MODES OF UPTAKE OF CADMIUM AND MERCURY IMPURITIES INTO GROWING GALENA CRYSTALS

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Three principally important mechanisms of impurity uptake by real crystals are associated with the phenomena of isomorphism, endocrypty and sorption. It seems to be difficult to get the features of relationships in this triad without detailed investigations in mineral surface chemistry. Commonly speaking, it is permissible to suppose that incompatible elements are preferentially occurred at the surface of a growing crystal and tend to form their own mineral forms thereon. If the incompatible element is adsorbed at the surface, this requires structural and chemical reconstruction to create the favorable surface sites for element retention. The entrapment of compatible element usually needs no appreciable surface reconstruction (see [1] for Sr on calcite). But it should be taken into account that the concepts of compatible and incompatible elements are conditional to some extent being dependent upon the real structure of crystal matrix. So, cadmium solubility in pyrrhotite can grow up to two orders of magnitude due to interaction with stoichiometric vacancies. In this case Cd behaves as a compatible element revealing no surface enrichment. In contrast, Cd poorly enters stoichiometric pyrrhotite and so could be easily detected at the surface [2]. It is quite important to clarify how the surface mechanisms of element uptake are acting at elevated P,T – parameters under the dynamic conditions of crystal growth. Although the question is crucial for endogenous ore formation, it is poorly covered in the literature. We have embarked on a study of this problem taking, as an example, toxic heavy metals (Hg, Cd) in galena. Most of the available data on sorption of these elements on sulfides cover a PT range of near-ambient conditions and rather contradictory [3-5] possibly because of the small chemical shifts for main forms of Hg and Cd. Moreover, the methods of surface spectroscopy (XPS, AES) have not very high sensitivity and cannot be used in the case of compatible elements for which isomorphous uptake prevails upon adsorption. This being so, we utilize an effective combination of ESCA methods and thermal atomic absorption analysis (TAA) providing possibility to discriminate element binding forms by use of temperature of its release from the sample [6]. The sensitivity of TAA reaches 0.1 ng for Cd and 1 ng for Hg allowing determination of there binding forms at concentration level of $>10^{-7}$-10^{-6}%.

The synthesis of galena crystals containing Hg and Cd impurities was performed using sealed tubes of silica glass of optical quality in NH_4Cl aqua solutions at 400°C and 500 bar. The starting material was PbS to which 0.1 to 0.5 wt.% of CdS and HgS was added. Silica glass ampoules were positioned in standard stainless steel autoclaves. Temperature gap of 10-15° for thermal gradient crystal growth was measured on the outer autoclave wall. The experiments were carried out for 8 days. Sulfur and oxygen activities in the experiments were defined with buffer mixtures placed in gold tubes closed but not sealed. To take a portion of high-temperature fluid, the silica-glass samplers were used. In the experiments we obtained mainly cubic galena crystals up to 3 mm. Their study by ESCA methods revealed rather different behavior of Hg and Cd. Mercury is located at a top of a surface layer in a sufficiently high concentration and escape from the surface after a short-term (10 min) ion bombardment (fig.1). This process is accompanied by the desorption of oxygen and partly chlorine which rather deeply penetrates into the crystal (Fig. B-C). The TAA study shows the temperature of Hg release to be more high than that one for physically adsorbed form and possibly, in accordance with Auger spectroscopic data (Fig. A-C), mercury is desorbed in oxy-chloride form. The position of peak Hg $4f_{7/2}$ in the XP-spectrum (100,0 eV) is found to be somewhat closer to cluster group Hg_2^{2+} than to Hg^{2+}. Cd is not detected at the surface by spectroscopic methods. Its total contents in crystals amount $1\text{-}2\cdot10^{-4}$% that is lower than the sensitivity level of ESCA but quite enough for reliable diagnostics of binding forms with TAA technique. These studies have showed that Cd is represented mainly by an isomorphous (structural) form amounting from 42 to 95% of total Cd binding forms contents in different runs. The mineral and adsorbed forms are found to be subordinate. It is relevant to note that the set of binding forms as well as their proportion varies from run to run. At the same time, the physical-chemical parameters of the growth medium are altered subtly (table 1): the SO_2 fugacity changes not more than one order of magnitude. This may indicate that the mechanisms of trace element uptake are highly sensitive to slight fluctuations of growth conditions.

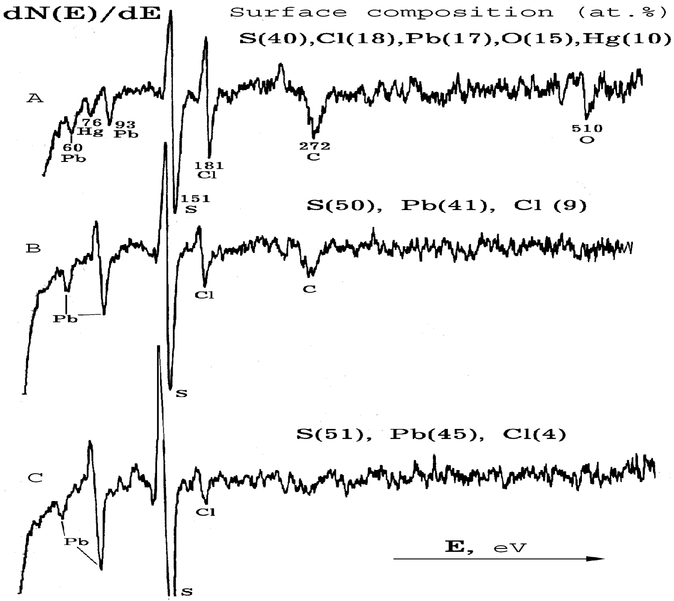

Fig.1. Differential Auger spectra of galena with Hg and Cd impurities
A – without ion etching;
B – etching 10 min;
C – etching 40 min.

Table 1

Activity of volatiles in experiments and relative quantities of Cd binding forms in PbS crystals obtained

Run No.	Fugacity of gases, bar			Relative contents of Cd binding forms	
	$-\lg f_{S_2}$ *	$-\lg f_{SO_2}$ **	$-\lg f_{O_2}$ ***	miner., %	struct./adsorb.
SBM1-1	>7.08	n.d.	n.d.	0	15.7
SBM1-2	7.08	2.95	23.67	30	9.0
SBM1-3	7.32	3.29	23.89	34	6.3
SBM2-1	7.56	3.62	24.10	40	2.3
SBM2-2	7.80	3.94	24.30	35	3.3
SBM2-3	7.56	3.62	24.10	0	4.3
SBM2-4	7.80	3.94	24.30	0	6.7
SBM2-6	7.80	3.94	24.30	0	19.0

*From pyrrhotite composition. **From reaction $Fe_3O_4 + \frac{5}{2}S_2 = \frac{3}{x}Fe_xS + 2SO_2$.

***From reaction $\frac{1}{2}S_2 + O_2 = SO_2$.

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