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A Preliminary Study on the Potential Source of Cadmium in the Boseong-Jangheung Mine District

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ABSTRACT : Cadmium occurs as a minor element in sphalerite ((Zn, Fe)S) from the Boseong-Jangheung gold-silver mine district. We analyzed the abundance of cadmium in sphalerite using an electron probe microanalyzer (EPMA) and discussed the natural sources of cadmium in terms of bedrock geochemistry, in order to preliminarily reconnoiter the potential cadmium contamination in mine districts. Cadmium contents of sphalerites from the Au-Ag mines (Bodeok, Mundeok, Jeonbo, Boknae, Keumsan) in the Boseong-Jangheung district are considerably high, compared with cadmium contents of sphalerites (average = 0.5 wt.% Cd, maximum = 4.4 wt.% Cd) in the world. Sphalerites from the Keumsan mine (average = 9.49 wt.% Cd, maximum=11.22 wt. Cd) are highly enriched in cadmium. Our data suggest that the Boseong-Jangheung area is an important potential site of cadmium contamination in Korea. Based on bedrock geochemistry, natural causes of cadmium enrichment in sphalerite from the mine district are thought to be the mixing of cadmium leached from organic-rich, metasedimentary rocks (including coal) and/or black shales. From this study, we propose that the pinpointing of potential sites of pollution by toxic heavy metals can be done effectively through detailed reconnaisance study on mineralogical compositions of ore minerals such as sphalerite from the mine area.

INTRODUCTION

The major effects of cadmium poisoning are experienced in the lungs, kidneys and bones. The dramatic toxic effect of cadmium is the development of Itai Itai disease (Nogawa, 1981). In natural soils, it derives mainly from zinc, lead and copper sulfide ore minerals such as sphalerite (ZnS) and tetrahedrite-tennantite ($(Cu, Zn)_2$ $(Sb, As)_4S_{13}$), whereas in cultivated soils it may be a component in fertilizers. Anthropogenic sources also locally raise cadmium concentrations in soil and plants. Cadmium behaves like most of the heavy metals in that it tends to be adsorbed in the humus-rich top soil but the cadmium may be more effectively leached during acidification (Jul Låg, 1990).

Cadmium has a strong geochemical affinity with sulphur, naturally forming CdS. The CdS usually occurs as a replacement compound in sphalerite (ZnS). The cadmium sulfide (CdS) is the stable species in reducing environments, however, in an atmosphere of dioxygen it is unstable and dissolves into soluble sulfate (Fergusson, 1982). Mine waters typically have low pH owing to the hydrolysis oxidation of sulfide minerals such as pyrite (FeS_2). Therefore, the cadmium in the mine water may be highly mobilized by the low pH, resulting in severe contamination of soils and surface and ground waters.

In order to find out the potential sites of the pollution by heavy metals including cadmium and zinc in Korea, we analyzed the sphalerites from several abandoned Au-Ag mines in Korea, because the average contents of cadmium in sphalerite (ZnS) give an useful information on the potential sites of cadmium. Previous literature data (Fleisher *et al.*, 1974) show that worldwide sphalerites (ZnS) contain minor amounts of cadmium (range = 0.02~1.4%; median value = 0.3%; maximum value = 5%). The tetrahedrite-tennantite ($(Cu, Zn)_2$ $(Sb, As)_4S_{13}$), an another source of cadmium (Nriagu, 1979), has a maximum level of cadmium around 2400 ppm (0.24%) and a median level of 600 ppm.

In this study, the Cd contents of sphalerite from the Boseong-Jangheung mine district has been investigated to find out the possibility of the pollution of soils and natural waters by cadmium in the district, and to discuss the natural spatial conditions of the occurrence of cadmium-rich sphalerites on the basis of bedrock geochemistry.

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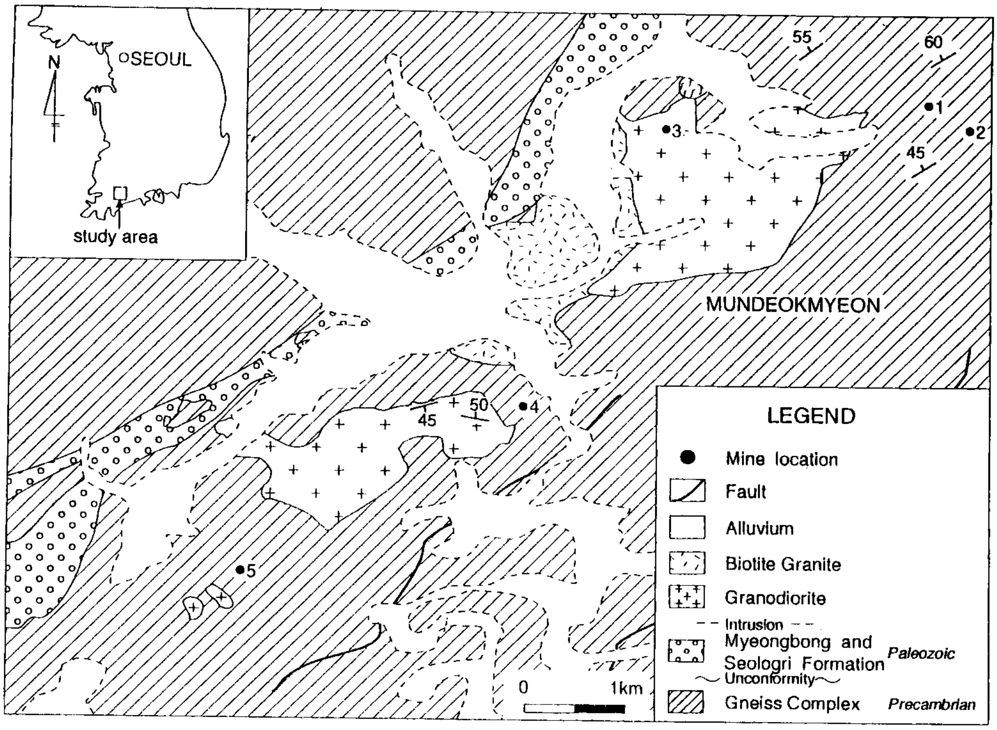

Fig. 1. General geologic map of the Boseong-Jangheung mine district. Mines: 1; Bodeok, 2; Mundeok, 3; Jeonbo, 4; Boknae, 5; Keumsan

Table 1. Summary of studied gold-silver mines in the Boseong-Jangheung district, Cheollanamdo-Province

Mine	Locality		Host rocks	References
Bodeok	34°54'45″N	127°13'E	paragneiss	So *et al.* (1993)
Mundeok	34°54'30″N	127°13'30″E	paragneiss	
Jeonbo	34°54'30″N	127°10'E	granite	
Boknae	34°52'N	127°08'30″E	paragneiss	So *et al.* (1995)
Keumsan	34°50'30″N	127°05'30″E	paragneiss	Heo, So (1995)

MATERIALS AND METHODS

Sample Collection and Preparation

Sphalerite-bearing ore samples from the five abandoned Au-Ag mines (Fig. 1, Table 1) including Bodeok (So *et al.*, 1993), Mundeok, Jeonbo, Boknae (So *et al.*, 1995), and Keumsan (Heo, So, 1995) were collected from tailings in dump sites. Ore samples were cut with a diamond saw and the 2.5 to 5 cm-sized samples were casted in two-piece cylindrical plastic mold (Craig, Vaughan, 1981). Successive grinding using 180-through 1200-mesh silicon carbide is followed to remove surface irregularities, to remove casting resin that covers the sample, to reduce thickness, and to prepare a smooth surface for polishing. Between

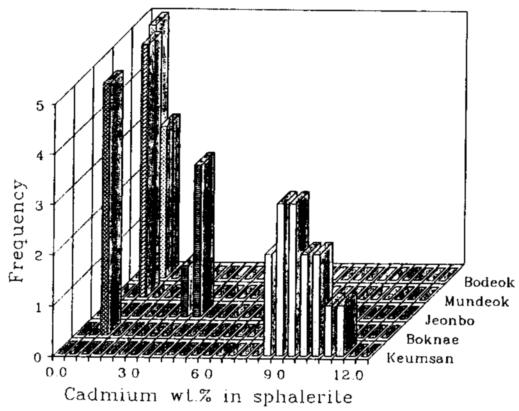

Fig. 2. Histograms of cadmium content (weight percent) in sphalerite from the Boseong-Jangheung gold-silver mine district.

steps samples are thoroughly wa- shed and cleaned with an ultrasonic cleaner. Finally, successive polishing using diamond pastes with grain size of 9 to ¼ microns is done to remove all of the remaining zone of surface deformation and the deeper scratches.

Chemical Analysis

Table 2. Representative chemical composition of sphalerites from the Boseong-Jangheung district. Cheollanamdo-Province.

Mine Name	wt.%		
	Fe	Mn	Cd
Bodeok	8.75	0.03	0.57
	8.61	0.00	0.55
	8.79	0.03	0.32
	7.79	0.02	0.24
	8.51	0.00	0.50
	9.07	0.00	0.38
	8.11	0.02	0.41
	7.65	0.04	0.58
Mundeok	7.96	0.04	0.68
	6.60	0.00	0.98
	7.76	0.00	0.87
	7.92	0.00	0.92
	8.04	0.00	0.77
	7.76	0.00	0.58
	3.76	0.00	0.71
	4.39	0.00	0.76
	3.61	0.00	0.62
Jeonbo	7.44	0.02	3.32
	6.54	0.00	3.69
	6.31	0.00	3.53
	6.97	0.01	3.89
Boknae	7.78	0.03	0.82
	6.74	0.04	0.82
	6.67	0.03	0.56
	5.59	0.03	0.86
	6.02	0.01	0.70
	6.21	0.03	0.75
Keumsan	7.34	0.01	10.95
	7.16	0.03	11.22
	7.39	0.07	10.35
	4.66	0.00	9.71
	4.16	0.09	9.24
	4.07	0.25	10.20
	6.50	0.00	8.98
	4.69	0.00	9.11
	4.68	0.00	9.17
	4.17	0.10	8.81
	6.64	0.09	8.44
	6.67	0.09	8.40
	4.92	0.05	9.63
	5.22	0.18	8.68

Chemical analyses of 41 polished ore samples containing sphalerite grains were performed with an electron microprobe analyzer operated in a wavelength dispersive (WDS) and energy dispersive spectrometer (EDS). In this study, the JEOL Superprobe JXA-8600 SX at the Center for Mineral Resources Research in Korea University with three-channel detecting system and a 40° X-ray take-off angle was used for analysis. Standard specimens used for quantitative measurements are synthetic compounds of CdS (for Cd), MnS (for Mn), FeS_2 (for Fe) and ZnS (for S). The instrumental settings of the EDS in quantitative microprobe analysis were as follows: X-ray excitation voltage (V_o) = 20 kV; absorption specimen current (i_{ab}) = 2.0 nA on Faraday cup; size of electron beams on specimen surface = 1~3 μm; method of X-ray intensity measurement = fixed-time counting mode; preset of period time = 100 second. After the correction for dead time and background values, matrix effect was corrected with reference to atomic number, absorption, and fluorescence (ZAF corrections). Standard errors of analytical data are less than 1 wt.%.

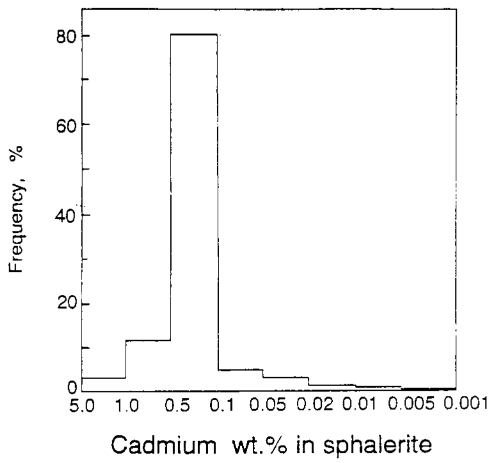

Fig. 3. Frequency distribution of cadmium content of worldwide 1027 sphalerites (after Muta, 1958).

RESULTS AND DISCUSSION

Cadmium contents (wt.% Cd) of sphalerites from the studied mines are as follows (Fig. 2 and Table 2): Bodeok, 0.24~0.58 (average = 0.44±0.12); Mundeok, 0.58~0.98 (average = 0.76±0.13): Jeonbo, 3.32~3.89 (average = 3.60±0.21); Boknae, 0.56~0.86 (average = 0.75±0.10); Keumsan, 8.40~11.22 (average = 9.49± 0.83). Average levels of cadmium in worldwide sphalerites (ZnS), the main natural source of cadmium contamination, lie in the range 0.02~1.4% (median around 0.3%, and a maximum level of 5%) (Fleisher *et al.*, 1974). Frequency distribution of 1027 data of worldwide sphalerites (Fig. 3) (Muta, 1958) shows a marked concentration in the range 1000~5000 ppm (equally, 0.1~0.5 wt.% Cd). Except the sphalerites from the Bodeok mine, those from other mines in the

Boseong-Jangheung district are significantly enriched in cadmium. To our knowledge, sphalerites from the Keumsan mine are highest in cadmium content in the world.

Compositional variation of cadmium in sphalerite from metallic ore deposits in Korea has been studied (Choi, 1993). The data indicate that sphalerites from the 'gold-dominant' (so-called 'mesothermal-type') deposits of Jurassic mineralization age typically have higher cadmium contents, whereas those from the 'silver-dominant' and 'gold-silver' deposits of Cretaceous age tend to have low cadmium. The previous studies (So *et al.*, 1993; So *et al.*, 1995; Heo, So, 1995) indicated that Au-Ag mines in the Boseong-Jangheung district show the characteristics with massive appearance of ore veins and simple ore mineralogy of the so-called 'gold-dominant' deposits. Nevertheless, sphalerites from the Boseong-Jangheung district are at least two or three-times enriched in cadmium contents.

In natural geochemical processes, cadmium is absorbed preferentially onto the organic carbon (Rose *et al.*, 1979). Compared to the average crustal abundance (about 0.2 ppm Cd), organic carbon-rich, coal (around 22 ppm), peat (around 190 ppm) and shale (around 8 ppm) are characteristically rich in cadmium. In terms of bedrock geochemistry and general geochemical behavior of cadmium in natural rocks, possible sources of cadmium enrichment in sphalerites from the Boseong-Jangheung mine district are thought as follows: 1) coal-bearing formation in the Hwasoon area, which is located northwest of the mine district; 2) organic-rich metasediments including the Myeongbong and Seologri formations; 3) black shale which characteristically occur at the Keumsan mine area.

Combined with general cadmium contents of sphalerites from metallic ore deposits in Korea (Choi, 1993), this close relationship between organic-rich rocks and the higher cadmium in sphalerites indicates that high potential of cadmium contamination in Korea is anticipated within areas of Jurassic metallic ore mineralization developed geologically within carbon-rich, metasedimentary rocks and/or black shales. The pinpointing of potential sites of pollution by toxic heavy metals can be done effectively through pilot study (using EPMA) on mineralogical compositions of ore minerals such as sphalerite from mine areas.

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전남 보성-장흥 광화대의 잠정적 카드뮴원에 대한 예비연구

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요 약 : 전라남도 보성-장흥 금은 광화대에서 산출되는 섬아연석 ((Zn, Fe)S)은 특징적으로 미량원소로서 카드뮴을 함유한다. 본 연구에서는 잠정적 독성원소로서의 카드뮴의 근원과 이동 및 분산을 고찰하기 위한 예비연구로서 연구지역 섬아연석내 카드뮴의 함량을 전자현미분석기 (EPMA)를 이용하여 분석하고, 환경지구화학적 관점에서 카드뮴의 기원물질을 토의하였다. 연구지역 광화대내 5개 금-은 광산 (보덕, 문덕, 전보, 복내, 금산)에서 산출되는 섬아연석은 세계적 평균치 (0.5 wt.% Cd) 및 최대치 (4.4 wt.% Cd)에 비교하여 상당히 높은 카드뮴 함량 (평균 3.96 wt.% Cd, 최대 11.2 wt.% Cd)을 갖는다. 특히, 금산광산의 섬아연석은 평균 9.49%에 이르는 특이하게 높은 함량을 나타낸다. 암석지구화학의 관점에서 보면, 연구지역 광화대내 섬아연석 카드뮴의 근원은 세가지로 판단된다: 1) 탄질물 (본 광화대의 북서부에 위치), 2) 연구지역내 광역적으로 분포하는 유기물이 풍부한 변성퇴적암 (예: 명봉 및 설옥리층), 3) 도처에 산재하는 소규모 흑색셰일 (예: 금산 광산 지역). 본 연구결과, 카드뮴과 같은 잠정적 독성원소의 근원을 밝히고 그분산을 제어하기 위하여 국내 휴 · 폐광산에서 산출되는 섬아연석의 광물조성 변화경향과 주변 지질을 파악함이 효율적임을 지시한다.