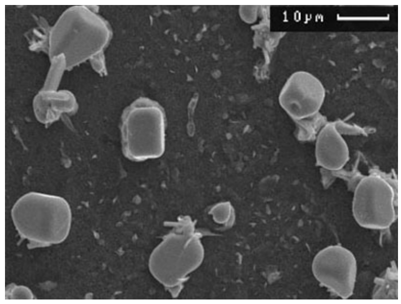


Fig. 4. Thallium iodide crystals.

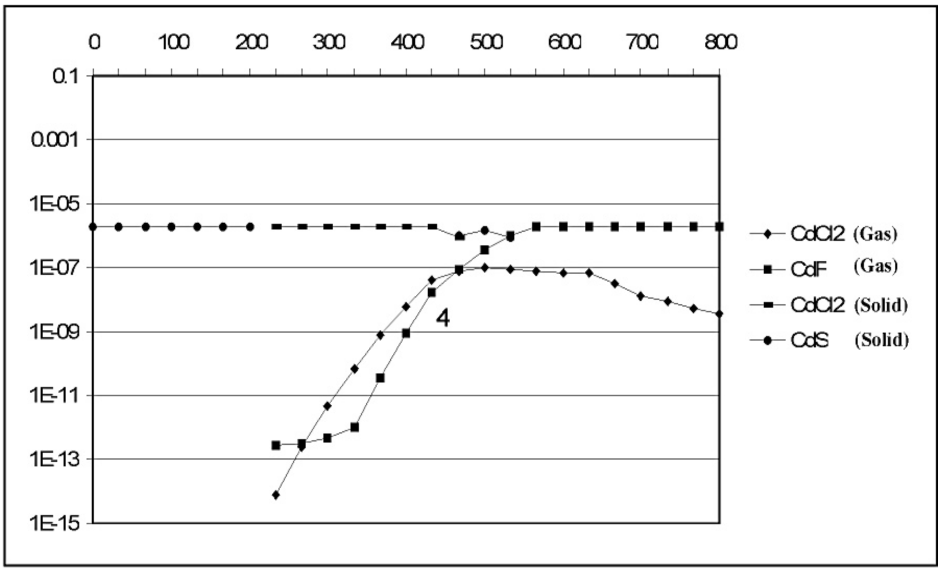
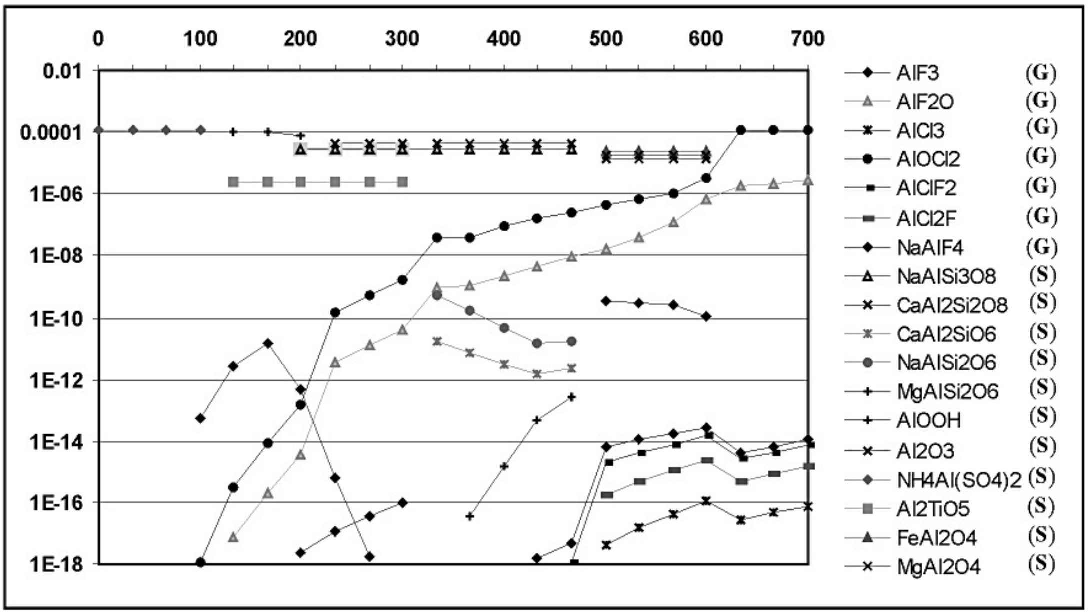


Fig. 5. Forms of cadmium compounds at T=0-800^{o}C and P=1 bar.



Fir. 6. Forms of aluminum compounds at T=0-700^{o}C and P-1 bar.