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ZINCIAN GREENOCKITE IN STRATIFORM LEAD-ZINC-SILVER MINERALIZATION AT LADY LORETTA, NORTHWEST QUEENSLAND

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ABSTRACT

At the Lady Loretta stratiform lead-zinc-silver deposit in northwest Queensland, Australia, zincian greenockite occurs in a thick, lead-rich, cadmium-anomalous zone in laminated sulfide mineralization. It is intergrown with galena, sphalerite and minor pyrite in galena-rich laminae and microscale veinlets. Electron-microprobe analyses show significant zinc-for-cadmium substitution in greenockite (7.1 - 18.4 mol.% ZnS, average 13.1 %); usually cadmium was found only in traces in coexisting sphalerite and was not detected at all in galena. Textural and geochemical considerations suggest that the cadmium-anomalous zone and the occurrence of zincian greenockite are primary depositional features of the mineralization. This indicates unusual physical or chemical conditions during sulfide deposition, resulting in a decoupling of the geochemical coherence of zinc and cadmium during the formation of a part of the deposit.

Keywords: cadmium, zinc, lead, greenockite, sphalerite, microprobe data, Lady Loretta deposit, Australia.

SOMMAIRE

Dans le gisement stratiforme de plomb-zinc-argent de Lady Loretta dans le Queensland du Nord-Ouest, en Australie, la greenockite zincifère se présente à l'intérieur d'une zone épaisse, riche en plomb et anomale en cadmium, au sein d'une minéralisation de sulfures laminés. Elle s'y trouve en intercroissance avec la galène, la sphalérite et un peu de pyrite dans des lamelles et filonnets microscopiques riches en galène. Les analyses à la microsonde électronique révèlent, dans la greenockite, un remplacement notable du cadmium par le zinc (7.1 - 18.4% mol. de ZnS, 13.1% en moyenne); mais d'ordinaire le cadmium ne se trouve qu'en traces dans la sphalérite contigue, et n'a pas été décelé du tout dans la galène. Sur la foi de considérations texturales et géochimiques, la zone anomale en cadmium et la présence de la greenockite zincifère seraient des indices de dépôt primaire de la minéralisation. Ces observations signalent des conditions physiques et chimiques anormales au cours du dépôt des sulfures, provoquant une dissociation de la cohérence géochimique du zinc et du cadmium pendant la formation d'une partie du gisement.

(Traduit par la Rédaction)

Mots-clés: cadmium, zinc, plomb, greenockite, sphalérite, analyse à la microsonde, gisement de Lady Loretta, Australie.

INTRODUCTION

During metallurgical evaluation of the Lady Loretta sulfide deposit, traces of apparently primary zincian greenockite were noted in polished sections of diamond-drill core. This occurrence is unusual because primary cadmium sulfides are seldom reported from ore deposits, and the mineral has not been previously recorded in the Proterozoic lead-zinc-silver deposits of northern Australia. In addition, cadmium usually shows a close geochemical coherence with zinc (Rankama & Sahama 1950, p. 708-714) and typically occurs as a trace element in sphalerite; its occurrence in a separate sulfide phase in such a zinc-rich environment is surprising, and suggests unusual geochemical conditions during formation of the deposit.

GEOLOGICAL AND CHEMICAL SETTING

The Lady Loretta deposit is a small but high-grade stratiform lead-zinc-silver deposit of Proterozoic age, situated about 115 km northwest of Mount Isa at Lat. 19°46′ S, Long. 139°03′ E in northwest Queensland. The style, geological setting and age of the deposit are similar to those of other Proterozoic stratiform lead-zinc-silver deposits in northern Australia, such as Mount Isa, Hilton and McArthur River. The regional geological setting is discussed by Plumb & Derrick (1975), Plumb *et al.* (1980) and Derrick (1982), and the geology of the deposit has been described by Alcock & Lee (1974) and Loudon *et al.* (1975). Aspects of the geology and isotope geochemistry of the deposit were discussed by Carr & Smith (1977).

Hole P116 was drilled on section 2420N into the eastern limb of the deposit (see Fig. 4 of Loudon *et al.* 1975); it intersected two zones of relatively high-grade lead-zinc mineralization. Down-hole profiles of lead, zinc and cadmium abundances in mineralized parts of P116 (Fig. 1) show a generally close correspondence between zinc and cadmium, except in a 25-m-thick lead-rich zone (estimated true thickness about 15 m) in which cadmium concentrations are considered higher than expected from zinc abundances. A scatter diagram shows a generally good correlation between zinc and cadmium throughout

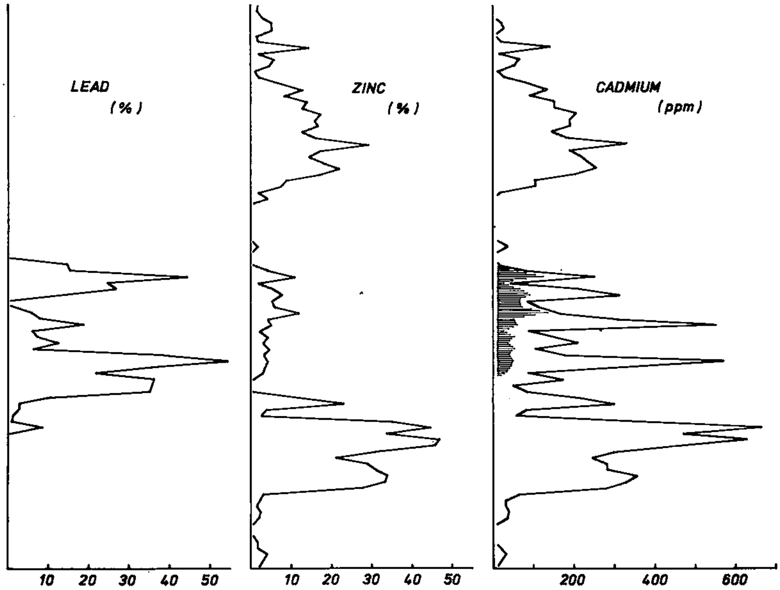

FIG. 1. Down-hole profiles of abundances of lead, zinc and cadmium in mineralized section of drill hole P116, Lady Loretta. Sample spacing is 1 metre within metal-rich zones. Shaded zone on cadmium profile is calculated contribution of cadmium contained in sphalerite over this interval, based on regression equation for Fig. 2B.

the hole, but with several outlying points (Fig. 2A). Omitting samples with over 5% lead, zinc and cadmium show an excellent linear relationship (Fig. 2B), but there is no simple relationship between lead and excess cadmium in lead-rich samples (Fig. 3).

OCCURRENCE AND PROPERTIES OF GREENOCKITE

Only a few samples were available from the lead-rich section of drill hole P116; greenockite was first observed in one polished section from that interval. Subsequent re-examination of all available material from the deposit revealed further greenockite in a lead-rich sample from an unknown location.

In both samples greenockite occurs in galena-rich laminae in finely banded massive sulfides, and to a minor extent in crosscutting, microscale veinlets of galena. Greenockite forms disseminated grains and patches from 10 to 1000 μm in diameter in galena, and is commonly intergrown with sphalerite and fine-grained euhedral or spheroidal pyrite. Sphalerite and fine-grained pyrite also occur disseminated throughout galena laminae and veinlets. Greenockite–sphalerite contacts are irregular to smoothly curved, whereas greenockite–galena contacts vary from irregular to planar, with occasional grains of greenockite approaching euhedral forms. Figure 4 shows typical morphologies and relationships of the grains.

In reflected light, greenockite has a slightly lower polishing hardness and slightly higher reflectance than the accompanying sphalerite, and is grey with a distinct blue-green tint; sphalerite has a faint pink tint in comparison, and this color contrast is accentuated under oil immersion. Most grains show abundant and intense internal-reflections, mostly clear yellow with occasional orange or red tints.

Electron-microprobe analyses of greenockite show significant substitution of Zn for Cd, with a compositional range of 7.1 to 18.4 mol.% ZnS (average 13.1%; Table 1, Fig. 5). Only traces of iron are present, and elements other than cadmium, zinc, iron and sulfur were not detected; in particular, manganese and indium were sought but not found. Individual grains of greenockite are homogeneous within the precision of the analyses.

X-ray powder-diffraction examination of a mixture of greenockite and its host galena gave a pattern similar to that of synthetic hexagonal CdS, with some displacement of lines. Calculated cell-parameters [*a* 4.08(1), *c* 6.64(1) Å] correspond to a ZnS content of about 15 mol.% (Hurlbut 1957), in good agreement with the range obtained from electron-microprobe analyses. No diffraction lines attributable to hawleyite were detected.

Sphalerite intergrown with greenockite and in isolated grains in laminae of greenockite-bearing galena contains minor amounts of iron and generally only trace amounts of cadmium. It is similar in composition to sphalerite in nearby sphalerite-rich laminae (Table 1, Fig. 5). Occasional analyses of sphalerite revealed over 1 wt.% Cd; this may reflect inclusions of greenockite at or below the surface of the polished sections, although none were seen in the areas analyzed. Etching of sphalerite with 1:1 HNO_3 did not reveal any patches that might be cadmium-enriched (*cf.* Chen & Dutrizac 1978). Electron-microprobe analyses of galena intergrown with greenockite detected only lead and sulfur.

Discussion

The Lady Loretta greenockite is clearly primary with respect to the present cycle of weathering. It occurs well below the base of significant oxidation, in samples showing no original oxidation or leaching, and only slight post-drilling oxidation. Mineral textures do not resemble those of secondary sulfides.

Some recrystallization of sulfides has occurred; sphalerite and galena show an approach to polyhedral "foam" textures, sphalerite has planar annealing-type twins, and there is some microscale veining of sphalerite laminae by galena ± greenockite ± sphalerite. This slight metamorphism is insufficient to explain the thick cadmium-anomalous zone, and equivalent or more intense recrystallization at Mount Isa and Hilton has not generated cadmium sulfides in ores of similar bulk-composition. Therefore, the occurrence of greenockite in a cadmium-enriched zone is most likely an original depositional feature of the mineralization.

The sulfur isotope data of Carr & Smith (1977) suggest that depositional or metamorphic temperature at Lady Loretta probably did not exceed 300°C. Compositions of zincian greenockite and coexisting sphalerite are far from the boundaries of the two-phase field in the ZnS–CdS system at these low temperatures (Tauson & Chernyshev 1977); thus the two minerals are not in equilibrium.

This occurrence of apparently primary zincian greenockite in the Lady Loretta deposit is of geochemical as well as mineralogical interest. The P116 intersection has a higher Zn/Cd ratio than the deposit as a whole, and the deposit is not enriched in cadmium in comparison to other Proterozoic, sediment-hosted lead–zinc–silver deposits in northern Australia (Table 2). In these deposits, cadmium typically occurs as a trace element in sphalerite at concentrations of a few thousand parts per million, and there is a good linear correlation between cadmium and zinc abundances (Smith & Walker 1971, Croxford & Jephcott 1972).

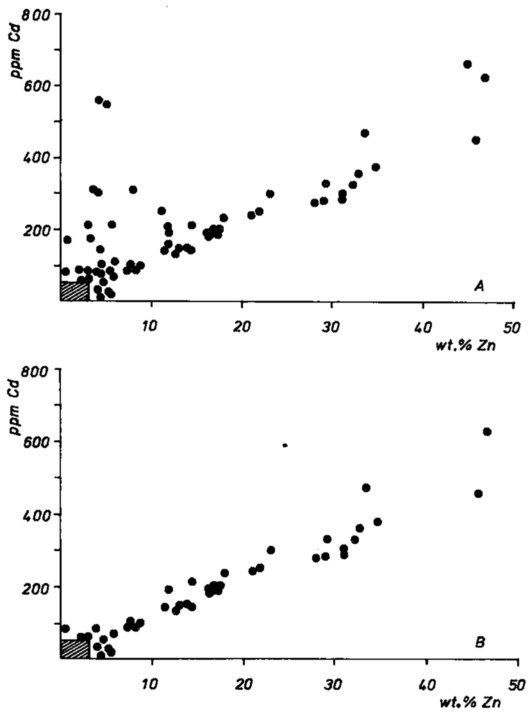

FIG. 2. Zinc–cadmium scatter plots for drill hole P116, Lady Loretta. A. All samples; shaded area contains 44 points. Least-squares regression equation is: amount of Cd (ppm) = 10.69 (Zn wt.%) + 37, correlation coefficient 0.802. B. Samples with less than 5% Pb; shaded area contains 42 points. Least-squares regression equation is: amount of Cd (ppm) = 11.12 (Zn wt.%) + 2, correlation coefficient 0.980.

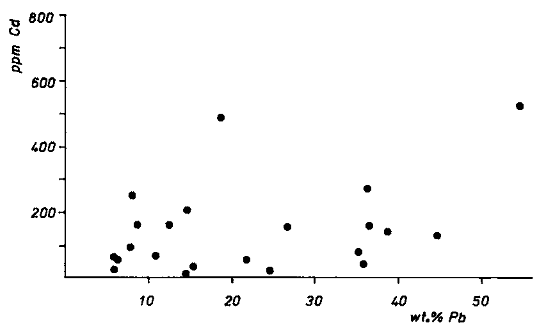

FIG. 3. Lead *versus* "excess cadmium" (total Cd minus Cd attributed to sphalerite, based on regression equation for Fig. 2B) for samples with 5% Pb or greater, in drill hole P116.

At Lady Loretta, there has been significant decoupling of the geochemical coherence of cadmium and zinc during the formation of a substantial thickness of mineralization, which presumably reflects changes in physical or chemical conditions

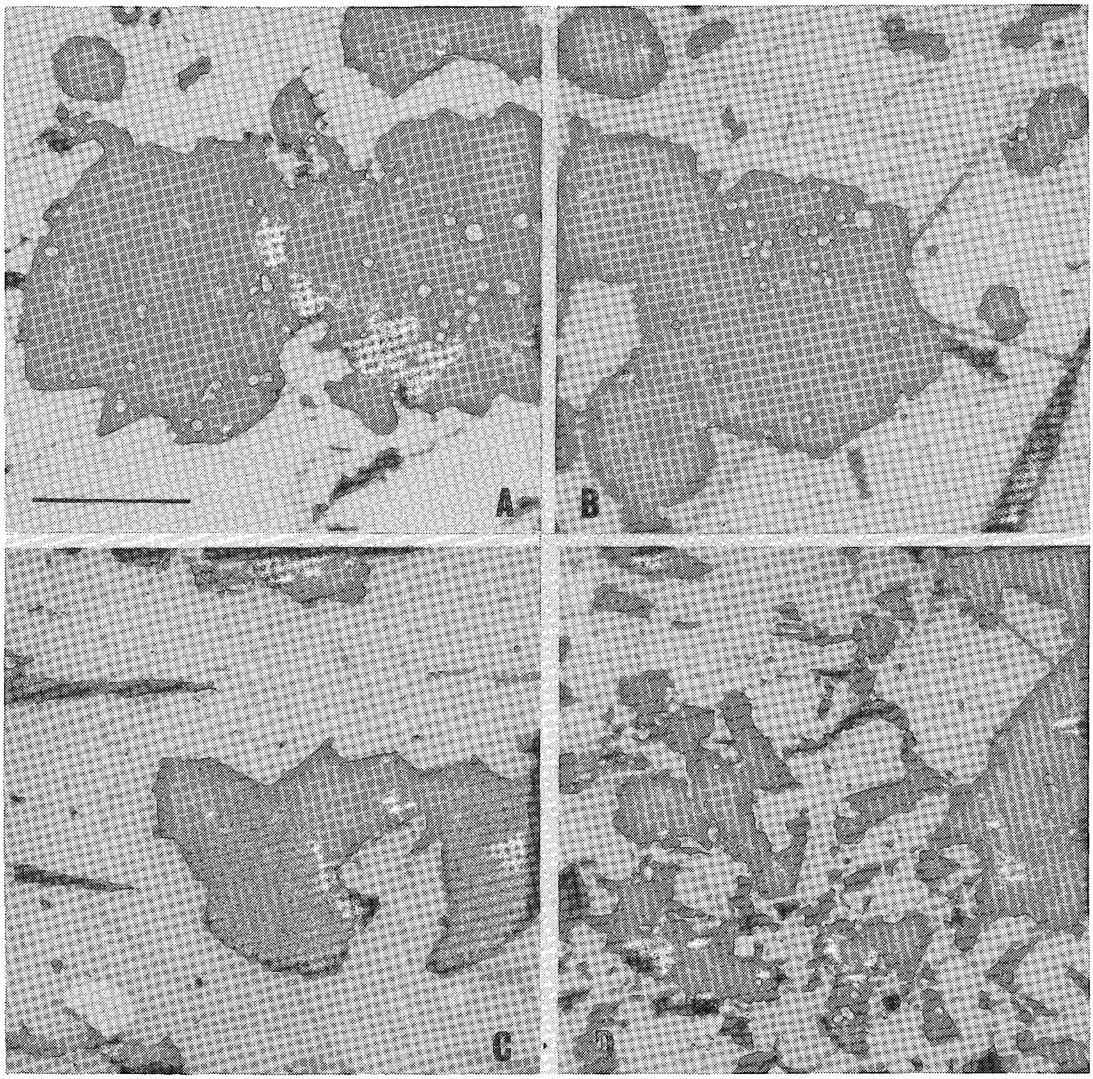

FIG. 4. Textural relationships of greenockite, sphalerite and galena at Lady Loretta. Scale bar represents 50 μm and applies to all photographs. All photographs taken under oil immersion. A. Irregular greenockite (medium grey) intergrown with galena (white) and sphalerite (dark grey, some with internal reflections). White euhedra of pyrite are included in greenockite. B. "Euhedral" greenockite in galena, intergrown with sphalerite and with fine-grained inclusions of pyrite. C. Irregular greenockite intergrown with galena and sphalerite; both greenockite and sphalerite have locally planar boundaries with galena. D. Graphic intergrowth of greenockite (with minor included pyrite) and galena.

during sulfide deposition. These may be related to local oxidizing conditions, as hematite and barite are common accessory minerals in the Lady Loretta mineralization, in contrast to other similar deposits in the region. Efficient separation of cadmium and zinc can occur in relatively oxidizing environments, as shown by the typical occurrence of cadmium sulfides as supergene minerals (Oen *et al.* 1974, Ramdohr 1980, p. 582).

ACKNOWLEDGEMENTS

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TABLE 1. COMPOSITION OF COEXISTING GREENOCKITE AND SPHALERITE FROM LADY LORETTA (ELECTRON-MICROPROBE DATA)

	1	2	3	4	5	6	7(a)	8(a)	9(b)	10(c,e)	11(c)	12(c)	13(d)	14(d)
Zn	7.0	7.4	3.9	5.2	8.9	7.5	64.2	64.0	64.9	62.7	65.4	65.3	65.5	65.2
Fe	tr	tr	tr	na	na	na	1.1	1.1	1.0	na	na	na	1.1	1.0
Cd	70.2	70.7	74.5	74.2	68.0	70.2	0.1	0.1	0.1	3.6	0.3	0.6	0.1	0.1
S	22.4	22.3	22.5	22.3	22.8	22.7	33.6	33.3	33.5	33.0	33.3	33.1	33.1	32.8
	99.6	100.4	100.9	99.9	99.7	100.4	99.0	98.5	99.5	99.3	99.0	99.0	99.8	99.1

1-6 Greenockite, 7-14 Sphalerite. Analyses in weight percent. tr = trace, na = not analyzed. (a) Intergrown with greenockite 1. (b) Intergrown with greenockite 2. (c) In same galena-rich lamina as greenockites 4-6.
(d) From massive sphalerite lamina adjacent to galena-rich band containing disseminated greenockite and sphalerite.
(e) High Cd in this sample may be due to inclusions of greenockite, although none were seen in the area analyzed. Analytical conditions: Pure ZnS, Fe, Cd standards, 20 kV, 0.025 mA, JEOL ZAF correction program. Analyses by P.D. Cheyne, Mount Isa Mines Limited.

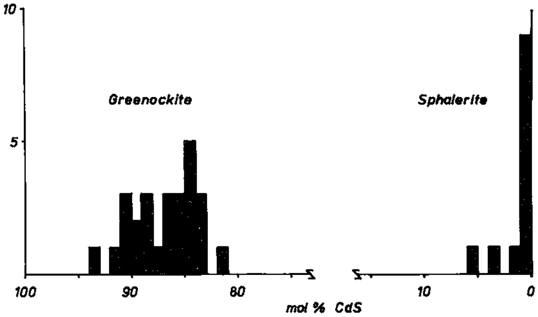

FIG. 5. Summary of compositional ranges of zincian greenockite and coexisting sphalerite at Lady Loretta. Zincian greenockite is close to pure (Cd,Zn)S, sphalerite contains in addition about 1 mol.% FeS. Sphalerite compositions shown as containing in excess of 1 mol.% CdS may be influenced by inclusions of zincian greenockite.

TABLE 2. APPROXIMATE Zn/Cd WEIGHT RATIOS IN NORTHERN AUSTRALIAN PROTEROZOIC STRATIFORM LEAD-ZINC-SILVER DEPOSITS

DEPOSIT	Zn/Cd
Mount Isa (a)	350
Hilton (b)	300
Lady Loretta (b)	450
McArthur - H.Y.C. (c)	500
Dugald River (d)	450

Sources: (a) Smith & Walker 1971. (b) Unpublished data, Mount Isa Mines Limited. (c) Croxford & Jephcott 1972. (d) Connor et al. 1982.

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