Minor and Trace Elements in the Polymetallic Stratabound Ore Deposits of the Central Peruvian Andes

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1 Introduction – Regional Metallogenetic Setting

The polymetallic province of central Peru forms a 120-km-wide-800-km-long belt which corresponds with the western Cordillera and the high plateaus of the Andes between 7 and 14°S (Bellido et al. 1969; De las Casas and Ponzoni 1969; Soler 1986). This province is limited to one segment of the liminar intracratonic Andean chain (Sillitoe 1974; Soler et al. 1986; Fig. 1).

Polymetallic vein and skarn deposits associated with Cenozoic magmatism are the principal metal producers (they account for 70, 87, and 96% of Zn, Pb, and Ag production respectively) (Soler 1986), but stratabound deposits have gained in importance during the past 20 years, mainly as Zn providers; currently they account for 30, 13, and 4% of Zn, Pb, and Ag production respectively. Two principal sedimentary metallotects have been identified.

– the Pucará limestone platform Group of Triassic-Liassic age, with volcano-sedimentary deposits (Soler 1986; Dalheimer this Vol.) and syndiagenetic deposits without associated volcanism (Fontboté this Vol.).

– the Santa limestone platform Formation of Valanginian age, with volcano-sedimentary deposits (Samaniego 1981).

Three additional stratabound deposits or districts have been described: the Jurassic exhalative-sedimentary deposit at Cercapuquio (Soler 1986; Cedillo this Vol. gives an alternative genetic hypothesis); the Cretaceous volcano-sedimentary district of Hualgayoc (Canchaya this Vol.); the Miocene lacustrine volcano-sedimentary deposit at Colquijirca (Lehne and Amstutz 1978; Soler 1986; Lehne this Vol.).

The variety in ages and types of polymetallic deposits made this province an especially attractive target for a comprehensive study of the distribution of minor and trace elements such as Ag, Bi, Cd, In, Ge, Ga, Sn, etc. in polymetallic ores on a regional scale.

Beyond its direct economic interest, such a study (Soler 1982, 1987; Soler and Lara 1983; Lara et al. 1983) provides a detailed quantitative and qualitative evaluation of the distributions of these elements in accordance with the characteristics of the deposits (geographic setting, metallogenetic type, nature and age of the country rock, time of mineralization, mineral associations, age and chemistry of

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Stratabound Ore Deposits in the Andes
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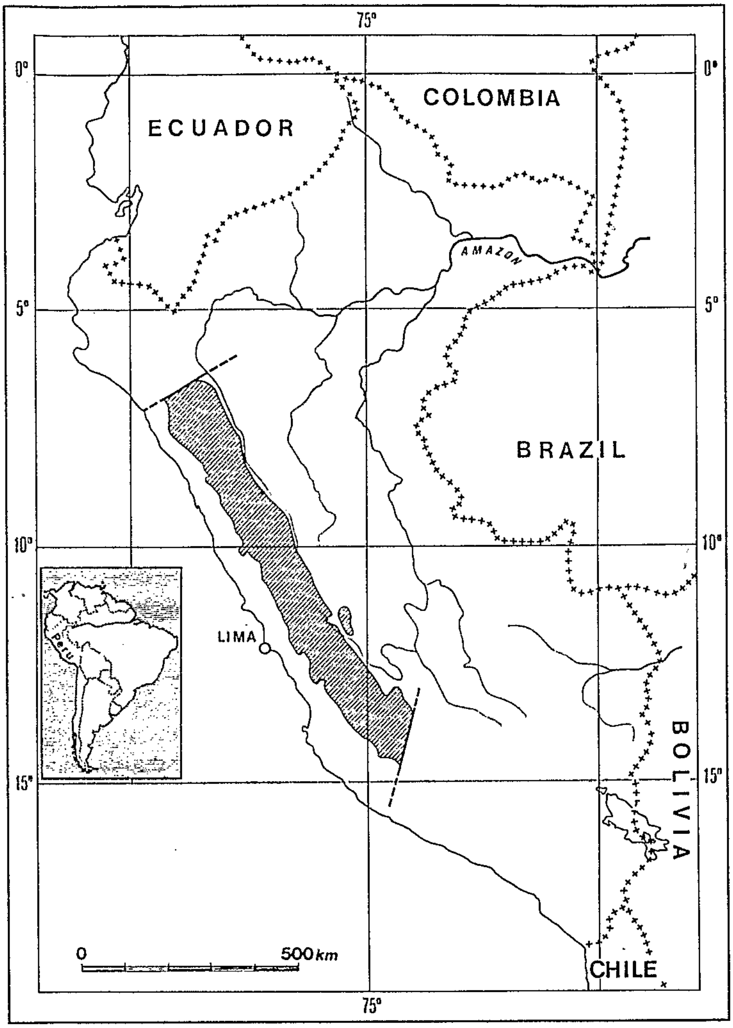

Fig. 1. The polymetallic belt of central Peruvian Andes (Soler et al. 1986)

associated magmatism, etc.) and shows that in absence of clear field evidence the knowledge of minor and trace elements contents in a deposit or a prospect of the studied province would permit, in various cases, determining the actual type of the deposit or prospect, with evident consequences for exploration.

In this chapter, we present data concerning the stratabound deposits defined above. The results concerning the polymetallic vein and skarn deposits associated with Cenozoic magmatism will be used for comparison, but will not be discussed in detail here (see Soler 1987).

The data were obtained from unsorted mine ore samples and Pb and Zn concentrates (see Appendix). Very few data are available for separate minerals, so that a detailed study of the actual minor and trace elements contents in sulfides and sulfosalts, and of the distribution of these elements between co-existing minerals, as discussed by MacIntire (1963), Ghosh Dastidar et al. (1970), or Bethke and Barton (1971), is not still possible here.

2 Minor and Trace Elements Associated with Zn (Cd, In, Ge, and Ga)

In the polymetallic ores, these four elements are known to concentrate preferentially in sphalerite (Fleisher 1955; Vlasov 1968; Ivanov 1966, 1968; Geldron 1983). As far as our samples are concerned, the highest Cd, In, Ge, and Ga contents are actually observed in Zn-rich ores and Zn concentrates. The contents in the Zn concentrates of polymetallic ore deposits are highly variable (by a factor of 100 for In, Ga, and Ge, by a factor of 10 for Cd; see Table 1). These elements do not appear under their proper mineralogic forms, except at Cercapuquio, where greenockite (CdS) is observed.

2.1 Cadmium and Indium Contents

Cadmium. Comparisons between the Cd contents observed in ores and those observed in Zn concentrates show that cadmium is found almost only in sphalerite. However, cadmium is observed in minerals other than sphalerite in the Pucará stratabound deposits without associated volcanism, where the relative Cd content as compared to Zn decreases considerably from the ores to the Zn concentrate. The Cd content in galena, which may be evaluated from the contents in Pb concentrates, is very low (< 5 g/t) and cannot account for the difference observed between ores and Zn concentrate. The Cd contents in the other ore-forming minerals

Table 1. Orders of magnitude of Cd, In, Ge and Ga contents in Zn concentrates from the stratabound polymetallic deposits of central Peru

	Maxima (ppm)	Deposits	Minima (ppm)	Deposits
Cd	5400	El Extraño	700	Carahuacra
In	290	Carahuacra	10	San Vicente
			10	Gran Bretaña
Ge	130	Shalipayco	< 10	Santa deposits
	90	Gran Bretaña		
Ga	855	Sayapullo	6	Shalipayco
	240	Hualgayoc	8	San Vicente
			12	Gran Bretaña

(pyrite, chalcopyrite) are also much too low (Fleisher 1955; Vlasov 1968) to account for it. Therefore cadmium probably occurs with considerable contents in some gangue minerals, possibly in the bituminous layers interbedded in the Pucará limestones and/or in smithsonite, a mineral which may contain commonly more than 2000 ppm of cadmium and is not concentrated by flotation.

In the province, the mean cadmium content of sphalerite varies considerably from one ore deposit to the other [the ratio Cd(ppm)/Zn(%) ranges from 10 to 120]. There is no rule which makes it possible to relate the Cd content to the temperature of ore formation. Some types of ore deposits are homogeneous in their Cd contents, while other types show contents which vary considerably from one ore deposit to the other.

Both types of stratabound deposits associated with the Pucará Group are homogeneous concerning the Cd contents, but with different level of content: the volcano-sedimentary ore deposits are characterized by low Cd contents ($Cd < 1000$ ppm in sphalerite), while the syndiagenetic stratabound deposits without associated volcanism are characterized by Cd contents in sphalerite amounting to about 2500 ppm. In the latter, in particular at San Vicente (Fontboté et al. this Vol.), Cd content is lower in light, diagenetically evolved sphalerite than in dark "primary" sphalerite, which may be interpreted as the result of a "diagenetic distillation" of sphalerite.

The Cercapuquio exhalative-sedimentary deposit (for another genetic interpretation, see Cedillo this Vol.) differs from all the other deposits in its very high Cd contents (higher than 1% in the ore) and the presence of greenockite.

The ore deposits of the Hualgayoc district are rather homogeneous and characterized by Cd contents ranging from 4500 to 7000 ppm in sphalerite, while the stratabound deposits associated with the Santa Formation are highly heterogeneous concerning their Cd contents in sphalerite, which range from 1500 ppm at Huanzalá to 7500 ppm at El Extraño.

The Colquijirca deposit presents an estimated Cd content in sphalerite in the range 2000–2500 ppm.

Cd content in sphalerite does not allow to distinguish stratabound deposits from vein and skarn deposits associated with Cenozoic magmatism. As a matter of fact, skarn deposits are characterized by Cd contents in sphalerite in the range 2000–4000 ppm, and vein deposits form a highly heterogeneous group with Cd contents in sphalerite ranging from 1000 to 8000 ppm, with a tendency to higher Cd contents in the deposits from the northern part of the polymetallic province (Soler 1987).

Indium. The hypothesis according to which indium is concentrated exclusively in sphalerite is inaccurate in almost all ore deposits. For the Pucará stratabound deposits without associated volcanism, the previous hypothesis with respect to cadmium remains valid. The other deposits, where the In/Zn ratio decreases considerably from the ores to the Zn concentrate, show complex mineral associations with abundant sulfosalts. Indium is much more ubiquitos than cadmium, and minerals such as chalcopyrite, enargite, wolframite, and mainly tin minerals (cassiterite, stannite) can contain large amounts of indium (Anderson 1953; Vlasov 1968).

In the province, the indium contents of sphalerite vary considerably from one deposit to the other; the ratio of In content (in ppm) to Zn content (in percent) (here referred as In/Zn) ranges from 0.2 to more than 5. There is no rule which makes it possible to relate the In content in sphalerite to the temperature of ore formation. It is classically considered that sphalerites from mesothermal and high-temperature deposits are richer in indium (Anderson 1953; Fleisher 1955) but, as it is emphasized by Fleisher, "numerous exceptions to this generalization have been noted".

Both types of stratabound deposits associated with the Pucará Group are homogeneous concerning the In contents, which at the same time makes it possible to distinguish the two groups: the volcano-sedimentary ore deposits are characterized by high In contents (In/Zn of about 3 to 5, that is to say 200 to 350 ppm In in sphalerite), while the syndiagenetic stratabound deposits without associated volcanism are characterized by very low In contents (In/Zn lower than 0.5, that is to say less than 30 ppm In in sphalerite).

The Cercapuquio deposit shows low In content (In/Zn = 0.54, that is to say 30 to 40 ppm In in sphalerite).

The ore deposits of the Hualgayoc district are more homogeneous and characterized by In contents in sphalerite ranging from 130 to 200 ppm, while the stratabound deposits associated with the Santa Formation are more heterogeneous concerning their In contents in sphalerite, which range from 180 ppm at Huanzalá to 13 ppm at El Extraño.

The Colquijirca deposit shows very high In contents (In/Zn of 8.7 in the ore).

In content in sphalerite does not allow to distinguish stratabound deposits from vein and skarn deposits associated with Cenozoic magmatism which form a highly heterogeneous group with estimated In contents in sphalerite ranging from 10–15 ppm to 200–300 ppm (Soler 1987).

When considering jointly Cd and In contents, two large groups of ore deposits can be distinguished (Fig. 2):

– A group of deposits with low to mean Cd contents and high In contents, the In/Cd ratio being higher than 0.10.
– A group of deposits with mean to high Cd contents and low to mean In contents, the In/Cd ratio being lower than 0.05.

The latter includes most of the Cenozoic skarn and vein deposits, the Pucará syndiagenetic deposits without associated volcanism, the Hualgayoc district, and the stratabound deposits of the Santa Formation. The former includes the Pucará volcano-sedimentary deposits, the Colquijirca deposit and some vein and skarn Cenozoic deposits, the common feature of which is the fact that they are situated in the Excelsior Formation of Lower Paleozoic and/or at the very bottom of the Meso-Cenozoic cover, within or around two dome structures of the Paleozoic basement (Soler 1987).

Both groups include a great variety of ore types, so that the occurrence of these two groups could not be related to the typology of ore deposits. The presence of lower Paleozoic country rock appears as the decisive factor concerning the high In content and the rather low Cd content of the deposits from the first group. The genesis of all the ore deposits belonging to this group is controlled by fluid circu-

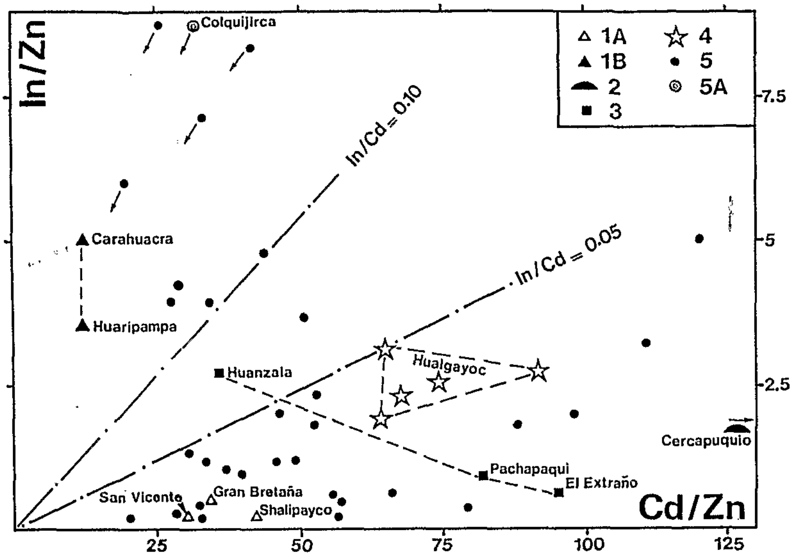

Fig. 2. Diagram Cd (ppm)/Zn(%) versus In(ppm)/Zn(%). *1* Strababound deposits in the Pucará Group (*A* syndiagenetic without associated volcanism, *B* volcano-sedimentary); *2* Jurassic sedimentary exhalative deposit; *3* volcano-sedimentary deposits in the Santa Formation; *4* Hualgayoc district; *5* deposits associated with Cenozoic magmatism (*A* skarn and vein deposits, *B* volcano-sedimentary deposit). The plotted data correspond to the contents in the Zn concentrates, except for a few deposits (*arrows*) where they correspond to the average ore analyses

lations related to magmatism (either to the Liassic volcanics or to the Cenozoic subvolcanic intrusions). The differences observed between these two groups suggest the contribution of elements extracted from the close country rock: In (and also Ga and Sn – see above) from the basement; Cd from the Andean cover. However, these differences appear as second-rate geochemical variations for the ore deposits linked to the Cenozoic magmatism which are very similar in their mineral associations, zonations, alterations, chemical composition of the associated calk-alkaline magmatic rocks whatever the country rock may be (Soler et al. 1986), which suggests that the metals (Cu, Pb, Zn, Ag) are not recycled from the immediate country rock and have a deep-sealed crustal or mantellic origin.

2.2 Germanium Contents

The results concerning germanium contents are summarized in Fig. 3.

Among the stratabound deposits associated with the Pucará Group, the volcano-sedimentary one deposits are characterized by very low Ge contents (lower than 10 ppm), while the syndiagenetic deposits without associated volcanism are characterized by mean to high Ge contents (130 ppm in Zn concentrate from Gran Bretaña). These high Ge contents are not surprising; it is quite normal to find such contents in low-temperature ore deposits such as, for instance, those of

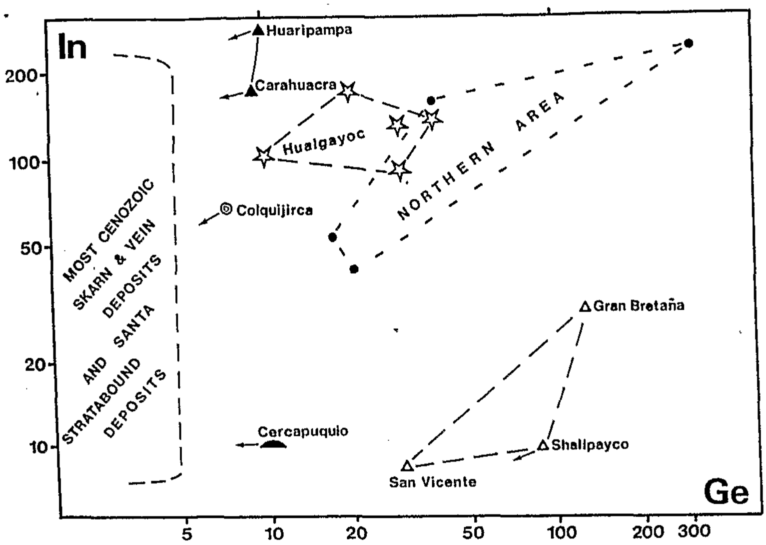

Fig. 3. Ge(ppm)-In(ppm) Diagram. (Symbols as in Fig. 2)

Mississippi valley type (Fleisher 1955; Vlasov 1968; Geldron 1983). The germanium contents observed in Peru remain low even when compared to those observed in other areas (Missouri, Poland, French Massif Central). In the case of germanium there is, as was noted for Cd and In, a "diagenetic distillation" of sphalerite. This phenomenon may account for the fact that the San Vicente ore deposit, where diagenetic recrystallization is considerable (Gorzawski et al. this Vol.), shows Ge contents which are lower than in the Shalipayco or Gran Bretaña (Azukocha) deposits where these phenomena are much less pronounced.

The Cercapuquio deposit shows low Ge contents (lower than 10 g/t), in agreement with the statement of Geldron (1983): "generally, syngenetic sphalerites are poor in germanium".

The stratabound deposits of the Santa Formation also show very low Ge contents and cannot be distinguished, in this respect, from the vein and skarn deposits associated with the Cenozoic magmatism in which, with a few exceptions, sphalerite are germanium-poor (contents lower than 5–10 ppm) (Soler 1987). This is a significant result from an economic and metallogenetic point of view, and it is after all rather unexpected as far as mesothermal and epithermal ore deposits are generally considered a priori as favorable to germanium concentrations (Fleisher 1955; Vlasov 1968; Geldron 1983). Some mesothermal vein deposits, all situated in the northern part of the province, are consistent with this general rule, and outstanding in the Peruvian context with high Ge contents in sphalerite (400 ppm in the Shalipayco deposit, 70 ppm in the Santo Toribio deposit) (Soler 1987).

The deposits of the Hualgayoc district show low to mean germanium contents (10 to 40 ppm in Zn concentrates) and therefore they differ from most of the deposits linked to Cenozoic magmatism. However, it would be risky to infer that this particular geochemical feature of Hualgayoc ores gives evidence of the specific origin of the deposits of this area (Canchaya this Vol.). In fact, the other volcano-sedimentary deposits of the province (associated with both Pucará Group and Santa Formation) show very low germanium contents and we have just seen that there is a regional "positive germanium anomaly" in the north of the province concerning the Cenozoic hydrothermal deposits. Therefore we may consider that the anomalous Ge contents of the Hualgayoc deposits are part of this regional Ge anomaly and are linked rather to Cenozoic hydrothermal processes than to Cretaceous volcano-sedimentary processes.

2.3 Gallium Contents

Of the four elements associated with Zn, Ga shows the most erratic distribution. The Ga contents in Zn concentrates vary considerably in the province and even in the same area. The ratio of Ga (expressed in ppm) to Zn (expressed in percent) (here referred to as Ga/Zn) ranges from 0.06 to 18. It is generally considered (Fleisher 1955; Vlasov 1968) that gallium is more abundant in epithermal deposits. In these case of the studied province, this rule does not apply, and gallium contents appear as quite independent of the temperature of ore formation.

The Pucará syndiagenetic stratabound deposits without associated volcanism and the Cercapuquio deposit are characterized by very low Ga contents (Ga/Zn lower than 0.2, that is to say less than 14 ppm Ga in sphalerite), while volcano-sedimentary deposits of the Pucará Group show higher, though erratic, Ga contents (Ga/Zn up to 3).

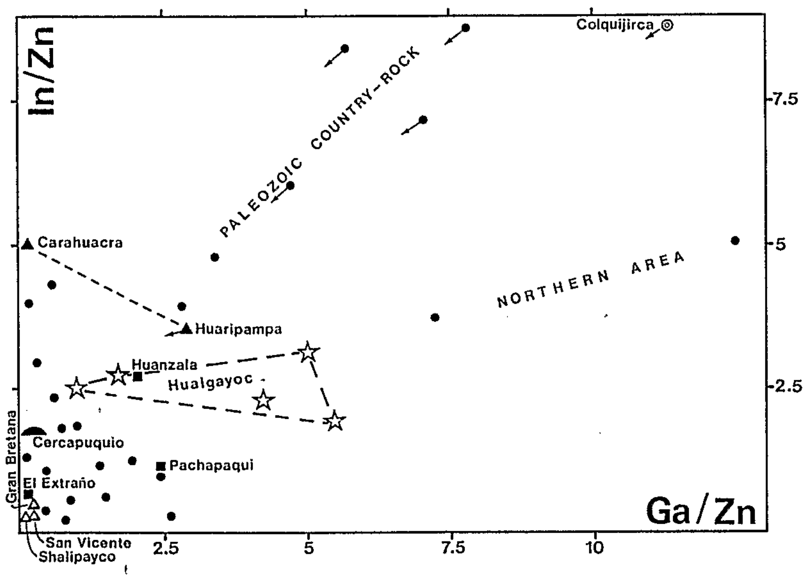

Fig. 4. Ga(ppm)/Zn(%)-In(ppm)/Zn(%) diagram (Symbols as in Fig. 2)

The stratabound deposit of the Santa Formation shows a large variation of Ga contents (Ga/Zn varies from 0.1 at El Extraño to 2.1 at Huanzalá) and cannot be distinguished, in this respect, from the Cenozoic hydrothermal deposits.

The deposits of the Hualgayoc district show mean gallium contents (Ga/Zn ranging from 1 to 6). The same observation can be made for gallium and for germanium or indium, namely that this positive anomaly is probably linked to Cenozoic hydrothermal processes, under regionally "anomalous" conditions, as suggested by the high Ga contents found in various mesothermal vein deposits of the northern part of the province (Soler 1987).

The deposits located within or near the domes of Paleozoic basement, previously characterized by a high In content, including the Colquijirca deposit, show also high Ga contents and a In-Ga correlation may be drawn (Fig. 4).

3 Silver Contents

In the Pucará stratabound ore deposits, silver contents are very low, both in the volcano-sedimentary deposits and the syndiagenetic deposits without associated volcanism. The latter are distinguished from the former by higher Pb contents and an excellent Pb-Ag correlation (Fig. 5). Galena is the only notable silver-bearing mineral in these deposits, with Ag contents ranging from 1400 to 1800 ppm.

The Cercapuquio deposit shows very low Ag contents associated with high Pb contents (Fig. 5). In this deposit galena is virtually Ag-free (Ag content < 10 ppm).

The stratabound deposits of the Santa Formation show Pb and Ag contents higher than those of the Pucará Group. Silver is concentrated mainly in galena with a content ranging from 1500 to 2500 g/t. On average, Ag contents remain low in the Santa deposits when compared to those observed in the Cenozoic hydrothermal vein deposits (Fig. 5).

The deposits of the Hualgayoc district and the Colquijirca deposit show Pb and Ag contents and Ag/Pb ratios which are similar to those observed in skarn and mesothermal vein deposits associated with Cenozoic magmatism (Fig. 5).

4 Bismuth Contents

Bismuth occurs as native bismuth, as proper minerals (bismuthinite, tellurobismuthinite, tetradymite, emplectite, etc.) and in replacement or micro-inclusions in sulfides and sulfosalts (mainly in pyrite, galena, and tennantite-tetraedrite).

Both syndiagenetic deposits without associated volcanism and volcano-sedimentary deposits of the Pucará Group are characterized by low to very low Bi contents (< 30 ppm) associated with their low Ag contents (Fig. 6). Bi contents do not allow discrimination between the two groups.

The Cercapuquio deposit is distinguished by its very low Bi content associated with its very low Ag content (Fig. 6).

The stratabound ore deposits of the Santa Formation show Bi contents ranging from 350 to 6 ppm. The latter vary in inverse proportion to Ag and the available data suggest a crude correlation with the temperature of ore formation, the most

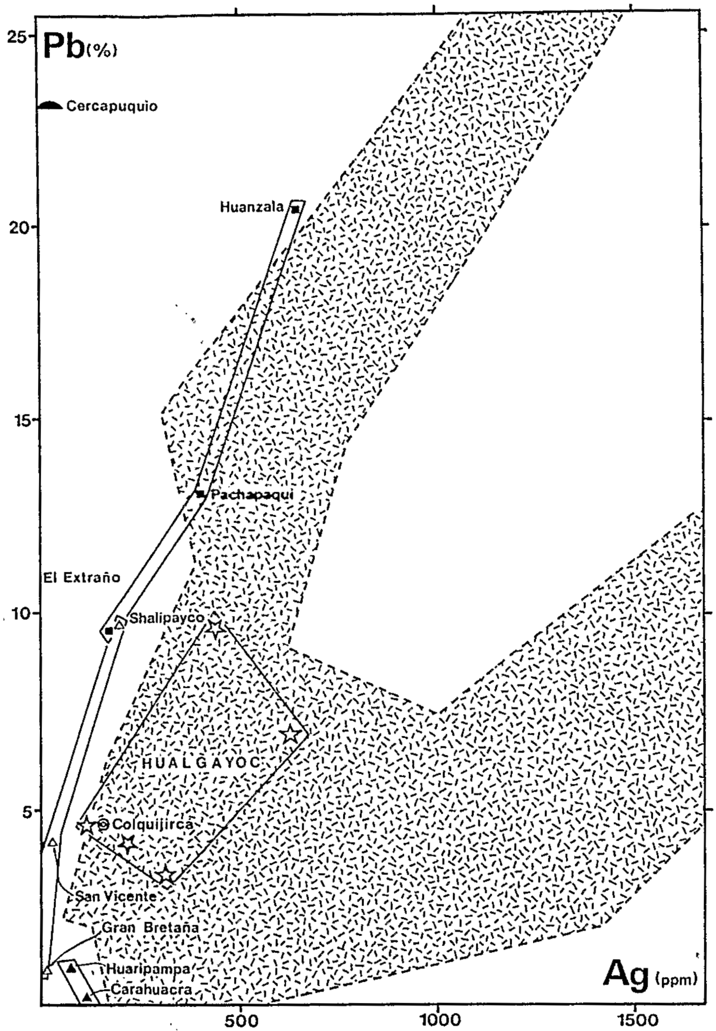

Fig. 5. Ag(ppm)-Pb(%) diagram (Symbols as in Fig. 2, but for each deposit the plotted data correspond to the average of ore analyses; the *dashed area* is the envelope of the data from the Cenozoic skarn and vein deposits, Lara et al. 1983)

proximal deposit (El Extraño) showing the highest Bi contents and the lowest Ag contents and inversely in the most distal deposit (Pachapaqui). A similar correlation between Bi content and temperature of ore formation has been demonstrated for the Cenozoic skarn and vein deposits (Soler 1987).

The ore deposits of the Hualgayoc district show Bi contents in the range 50–100 ppm, similar to those presented by Cenozoic mesothermal vein deposits, while Bi contents in the Colquijirca deposit are close to those found in Cenozoic skarn deposits (Fig. 6).

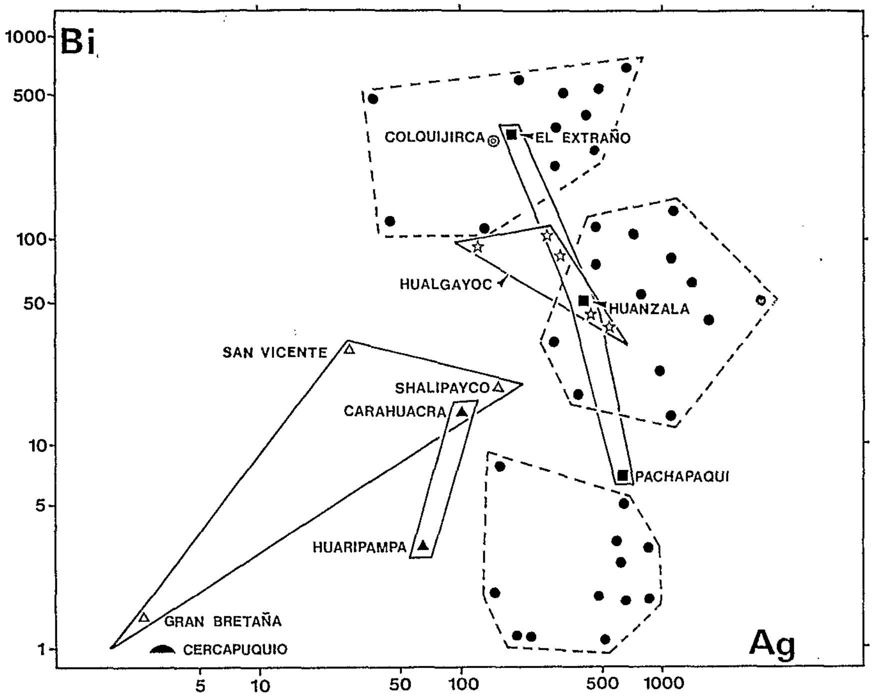

Fig. 6. Ag(ppm)-Bi(ppm) diagram (Symbols as in Fig. 2 but for each deposit the plotted data correspond to the average of ore analyses)

5 Tin Contents

Tin is systematically present in the ore deposits of the province either in its proper mineralogic forms (seldom cassiterite, most often stannite, stannoidite etc.) or in replacement mainly in sphalerite, chalcopyrite, and tennantite-tetraedrite, the Sn content of ores ranging from less than 10 to more than 1000 ppm (Soler 1987).

In the stratabound deposits, the range of Sn contents is more limited (16–181 ppm), but Sn content cannot be used for metallogenetic discrimination. Both types of stratabound deposits of the Pucará Group and the Cercapuquio deposit show mean to low Sn contents (102 ppm at Gran Bretaña, 93 ppm at Shalipayco, 16 ppm at San Vicente, 181 ppm at Huaripampa, 19 ppm at Carahuacra, 32 ppm at Cercapuquio), with a clear Sn-Hg correlation in the syndiagenetic deposits without associated volcanism. In the stratabound deposits of the Santa Formation, Sn contents fall in the same range (151 ppm at Huanzalá, 127 ppm at Pachapaqui, 20 ppm at El Extraño). Similar contents (40–130 ppm) are observed in the deposits of the Hualgayoc district.

The Colquijirca deposit, with 1070 ppm of tin (average analysis of ore samples), constitutes an exception; such high Sn contents are also found in various vein deposits associated with Cenozoic magmatism and located in the lower Paleozoic basement. For these deposits, including Colquijirca, the Sn positive anomaly correlates with the above discussed In and Ga positive anomaly.

6 Conclusions

The main geochemical features of polymetallic ores from the stratabound deposits of the polymetallic belt of central Peru are summarized in Table 2.

Among these deposits, three families are demonstrated to present specific distinctive geochemical features:

- the syndiagenetic deposits without associated volcanism and the volcano-sedimentary deposits of the Pucará Group, with low Ag and Bi contents and very low Cu contents. The metallogenetic distinction between the two Pucará Groups, suggested by Soler (1986), is confirmed through geochemical features of the ores. The two groups differ largely by their Ge and Hg contents (characteristically high in the syndiagenetic deposits), and Pb, In, Cd, Mn, and Hg contents (Table 2).

Table 2. Summary of the principal geochemical features of ores from the stratabound deposits of the central Peruvian Andes

Country rock and type	Principal geochemical features	
1. Pucará Group (Trias-Lias)	*Common features*	*Specific features*
A) Syndiagenetic without associated volcanism	Low Ag contents Low Bi contents Absense of Cu Low Ga contents Low Se contents	*High Ge contents* – *Low In contents* Pb-Ag correlation High Hg contents with a Sn-Hg correlation[a] – Low Mn contents[a]
B) Volcano-sedimentary		*High In contents* – Low Ge contents *Very low Cd contents* *Absence of Pb* Very low Hg contents[a] – High Mn contents[a]
2. Chaucha Formation (Malm) Sedimentary-exhalative (Cercapuquio)	*Very high Cd contents* *High Pb contents associated with very low Ag contents* Low Ge and Ga contents – Mean to low In contents *Very low Bi contents* Very low Se and Hg contents	
3. Santa Formation (Valanginian) Volcano-sedimentary	Very low Ge contents Mean to low Ag contents (higher in the more distal deposits, lower in the more proximal deposits) Ag-Pb correlation and inverse Ab-Bi correlation High Sn contents – Low Cu contents	
4. Hualgayoc district (Cretaceous) Volcano-sedimentary with superimposed Cenozoic skarn and vein	Mean to high In, Ga and Ge contents Mean Bi contents Notable Hg and Sn contents	
5. Calera Formation (Miocene) Miocene lacustrine volcano-sedimentary (Colquijirca)	Very low Ge contents High In, Ga, and Sn contents Very low Mn contents[a] High Bi, Hg and Se contents Presence of U[a]	

[a] Not discussed in the text, see Soler (1987).

– the exhalative-sedimentary deposit at Cercapuquio with very high Cd contents, very high Pb contents associated with very low Ag contents, and very low Bi contents.

On the contrary, the geochemical features of the stratabound deposits of the Santa Formation and of the Hualgayoc district, and of the Colquijirca deposit, appear as hardly specific. They do not permit a real discrimination between these volcano-sedimentary deposits and the skarn and vein deposits associated with Cenozoic magmatism, and therefore do not introduce new arguments into the present metallogenetic discussions with respect to the genesis of these stratabound deposits. Hence it may be inferred that there are no fundamental differences in composition and nature between the fluids responsible for the formation of the Cretaceous and Miocene stratabound volcano-sedimentary deposits and those responsible for the Oligocene and Miocene skarn and vein deposits, although geometric features and the current process of deposition of ores are different. This suggests a similar source for these fluids, which may be related with the Andean calk-alkaline magmatic activity associated with the subduction process.

Appendix. This study has been realized as part of a research program conducted jointly by the Peruvian Instituto Geológico, Minero y Metalúrgico (INGEMMET) and the French Institut Français de Recherche Scientifique pour le Développement en Coopération-ORSTOM, with financial and analytical support by the Société Minière et Métallurgique de Peñarroya through an ORSTOM-Peñarroya settlement and with financial support from the Compañia Minera Huarón S. A. and the Compañia Minera Milpo S. A. through a settlement between INGEMMET and both mining companies.

Minor and trace elements were determined in the laboratory of the Peñarroya smelting plant at Noyelles-Godault (France). Zn, Pb, Cd, In, Ge and Sn analyses were carried out through XRF spectrometry, Hg, Ga and Bi analysis through AA spectrometry, and Ag analyses through dry process.

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