Paragenesis and mineral chemistry of alabandite (MnS) from the Ag-rich Santo Toribio epithermal deposit, Northern Peru

G. R. OLIVO* AND K. GIBBS†

Department of Geological Sciences and Geological Engineering, Queen’s University, Kingston, Ontario, Canada K7P 2L7

ABSTRACT

The Miocene, epithermal, Ag-rich polymetallic Santo Toribio deposit is hosted by the volcanics of the Quiruvilva-Pierina subbelt, Northern Peru, which also comprises the world-class, high sulphidation Pierina deposit. The Ag-rich, alabandite-bearing veins of the Santo Toribio deposit formed during two major stages. The early stage is characterized by deposition of arsenopyrite, pyrite, quartz, Mn-sphalerite, stannite, alabandite and minor miargyrite. Sphalerite associated with this stage is exceptionally enriched in Mn (up to 14.5 wt.%) and alabandite is optically and mineralogically zoned. Its brown zones have greater Fe+S bands and smaller Mn contents than the green zones and Fe+S replaces Mn in its structure. During this early stage, \( f_{\text{O}_2} \) must have been high to allow the stabilization of alabandite relative to rhodochrosite. In the second stage, the physicochemical conditions changed and the \( \text{CO}_2/\text{S} \) ratio increased, causing dissolution of alabandite and the deposition of abundant rhodochrosite and a second generation of arsenopyrite, pyrite and quartz, sphalerite with chalcopyrite inclusions, mirargyrite, ramdohrite, and finally stibnite. This polymetallic ore probably formed due to an abrupt decrease in \( \text{H}^+ \) and/or \( \text{Cl}^- \) concentration caused by boiling or dilution of the high-salinity hydrothermal fluids and constitutes an example of “intermediate sulfidation-state” epithermal deposits.

KEYWORDS: alabandite, Santo Toribio epithermal deposit, Peru.

Introduction

ALABANDITE, which is an isometric manganese sulphide dimorphic with rambervigite (MnS, hexagonal), occurs in a diversity of geological settings, including Mn-rich sedimentary rocks (Vassileff, 1987; Mücke et al., 1999), veins in contact-metamorphosed Mn-rich sedimentary rocks and/or skarns (Törnroos, 1982; Dobbe, 1992; Ragu, 1993), Pb-Zn-Ag replacement deposits in carbonate sequences (Hewett and Rove, 1930), mesothermal veins in pyrite-rich sedimentary rocks (Graham, 1978), Ag-rich polymetallic volcanic-hosted epithermal deposits (Hewett and Rove, 1930; Burbank, 1933), and meteorites (Skinner and Luce, 1971).

Although alabandite has been commonly reported in sediment-hosted ores, little information is available on its mode of occurrence and paragenesis in Ag-rich volcanic-hosted, epithermal deposits and there are no data on its mineral chemistry in this environment. We present in this paper, the results of a detailed petrographic and mineral chemistry investigation of alabandite and its associated vein minerals from the Ag-rich Santo Toribio epithermal deposit, to further our understanding of the processes responsible for the formation of Mn- and Ag-rich polymetallic ore in volcanic-hosted epithermal systems.

Mode of occurrence and paragenesis

The Santo Toribio ore is a low-sulphidation epithermal Ag-rich polymetallic deposit hosted
in the Quiruvilva-Pierina subbelt, which also contains the world-class, high sulphidation Pierina deposit (Noble and McKee, 1999). Both deposits are hosted by upper Oligocene-middle Miocene andesitic to rhyolitic, subaerial, volcanic rocks of the upper Calipuy Group (also referred to as the Huaraz Group), and formed between 16.5 to 13.3 Ma (Strusieva et al., 2000).

The Santo Toribio deposit is regionally controlled by NW–SE-trending lineaments (Chamorro, 1984) and has been intermittently mined since 1951. It comprises NW-, NE- and EW-striking quartz and/or carbonate veins (up to 220 m in length; Chamorro, 1984) with variable proportions of sulphides, mainly pyrite, arsenopyrite, sphalerite and alabandite. The Ag and Au grades in the polymetallic ore average 744 and 220 m length; Chamorro, 1984) with variable proportions of sulphides, mainly pyrite, arsenopyrite, sphalerite and alabandite. The Ag and Au

The alabandite-rich layer (Fig. 1a–f) is breciated and composed of fractured and corroded grains of alabandite (up to 85 vol.% of the layer), euhedral quartz crystals, rhodochrosite, pyrite, arsenopyrite, Mn-bearing sphalerite, stannite (Cu2FeSnS4), ramdohrite (Ag3Pb6Sb11S24), miar- gyrite (AgSbS2) and stibnite (Sb2S3). Alabandite grains exhibit complex, concentric green and brown zones (Fig. 1a). Quartz crystals are oriented with the long axes perpendicular to the layer boundary, and contain inclusions of pyrite and arsenopyrite. Miargyrite (Fig. 1g) and sphalerite with abundant irregular inclusions of chalcopyrite occur as isolated irregular grains and sphalerite locally fills corroded zones in pyrite II (Fig. 1h). Supergene manganese and goethite (Fig. 1g) locally occupy fractures and corroded zones in rhodochrosite, pyrite and sphalerite.

Based on the textural relationships described above, the following paragenetic sequence has been proposed for the Mn-rich hydrothermal ore of the Santo Toribio deposit (Fig. 2). The first phases that started to precipitate were pyrite I and arsenopyrite I, which commonly occur included in other minerals. Subsequently, alabandite, quartz, Mn-sphalerite-stanite, and minor miargyrite were deposited, followed by arsenopyrite II, pyrite II

![Fig. 1. Photomicrographs of the alabandite-bearing vein. (a) The three major layers: alabandite-rich (left), quartz-pyrite (QPL, centre) and carbonate-quartz (right) (reflected light). (b) Concentric green and brown zones in fractured and corroded alabandite grains (transmitted, plain-polarized light). (c) Quartz, pyrite and arsenopyrite included in alabandite (reflected light). (d) Stannite, sphalerite and miargyrite included in alabandite (reflected light). (e) Alabandite grains with an inclusion of miargyrite and corroded rims and fractures filled with rhodochrosite, pyrite and miargyrite (reflected light). (f) Alabandite with inclusions of composite grains of stannite-sphalerite. Note interstitial quartz grains and rhodochrosite and pyrite filling fractures and embayments in alabandite (reflected light). (g) Miargyrite interstitial to rhodochrosite in carbonate-quartz layer (reflected light). (h) Corroded pyrite grains filled with sphalerite and stibnite (reflected light). Ald = alabandite, Aspy = arsenopyrite, Cpy = chalcopyrite, Goe = goethite, Mi = miargyrite, Mnt = manganite, Py = pyrite Qz = quartz, Rd = rhodochrosite, Sph = sphalerite, Stb = stibnite, Stn = stannite (II denotes second generation).](image-url)
and quartz, rhodochrosite, sphalerite with chalcopyrite inclusions, mirargyrite, ramdohrite and finally, stibnite.

**Mineral chemistry**

Quantitative analyses of minerals of the Mn- and Ag-rich Santo Toribio ore were conducted using the Jeol JXA-8900L automated wavelength-dispersion electron microprobe (EMP) at McGill University in Montreal. The analyses were conducted with an accelerating voltage of 20 kV and a beam current of 30 nA. Beam diameters of 10 µm and 5 µm were used for analysis of carbonate and sphalerite, respectively, and of 2 µm for mirargyrite and alabandite. Carbonate analysis was calibrated using internal standards of dolomite (CaO and MgO), strontianite (SrO) and siderite (FeO and MnO). The standards used for calibration for the analysis of the sulphide minerals include: spessartine (Si, Mn and Al), diopside (Mg), AgBiSe² (Ag), CanMet ZnS (Zn and S), CanMet pyrite (Fe and S), CanMet stibnite (Sb) and CanMet pentlandite (Ni).

Electron microprobe data were collected from 206 points along straight lines across four concentrically zoned alabandite grains (Table 1) and single element scans for Mn, S, Fe and Sb were conducted in selected grains (Fig. 3) in order

![FIG. 2. Paragenetic sequence for the alabandite-bearing veins from Santo Toribio.](image)

**Table 1. Composition of alabandite from the Santo Toribio deposit.**

<table>
<thead>
<tr>
<th></th>
<th>Green zones (N = 96)</th>
<th>Brown zones (N = 113)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>Wt.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>61.6–62.9</td>
<td>62.3</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0–1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Sb</td>
<td>0–0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>35.9–36.7</td>
<td>36.3</td>
</tr>
<tr>
<td>a.p.f.u.*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.986–1.006</td>
<td>0.999</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0–0.016</td>
<td>0.004</td>
</tr>
<tr>
<td>Sb</td>
<td>0.0–0.002</td>
<td>0.00</td>
</tr>
<tr>
<td>Σ</td>
<td>1.003</td>
<td>1.002</td>
</tr>
<tr>
<td>S</td>
<td>0.988–1.002</td>
<td>0.997</td>
</tr>
</tbody>
</table>

* Ag, Al, Ca, Mg, Ni, Zn were also analysed and were not detected or are lower than 0.1 wt.%

* The atomic proportions are based on 2 atoms per formula unit (a.p.f.u.)
Fig. 3. (a) Photomicrograph of the alabandite grain selected for single-element scanning. (b) Back-scattered electron image of the selected grain. (c,d,e,f) Single element scans for Mn, S, Sb and Fe, respectively.
to document the variation of their composition. The results reveal that alabandite contains minor amounts of Fe and Sb and the brown zones have higher Fe + Sb and lower Mn contents than the green zones (Fig. 3). Manganese correlates negatively with Fe+Sb in the brown zones (correlation coefficient: $R^2 = 0.91$; Fig. 4), suggesting that Mn is replaced by Fe+ Sb. In the green zones, this correlation is less evident ($R^2 = 0.53$), probably because Fe and Sb contents are near background levels in most of the analyses. This is the first time that Sb has been reported in alabandite.

Sphalerite, previously referred to as Mn-sphalerite, forms composite grains with stannite and contains up to 14.5 and 5 wt.% Mn and Fe, respectively (Table 2). Zinc correlates negatively with Mn+Fe ($R^2 = 0.97$) indicating that it is replaced by Mn+Fe. Based on this assumption and using the average composition, the Mn-sphalerite formula was calculated as $(\text{Zn}_{0.70}\text{Mn}_{0.23}\text{Fe}_{0.08})\Sigma_{1.01}\text{S}$. To our knowledge, this is the highest Mn content in sphalerite reported in the literature. Mirargyrite analyses yielded (wt.%): 36.78 Ag, 40.74 Sb and 21.24 S and rhodochrosite contains on average (mol.%) 77.7 MnCO$_3$, 20.0 CaCO$_3$, 1.9 MgCO$_3$ and 0.4 FeCO$_3$.

Energy-dispersive spectral analyses were also conducted on ramdohrite, stibnite, stannite and pyrite II in the alabandite-rich layer. These

![Graph](image.png)

**Fig. 4.** A plot of Mn vs. Fe+Sb (in atomic proportions), comparing the composition of the green (squares) and brown (circles) zones in alabandite.

**Table 2.** Composition of Mn-sphalerite from the alabandite-rich layer.

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
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<tr>
<td>Zn</td>
<td>49.02</td>
<td>47.90</td>
<td>47.55</td>
<td>46.99</td>
<td>48.99</td>
<td>49.39</td>
<td>48.00</td>
<td>47.96</td>
<td>50.02</td>
<td>47.19</td>
<td>47.36</td>
<td>47.85</td>
</tr>
<tr>
<td>Fe</td>
<td>4.26</td>
<td>4.61</td>
<td>4.87</td>
<td>4.78</td>
<td>4.12</td>
<td>3.95</td>
<td>3.99</td>
<td>3.89</td>
<td>3.83</td>
<td>5.01</td>
<td>4.87</td>
<td>4.92</td>
</tr>
<tr>
<td>S</td>
<td>33.44</td>
<td>33.38</td>
<td>33.91</td>
<td>34.01</td>
<td>33.46</td>
<td>33.44</td>
<td>33.24</td>
<td>33.30</td>
<td>33.63</td>
<td>33.12</td>
<td>33.63</td>
<td>33.52</td>
</tr>
<tr>
<td>Total</td>
<td>98.84</td>
<td>99.36</td>
<td>100.12</td>
<td>100.27</td>
<td>98.76</td>
<td>98.79</td>
<td>98.78</td>
<td>98.55</td>
<td>99.75</td>
<td>98.81</td>
<td>99.39</td>
<td>99.39</td>
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<td>a.p.f.u.##</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Zn</td>
<td>0.718</td>
<td>0.698</td>
<td>0.686</td>
<td>0.676</td>
<td>0.717</td>
<td>0.725</td>
<td>0.705</td>
<td>0.703</td>
<td>0.727</td>
<td>0.691</td>
<td>0.687</td>
<td>0.696</td>
</tr>
<tr>
<td>Mn</td>
<td>0.211</td>
<td>0.233</td>
<td>0.236</td>
<td>0.247</td>
<td>0.212</td>
<td>0.209</td>
<td>0.236</td>
<td>0.233</td>
<td>0.211</td>
<td>0.234</td>
<td>0.234</td>
<td>0.226</td>
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<tr>
<td>Fe</td>
<td>0.073</td>
<td>0.078</td>
<td>0.082</td>
<td>0.080</td>
<td>0.071</td>
<td>0.067</td>
<td>0.068</td>
<td>0.066</td>
<td>0.065</td>
<td>0.086</td>
<td>0.083</td>
<td>0.084</td>
</tr>
<tr>
<td>Σ</td>
<td>1.002</td>
<td>1.009</td>
<td>1.004</td>
<td>1.003</td>
<td>1.001</td>
<td>1.001</td>
<td>1.007</td>
<td>1.003</td>
<td>1.003</td>
<td>1.011</td>
<td>1.004</td>
<td>1.006</td>
</tr>
<tr>
<td>S</td>
<td>0.998</td>
<td>0.991</td>
<td>0.996</td>
<td>0.997</td>
<td>1.000</td>
<td>0.999</td>
<td>0.993</td>
<td>0.997</td>
<td>0.997</td>
<td>0.989</td>
<td>0.996</td>
<td>0.994</td>
</tr>
</tbody>
</table>

*Ag, Al, Mg, Sb and Si were also analysed and were not detected or are <0.1 wt.%

## The atomic proportions are based on 2 atoms per formula unit (a.p.f.u.)
analyses were valuable in confirming their optical identification and showed that Mn is a common minor element in all of these phases.

Discussion

The detailed petrographic and mineral chemistry investigation of the Mn-rich ore of the Santo Toribio deposit demonstrated that it is a polymetallic system with Fe, Zn, Cu, Pb, Mn, Sn, Ag, S and Sb-bearing minerals. Two major stages of ore formation were identified: the early one is characterized by the stability of alabandite and the later one by partial dissolution of alabandite and precipitation of rhodochrosite. The compositional zoning of alabandite, with Fe+Sb replacing Mn, indicates that the physicochemical conditions oscillated during its deposition. During the early stage, $f_S$ must have been high to allow the stabilization of alabandite relative to rhodochrosite, according to reaction 1:

$$2\text{MnS} + 2\text{CO}_2 + \text{O}_2 = 2\text{MnCO}_3 + \text{S}_2$$

and according to Krauskopf and Bird (1995).

In addition, Sb concentration was probably relatively high as inferred by its incorporation in alabandite zones and the precipitation of a silver antimonide (miargyrite). In the second stage, the physicochemical conditions changed and the CO$_2$/S ratio increased, causing deposition of abundant rhodochrosite that partially replaced alabandite (reaction 1). Significantly, Ag-, Pb- and Sb-bearing minerals (i.e. miargyrite, rammohrite and stibnite) are more common in rhodochrosite layers and patches.

Epithermal, Mn-rich polymetallic veins with a high Ag/Au ratio, similar to the samples investigated here, may have been formed by high-salinity fluids (Henley, 1985; Gammons and Seward, 1996), which are favourable for transporting Mn and Ag as Cl complexes. In these systems, the Ag/Au ratio is high because Au does not form stable chloride complexes (Gammons and Williams-Jones, 1995). In high-salinity fluids, at temperatures lower than 300°C, rhodochrosite may have precipitated due to an abrupt decrease in H$^+$ and/or Cl$^-$ concentration, which may be caused by boiling or dilution of the hydrothermal fluids (Gammons and Seward, 1996). These changes would also cause the precipitation of Ag, according to reaction 2:

$$\text{Ag}_2(\text{s}) + 2\text{Cl}^- + \text{H}^+ + \frac{1}{2}\text{O}_{2(g)} = \text{AgCl}_2^- + \frac{1}{2}\text{H}_2\text{O}$$

(Gammons and Williams-Jones, 1995), which explains the occurrence of Ag-bearing minerals associated with rhodochrosite.

Implications for exploration

The geological setting and the mineral assemblage of the Mn-rich ore of the Santo Toribio deposit are similar to the subset of low-sulphidation epithermal deposits, defined as “intermediate sulphidation-state” (Hedenquist et al., 2000). The Santo Toribio deposits and the intermediate sulphidation-state deposits are hosted by andesite-rhyodacite-rhyolitic sequences, are Ag-, Mn- and base metal-rich, have high Ag/Au ratio, and occur in belts that host high-sulphidation deposits. Because both high-sulphidation and intermediate-sulphidation-state epithermal deposits are commonly associated with porphyry deposits (e.g. Lepanto District; Hedenquist et al., 2000), the Quiruvilva-Pierina subbelt, which has traditionally been explored for epithermal Au-Ag deposits, should also be explored for porphyry Cu deposits.

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