ABSTRACT

Manganese oxide mineralization on the eastern coast of Baja California Sur is intimately related to the Neogene tectonic evolution of the Gulf of California. Manganese is closely associated with the Cu-Co-Zn mineralization of the Boleo district and nearby deposits of Santa Rosalía region and Concepción peninsula. Trace element and rare earth element geochemistry of the manganese oxides provides clear evidence of a hydrothermal origin and excludes the hydrogenous nature for these deposits. Lead isotope data suggest that metal sources for the manganese mineralization along the eastern coast Baja California Sur are mostly the Miocene Andesite of Sierra Santa Lucía volcanics and the Peninsular Ranges batholith rocks. The strontium isotope data indicate that the mineralizing fluids involved in the manganese mineralization from Boleo district resulted from the interaction of two end-members: (1) the Sierra Santa Lucía volcanic rocks and (2) the gypsum member of the Boleo Formation. The geological observations and the available isotope and geochronological data suggest a southward migration of the hydrothermal processes in response to the evolving tectonic context of the opening of the Gulf of California.

Keywords: manganese oxide, mineralization, rare earth elements, Pb-Sr isotopes, REE geochemistry.

RESUMEN

La mineralización de óxidos de manganeso de la porción oriental de Baja California Sur está íntimamente relacionada a la evolución tectónica del Golfo de California durante el Neógeno. Estos depósitos de manganeso están a su vez relacionados a la mineralización de Cu-Co-Zn del distrito El Boleo y otros sitios en los alrededores de Santa Rosalía y la Península de Concepción. La geoquímica de elementos traza y elementos de las tierras raras de los óxidos de manganeso muestra claramente un origen hidrotermal y excluye la naturaleza hidrogénica para estos depósitos. Los análisis de isótopos de plomo sugieren que las fuentes del manganeso pudieron haber sido las rocas volcánicas del Mioceno de la
INTRODUCTION

The tectonic evolution of the Gulf of California has produced several isolated basins, magmatism, volcanism, and hydrothermal activity along the gulf (Karig and Jensky, 1972; Atwater, 1989; Hausback, 1984; Sawlan and Smith, 1984; Lonsdale, 1989; Sawlan, 1991; Canet et al., 2005). Different occurrences and metal endowment are present in the Miocene to Pliocene (Au, Ag, Cu, Co, Zn, and Mn) and recent (Au, Ag, Cu, Zn, and Mn) mineral deposits in the eastern coast of Baja California Sur (Wilson and Rocha, 1955; González-Reyna, 1956; Terán-Ortega and Ávalos-Zermeño, 1993; Ochoa Landín et al., 2000; Prol-Ledesma et al., 2004; Conly et al., 2006, 2011; Rodríguez-Díaz et al., 2010). Among these metals, manganese is a key metal in these deposits because its usefulness to constrain metallogenic processes in space and time in the Baja California province.

Manganese oxide mineralization has been classified on the basis of mineralogy and geochemistry to constrain the depositional environments and the origin of the manganese deposits (Bonatti et al., 1972; Crerar et al., 1982; Nicholson, 1992; Roy, 1992). In general, manganese oxides are deposited in a variety of continental and marine environments as a consequence of hydrogenetic, supergene, and hydrothermal processes (Nicholson, 1992; Roy, 1992).

The purpose of this study is to trace the metal sources and examine the geochemistry of the mineralizing fluids involved during the manganese oxide precipitation. In order to elucidate the genesis of the manganese oxide mineralization, the present study uses Pb and Sr isotopic systematics to trace the metal sources involved in the mineralization. Also, the geochemistry of rare earth elements (REE) and other trace elements in the manganese mineralization is employed to characterize the genesis of the manganese mineralization present at the different mineralized mantos in the Boleo district and surroundings areas.

GEOLOGICAL SETTING

The Gulf of California formed as a result of continental rifting and slow transfer of the Baja California Peninsula from North America to the Pacific plate (Lonsdale, 1989; Spencer and Normark, 1989). The Santa Rosalía basin is an incipient rift basin, formed as a result of northwest- to southeast-trending pre-Gulf continental rifting during Late Miocene (Karig and Jensky, 1972; Stock and Hodges, 1989). This basin hosts the Cu-Co-Zn mineralization from the Boleo district as well as the manganese oxide deposits of nearby areas. The Santa Rosalía basin is bounded to the north-northwest by the Pliocene-Quaternary Tres Virgenes volcanic field and La Reforma caldera, and to the west-southwest by the 24–12 Ma Andesite of Sierra Santa Lucía (ASL) volcanic rocks, and to the east by the Gulf of California (Figure 1).

The oldest rock in the region is a biotite quartz-monzonite dated at 91.2 ± 2.1 Ma (Schmidt, 1975). This intrusive rock corresponds to the southeastern extension of the Mesozoic Peninsular Ranges batholith complex that represents the crystalline basement of Baja California (Gastil et al., 1975). The ASL suite unconformably lies over the biotite quartz-monzonite intrusive. It is more than 1 km thick and mostly consists of andesite, basaltic andesite and basalt flows, tufts, breccias, agglomerates and tuffaceous sandstones, predominantly of andesitic composition (Sawlan and Smith, 1984). K-Ar geochronology in the ASL volcanic rocks from Santa Rosalía region yielded ages between 24 and 13 Ma (Sawlan and Smith, 1984; Conly et al., 2005). The ASL suite is the result of the oblique subduction of the Farallon-Guadalupe plate under the North American plate along the western margin of Baja California (Atwater, 1989; Lonsdale, 1989; Stock and Hodges, 1989). These volcanic rocks are medium-K calc-alkaline and are widely exposed through the Boleo district and the Concepción Peninsula (Sawlan and Smith, 1984). The final stage of the arc volcanism is represented by the Santa Rosalía dacite unit, which consists of lavas, erupted between 13 and 12 Ma (Conly et al., 2005).

Subsequent volcanic activity records the transition from arc to rift volcanism associated with the initial opening of the Gulf of California (Conly, 2003; Conly et al., 2005). The rift-related suite was unconformably emplaced over the ASL volcanic rocks (Figure 2), and consists of three volcanic groups (Conly et al., 2005): 1) the 11–9 Ma lava flows of the Boleo basalts and the basaltic andesites; 2) El
Morro tuff, a 9–8 Ma felsic lapilli tuff to ignimbrite unit; and 3) the 9.5 to 7.7 Ma high-K andesitic lava flow of the Cerro San Lucas unit.

The Miocene ASL and rift-related volcanic rocks in the Santa Rosalía region are overlain by a series of sedimentary marine and non-marine formations including the Boleo Formation (Wilson and Rocha, 1955). The thickness of the Boleo Formation varies from 250 to 350 m, and is divided into four members: the basal conglomerate member, the limestone member followed by the gypsum member, and the upper clastic member (Figure 2; Wilson and Rocha, 1955). The basal conglomerate has a maximum thickness of 10 m, and is composed of angular to sub-angular boulders and pebbles derived from the ASL volcanic rocks, supported by a brownish sandy matrix (Wilson and Rocha, 1955); the basal conglomerate is directly overlain by 4 m-thick, red-
Manganese oxide mineralization in the Boleo region and Concepción Peninsula, Baja California

**MANGANESE MINERALIZATION IN THE BOLEO REGION**

**Boleo deposits**

The mineralization in the Boleo district consists of laterally extensive and stratiform ore bodies (known as mantos) of disseminated Cu-Co-Zn sulfides and manganese oxides, constrained within the fine-grained facies at the base of each cycle of the Boleo Formation (Figure 2; Wilson and Rocha, 1955; Ochoa-Landin, 1998; Conly, 2003). The mantos are numbered from 4 to 0, with manto 4 being the lowest in the stratigraphic column and manto 0 the uppermost (Wilson and Rocha, 1955).

Manto 4 is commonly related to faults that affected the ASL rocks; these fault zones show evidence of Cu and Mn mineralization (Ochoa-Landin 1998). Manto 4 occurs either above the limestone or the ASL rocks, within the fine-grained facies of the first sedimentary cycle of the Boleo formation, and consists of 1 m-thick laminar calcareous mudstone overlain by a 2 m-thick monomictic breccia with high Mn and Fe oxide content (Wilson and Rocha, 1955). Locally, the Mn and Fe oxides are mixed with jasper that replaced the limestone. The Mn-oxide mineralization in manto 4 occurs directly over the ASL volcanic rocks, and shows dendritic textures within the fine-grained sediments of the Boleo Formation.

Manto 3 is the more extensive and can be continuously traced over an area of 6 × 3 km. The fine-grained facies that host manto 3 consist of a 0.25 to 0.5 m-thick interval of calcareous mudstone at the bottom and a 1 to 20 m-thick fine-laminar claystone-siltstone interval at the top. The later contains a chaotic breccia zone with claystone-siltstone fragments ranging in diameter from 1 to 5 cm, in a claystone-siltstone matrix. The mineralization occurs along the laminar structures of the brecciated fragments and rarely in the matrix (Ochoa-Landin, 1998); however, some authors determined that sulfide mineralization is present in both the fragments and matrix (Bailes et al., 2001; Conly, 2003; Conly et al., 2006; Conly et al., 2011). This manto is important in the district because of its high content of copper minerals, including chalcocite, covellite, chalcopryrite, bornite, native copper, and minor cuprite (Wilson and Rocha, 1955; Ochoa-Landin, 1998). Manganese oxides are present within and above the copper-rich zone, usually as thin horizons along with chrysocolla veinlets, and as small nodules. Locally, the manganese oxide mineralization in manto 3 occurs as nodules, with diameter ranging from 8 to 15 cm, hosted within the fine-grained sediments.

Manto 2 is less extensive, and is also hosted within the fine-grained sediments. The base of the sedimentary sequence consists of a 1 m-thick mudstone, and a 2.5 m-thick breccia zone with siltstone and sandstone fragments in a silty sandstone matrix. The mineralization consists of copper sulfides, mostly chalcocite, along with disseminated pyrite. The manganese content is usually higher at the top...
of the mineralized manto as seen in manto 3. Many of the ores in manto 2 are manganiferous and ferruginous, and are associated with NW-SE silicified structures (Wilson and Rocha, 1955).

A few manganiferous horizons with small quantities of copper are found between mantos 1 and 2, and between mantos 2 and 3. These horizons are commonly discontinuous, thin, and in general, low-grade (Wilson and Rocha, 1955). Manto 1 is the second most important manto after manto 3 as a producer, with ore grade ~4.5% Cu. This manto is the most extensive in the district, but has been productive only in the southeastern portion of the district (Wilson and Rocha, 1955). Manto 0 is the least important of the mantos in the Boleo district. It is commonly manganiferous and ferruginous, and the copper grade is as high as 1% Cu (Wilson and Rocha, 1955).

**Neptuno area**

The manganese mineralization in Neptuno area correlates with manto 4. It is mostly located near the base of the first sedimentary cycle of the Boleo Formation and is hosted by siltstones and sandstones. These manganese oxide bodies were deposited in lenticular basins (10–15 m) with depths of ~2 m and directly on top of the ASL rocks. These lenticular basins were geomorphic traps that favored the preservation of manganese oxides. In these basins, the Mn and Fe oxides show a strong zonation similar to that observed at the Lucifer deposit. Other manganese oxide outcrops are located directly above the limestone, restricted to N–S fault-controlled depressions. Some manganese oxides with botryoidal morphology are intercalated within the fine-grained sediments below manto 3. In addition to the Mn mineralization in manto 4, the Neptuno area also has evidence of mineralization corresponding to manto 3 just a few meters above manto 4 (Wilson and Rocha, 1955). The mineralization in manto 3 consists of a thin horizon less than 30 cm thick, hosted within claystone-siltstones of the sedimentary cycle 2.

**Lucifer deposit**

The Lucifer manganese deposit is a stratiform manto deposit hosted within the first sedimentary cycle of the Boleo Formation (manto 4, Figure 2); however, 1 to 5 mm wide manganese oxide veinlets, filling a NW–SE fracture that crosscuts a weakly argillized zone in the ASL rocks has been pointed out by Freiberg (1983). The lower zone of
the Lucifer deposit is composed of a fine-grained sandstone sequence that overlies the limestone member. It contains thin manganese oxide lenses of about 40 cm thickness interbedded within the fine-grained sequence (Freiberg, 1983). These manganese oxide horizons mostly consist of pyrolusite and cryptomelane, and are crosscut by 2 to 5 mm thick silica veins, and are overlain by a 10 m-thick horizon of chaotic breccia, containing angular manganese oxide fragments composed by pyrolusite, cryptomelane, and to todorokite. The angular fragments (1 to 5 cm in diameter) represent around 30% of the horizon and are supported in a matrix of Mn oxide. This unit is overlain by a 5 m thick horizon with a brecciated lens composed of angular manganese oxide fragments of similar composition, but with minor content of Fe oxides (hematite and goethite), and jasper fragments, all ranging from 5 to 15 cm in diameter. This lens constitutes the richest manganese ore in the Lucifer deposit, with about 40% Mn. This horizon is overlain by other brecciated lenses, which are massive bodies composed mainly of brecciated jasper. The jasper bodies contain Fe oxides such as goethite and hematite, and are overlain by a breccia with jasper fragments and minor Mn oxide fragments, both ranging from 5 to 20 cm in diameter, supported by a manganese oxide and jasper matrix. The distal facies of the main Mn orebodies in the Lucifer deposit have minor manganese mineralization within fine-grained sediments. The incipient Mn mineralization consists of thin manganese oxide horizons (10–15 cm thick), associated with clay that shows load structures caused by the boulders and pebbles of the conglomerate member.

**MANGANESE MINERALIZATION IN THE CONCEPCIÓN PENINSULA**

Several localities with manganese oxide mineralization occur along the Concepción Peninsula to the southern part of the Mencenares volcanic field (Figure 1). The manganese mineralization is hosted by volcanic and volcanoclastic rocks, and is constrained by NW-SE fault systems, similarly as in the Santa Rosalía region.

The Gavilán deposit is located at the northeastern tip of the Concepción Peninsula, 15 km east of Mulegé (Figure 1). The hosting rocks in Concepción Peninsula are part of the upper Oligocene to middle Miocene Comondú Group (Hausback, 1984). These volcanic rocks essentially belong to the same volcanic episode that formed the ASL rocks (Sawlan and Smith, 1984). Several name discrepancies exist for these Oligocene-Miocene volcanic rocks (Umhoefer et al., 2001, and references therein). In this work, the nomenclature used for the volcanic rocks from the Concepción Peninsula is from Hausback (1984), since some of the formations that host the manganese mineralization are time constrained.

The manganese mineralization is hosted by andesitic-basaltic lavas of the Pilares Formation from the upper Oligocene to middle Miocene Comondú Group (Camprubi et al., 2008), and consists of a series of NW–SE-oriented manganese oxide veins, which crosscut highly fractured volcanic flows of this formation (Wilson and Veytia, 1949; Noble, 1950). Two types of veins can be distinguished: (1) veins with massive or laminated manganese oxides, and (2) laminated veins with dolomite and quartz that might contain minor manganese oxides (Camprubi et al., 2008). These veins are separated between 2 to 3 m (Wilson and Veytia, 1949), and, in most cases, they are 1 to 10 cm thick, although, some can exceed 0.5 m along fault zones. Also, the manganese mineralization occurs as stockwork with veinlets 1–12 cm thick consisting of pyrolusite with minor coronadite and romanechite, along with dolomite, barite, and vanadinite (Camprubi et al., 2008). The manganese oxides also occurs as breccia matrix; the fragments consist of basaltic and basaltic-andesite lavas with an average diameter around 10 cm. The matrix assemblage is composed by coronadite and minor pyrolusite, and dolomite (Camprubi et al., 2008).

Other less important manganese deposits are present along the Concepción Peninsula (Guadalupe, Minitas, Pilares, Trinidad, Santa Teresa, Azteca mine), and most of them share similar geological features. The manganese mineralization mostly consists of pyrolusite and romanechite, and grades between 4 and 42 wt% Mn. It occurs generally in NW-SE veins systems, hosted in volcanic and volcanoclastic rocks from the Comondú Group (Camprubi et al., 2008). Only two manganese deposits (Santa Rosa and San Juanico mines) show slight differences. The mineralization at the Santa Rosa mine, located south of the Concepción Peninsula, occurs along N-S vertical veins hosted in Pliocene alluvial conglomerates, although the mineralization also replaces the matrix of the same conglomerates (Camprubi et al., 2008; Rodíguez-Díaz et al., 2010). The manganese mineralogy consists of botzoidal romanechite or coronadite, along with opal and phanerocrystalline barite. San Juanico mine is located south of the Concepción Peninsula near Cerro Mencenares volcanic field. The mineralization is related to fault zones within the Comondú Group volcanic rocks and Pliocene limestones of the Inferno Formation, and consists of pyrolusite and romanechite, with Fe oxides and quartz (Camprubi et al., 2008).

**ANALYTICAL PROCEDURES**

**Major and trace elements**

Manganese oxides were analyzed for major elements (Mn, Cu, Fe) and some trace elements, including the rare earth elements (REE). For the analysis, pure manganese oxide samples were digested using HClO₄ at around 100°C for a few hours, and then the solutions were evaporated to dryness. This step was repeated three times in order to ensure total digestion. Subsequently, the samples were treated with
Analysis were performed with an Elan DRC-II inductively coupled plasma – mass spectrometer (ICP-MS) system and a Perkin-Elmer inductively coupled plasma – optical emission spectrometer (ICP-OES) model Optima 4200 DV. Results for the Boleo district samples are shown in Tables 1 and 2, along with data for the Neptuno, Lucifer and Gavilán manganese deposits reported by Del Rio Salas et al. (2008).

Whole rock powdered samples were digested using Savillex teflon containers in a 5:1 mixture of HF and HNO₃. The samples were evaporated to dryness and treated with HClO₄. After evaporation, concentrated HNO₃ was added to the samples and evaporated to dryness. The samples were treated with 8N HCl and evaporated to dryness. Some steps described above were repeated to ensure total digestion of the samples. Powders from micro-drilled manganese ore were subjected to the same digestion procedures.

Notes: (na) Not analyzed; (nd) below detection limit; (-) not calculated; (*) manganese oxide vein within the Andesite of Sierra Santa Lucía (ASL) rocks; (º) Manganese oxide horizon in sediments from the base of Gloria Formation; (j) Jasperoid. Sources (1) Del Rio Salas et al. (2008); (2) present study.
Manganese oxide mineralization in the Boleo region and Concepción Peninsula, Baja California

samples were extracted using lead-free tungsten-carbide dental drill bit. The powders were digested using the same procedure described above.

Sr and Pb were separated from the resulting solutions using a chromatographic method following the procedure described by Thibodeau et al. (2007). Lead isotope analyses were conducted using a GV Instruments multicollector–inductively coupled plasma – mass spectrometer (MC-ICP-MS) according to the methods discussed in Thibodeau et al. (2007). Analysis of NBS-981 standard produced the following results: 206Pb/204Pb = 16.9405 (± 0.0029 2σ), 207Pb/204Pb = 15.4963 (± 0.0034 2σ), and 208Pb/204Pb = 36.7219 (± 0.0099 2σ).

The strontium solution separates were loaded on tantalum filaments with Ta gel to enhance ionization following the procedure in Chesley et al. (2002). The isotopic analyses were performed by negative thermal ionization mass spectrometry (N-TIMS) using a VG 54 mass spectrometer, according to Chesley et al. (2002). Analytical uncertainties (2σ) are 87Sr/86Sr = 0.0011% or better.

The obtained lead and strontium isotope data for the manganese oxide mineralization in the Boleo, Neptuno, Lucifer, and Gavilán deposits are shown in Table 3.

RESULTS

Major and trace elements in manganese oxides

In general, the manganese concentration in manto 4 is greater than the concentrations in mantos 3 and 2 (1.2 to 52.7 wt%), with an average concentration of 25.9 wt%. However, copper concentrations in the manganese oxides are lower than those of mantos 3 and 2, ranging from 0.2 to 8.4 wt%. Zinc and cobalt concentrations range from 0.4 to 1.7 wt%, and 32 to 1600 ppm, respectively.

The manganese concentrations from manto 3 range from 0.8 to 19.7 wt%. The copper concentrations in the manganese oxides are higher than in the rest of the mantos and range from 0.03 to 68 wt%. The zinc and cobalt concentrations are higher than concentrations in manto 4, and range from 0.2 to 1.6 wt% and 393 to 4600 ppm, respectively. Mantos 3A and 2 show lower manganese concentrations (~2.5 wt%), and exhibit lower copper content (5.5 and 13.4 wt%, respectively), and higher cobalt and zinc concentrations than manto 3 and 4 (Table 1).

The REE abundances, normalized to the North American shale composite (NASC) from Gromet et al. (1984), are shown in Figure 3. The shaded area in Figure 3a represents the REE-normalized trend for the manganese oxides from the different mineralized mantos in the Boleo district. The NASC-normalized La/Sm and Gd/Yb ratios (Table 2) are variable, yielding an average of 2.9 and 1.1, respectively. In general the REE spectrum is relatively flat (Figure 3), yielding an average (La/Yb), ratio of 2.4 (Table 2), and is characterized by a positive Eu anomaly.

Pb and Sr isotopes

The lead isotope ratios of the manganese mineralization from manto 4 of the Boleo district are 206Pb/204Pb = 18.726 to 18.833, 207Pb/204Pb = 15.589 to 15.595, and 208Pb/204Pb = 38.471 to 38.499. The Pb isotope values for the manganese mineralization from manto 3 are 206Pb/204Pb = 18.708 to 18.800, 207Pb/204Pb = 15.588 to 15.598, and 208Pb/204Pb = 38.452 to 38.511. The lead data in the manganese oxides from manto 3A is 206Pb/204Pb = 18.751, 207Pb/204Pb = 15.591 to 15.593, 208Pb/204Pb = 38.483 to 38.494. A single manganese oxide from manto 2 has 206Pb/204Pb = 18.721, 207Pb/204Pb = 15.589, 208Pb/204Pb = 38.469.

The lead isotope analysis of manganese oxide from the Lucifer deposit yielded 206Pb/204Pb = 18.743 to 18.788, 207Pb/204Pb = 15.597 to 15.606, and 208Pb/204Pb = 38.512 to 38.590. A single lead data of the ASL rocks and a manganese oxide vein from the Gavilán deposit have 206Pb/204Pb = 18.621, 207Pb/204Pb = 15.584, and 208Pb/204Pb = 38.432, and 206Pb/204Pb = 18.612, 207Pb/204Pb = 15.579, 208Pb/204Pb = 38.421, respectively.

The Sr isotope data for the manganese oxide mineralization from the Boleo district mantos range from 0.7043 to 0.7067. The strontium isotope data for manganese mineralization from Lucifer deposit range from 0.7050 to 0.7052. The single data for the Neptuno and Gavilán deposits are 0.7067 and 0.7052, respectively.

DISCUSSION

Manganese mineralization and hydrothermal activity

In the Boleo district, the NW-SE structures constituted by manganese oxides and copper silicates crosscut the Andesite of Sierra Santa Lucía (ASL) rocks. Manganese oxide mineralization is also related to the NW-SE structures crosscutting the ASL volcanic rocks in the Lucifer area (Del Rio Salas et al., 2008). The NW-SE structures served as conduits for the ascent of the mineralizing fluids that were discharged into the Santa Rosalia basin. The fact that the mineralizing fluids ascended through these structures is inferred by the juxtaposition of high-grade Cu ± Co zones and localized discordant to stratabound zones of pervasive Mn-Fe-Si alteration (Conly et al., 2006).

Equilibration temperatures using the quartz-pyrolusite geothermometer from Zheng (1991) produced a range of temperatures between 18 and 118 °C for the manganese oxide mineralization in the different Boleo mantos (Conly, 2003; Conly et al., 2006). The mineralogy and geochemical data suggest a conservative mineralization temperature range between 70 and 118 °C.

Late Cenozoic hydrothermal activity along a 200 km segment of the eastern coast of Baja California Sur is evidenced by a series of mineralized localities (Figure 1). North of Tres Virgenes volcanic field, evidence of hydro-
thermal activity is recorded by the copper and manganese mineralization within the ASL rocks in the San Alberto prospect, and copper mineralization at the Caracol alteration zone (Figure 1). South of Boleo district, the hydrothermal activity is mostly represented by manganese deposits such as Mantitas, Gavilán, La Trinidad, Pilares, Las Minitas, Santa Teresa, and Azteca (Bustamante-García, 1999; Camprubí et al., 2008). Fluid inclusion microthermometry on barite samples from the Mn-Ba Santa Rosa deposit, southern Concepción Peninsula, yielded a temperature range between 97 and 160 °C, with two fluid inclusions population: (1) average \( T_h = 136.5 \) °C and 4.2 wt. % equivalent NaCl, and (2) average \( T_h = 136 \) °C and 11.4 wt. % equivalent NaCl (Rodríguez-Díaz et al., 2010).

The geothermal waters from springs and wells in and around the Tres Virgenes and La Reforma caldera fields located north of the Boleo district (Figure 1) are characterized by temperatures from 21 to 98 °C (Portugal et al., 2000). South of the Boleo district, localities such as Saquicismunde and Los Volcanes (Figure l), are current

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comment</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>ΣREE (La/Sm)</th>
<th>(Gd/Yb)</th>
<th>(La/Yb) Ref.</th>
</tr>
</thead>
</table>
Manganese oxide mineralization in the Boleo region and Concepción Peninsula, Baja California

Example of hydrothermal activity that may correspond in type to that responsible for the mineralization in the Boleo district. These geothermal emanations are geographically quite dispersed, and all of them share similar geological features such as the structural northwest-southeast control, the evidence of hydrothermal alteration, the occurrence within the Miocene volcanic or volcanoclastic rocks, and the low temperatures range between 38 to 94 ºC (Casarrubias and Gómez-López, 1994; Bustamante-García, 1999; Camprubí et al., 2008). Hydrothermal activity is also present along the western coast of Concepción Bay, between the Santispac and the Mapachitos areas (Figure 1). Temperatures of hydrothermal fluids range between 72 to 87 °C in submarine diffusive venting areas (Canet et al., 2005). Although some of these geothermal emanations occur within the shallow submarine environment (<20 m depth), they share similar features than those exposed above (Prol-Ledesma et al., 2004; Canet et al., 2005).

Mineralization age

The age of the Boleo Formation in the Santa Rosalía region has been previously constrained by Holt et al. (2000). The age was calculated using isotope data in conjunction with magnetostratigraphy, which is correlated with the geomagnetic polarity time scale. The most likely correlation

Table 3. Lead and strontium isotope data of samples from the Boleo district and adjacent deposits in Baja California Sur, Mexico.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Locality</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>$^{206}$Pb/$^{204}$Pb</th>
<th>$^{207}$Pb/$^{204}$Pb</th>
<th>$^{208}$Pb/$^{204}$Pb</th>
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<td>BO1007</td>
<td>Mn Manto 2</td>
<td>Boleo</td>
<td>-</td>
<td>18.721</td>
<td>15.589</td>
<td>38.469</td>
</tr>
<tr>
<td>95-231b</td>
<td>Mn Manto 3A</td>
<td>Boleo</td>
<td>-</td>
<td>18.751</td>
<td>15.593</td>
<td>38.494</td>
</tr>
<tr>
<td>95-231b(r)</td>
<td>Mn Manto 3A</td>
<td>Boleo</td>
<td>0.7063</td>
<td>18.751</td>
<td>15.591</td>
<td>38.483</td>
</tr>
<tr>
<td>95-231e</td>
<td>Mn Manto 3</td>
<td>Boleo</td>
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<td>18.720</td>
<td>15.593</td>
<td>38.481</td>
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<td>BO0107</td>
<td>Mn Manto 3</td>
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Note: (r) repeated sample; (-) not analyzed.
yielded an age of 7.09–6.93 Ma for the base and 6.27–6.14 Ma for the top of the Boleo Formation (Holt et al., 2000). The manganese mineralization in the Boleo deposit has yielded an age of 7.0 ± 0.2 Ma (Conly et al., 2011), which is stratigraphically and chronologically in agreement with the deposition age for the base of the Boleo Formation. Moreover, the manganese mineralization age is also in agreement with the geochronologic data for the underlying lithologic units in the Santa Rosalia region, which include the 24–13 Ma ASL, the 11–9 Ma Boleo basalts and Boleo basaltic andesites, and the 9–8 Ma El Morro tuff (Conly et al., 2005).

Moreover, the Gulf of California region has been subjected to intense volcanism and tectonic activity (Sawlan 1991). Around the Santa Rosalia region, Conly et al. (2005) reported K–Ar ages for the high-K andesites from Cerro San Lucas suite, which represents volcanic activity during the transition from arc- to rift magmatism between 9.5 and 7.7 Ma. Furthermore, Pallares et al. (2008) reported geochronologic data supporting the continuation of volcanic activity until the Pleistocene, following the end of the calc-alkaline volcanism northern Santa Rosalia region.

**Geochemistry of manganese oxides**

Discrimination diagrams for the origin of manganese deposits have been proposed on the basis of the cation-adsorption capacity of manganese oxides, considering the concentrations of specific trace elements present in manganese oxides. These discrimination diagrams have been used to distinguish between a hydrothermal (continental or marine) and a hydrogenous origin. The term hydrothermal refers to manganese oxides deposited directly from geothermal waters around hot springs and pools in continental environments or sedimentary exhalative manganese mineralization deposited in marine environments (Nicholson, 1992 and references therein). The term hydrogenous refers to deposits formed by slow precipitation or adsorption of dissolved components from seawater (Bonatti et al., 1972; Crerar et al., 1982; Nicholson, 1992).

Elements such as Ba, Cu, Ni, Co, Pb, Sr, V, and Zn are frequently found in hydrothermal manganese-rich systems (Nicholson, 1992). These elements are present in significant concentrations in the manganese oxide mineralization from Santa Rosalia region and Concepción Peninsula (Table 1). Hydrothermal oxides have lower Co, Cu, Ni, and Zn concentrations, relative to hydrogenous deposits (Nicholson 1992 and references therein); hence, high cobalt concentrations are indicative of marine environments (hydrogenous). Nicholson (1992) proposed discrimination diagram for hydrothermal and supergene manganese oxide deposits based on the abundance of trace elements (Figure 4); in this diagram the manganese oxides from marine and freshwater environments are included within the supergene field.

Previous studies in Lucifer deposit and the manganese oxides from Concepción Peninsula have documented the hydrothermal nature of the manganese oxide deposits (Canet et al., 2005; Camprubí et al., 2008; Del Rio Salas et al., 2008; Rodriguez-Diaz et al., 2010). In Figure 4, the manganese ore samples reported from Baja California Sur and those from the Boleo mantos plot within the hydrothermal field. In general, the samples from Concepción Peninsula are characterized by lower Co and Ni concentrations, like those from the Lucifer deposit (Figure 4). The data from the Neptuno area plot above the Lucifer and the Concepción Peninsula deposits, and are characterized by higher concentrations of Co and Ni. The Boleo manto samples are relatively richer in Co and Ni compared with the samples mentioned before. Within the Boleo samples, it is possible to notice a relative enrichment from manto 4 to manto 2. The trace element concentrations in the manganese oxides indicate a clear hydrothermal origin for all manganese deposits in the Santa Rosalia region and the Concepción Peninsula.

The shaded area in Figure 3a represents the NASC-normalized REE spectrum for the manganese oxides in the Boleo mantos. No particular difference is observed in the REE enrichment of the different mantos; the entire spectrum is relatively flat and displays a subtle enrichment of the light rare earth element (LREE) over the heavy rare earth element (HREE), as pointed out with the normalized La/Yb ratios, as well as the noticeable positive Eu anomaly. The normalized REE spectrum of the manganese mineralization from Neptuno area displays also a positive Eu anomaly with relatively flat trends, except for sample LF-46, which is the most enriched in the LREE relative to the NASC, as noticed by the high normalized La/Yb ratio (Table 2) (Del Rio Salas et al., 2008). The REE pattern of the manganese oxides from Lucifer deposit is flat (Figure 3c) as noticed by an average normalized La/Yb ratio of
2.0 (Table 2), and they signatures are characterized by the absence of either positive or negative Ce or Eu anomalies (Del Rio Salas et al., 2008).

The available REE data for the manganese oxides from Concepción Peninsula are presented in Figure 3d. A sample from the Gavilán deposit has REE concentrations that are lower than NASC, and a relatively flat REE pattern with an average normalized La/Yb of 0.9, and slightly negative Ce and Eu anomalies (Figure 3d) (Del Rio Salas et al., 2008). Figure 3d also shows the REE data from Santa Rosa manganese oxides, which is depleted in REE with respect to NASC, and has a relatively flat spectrum with slightly Ce and clear Eu negative anomalies (Figure 3d) (Rodríguez-Díaz et al., 2010). In general, the available REE data of the manganese oxides from Concepción Peninsula exhibit relatively flat patterns, characterized by slightly negative Ce and Eu anomalies.

Table 4 shows the average of the total REE abundances of various manganese oxide deposits of hydrothermal and hydrogenous nature. The total REE concentrations in hydrothermal deposits range from 45 to 648 ppm, whereas those for hydrogenous deposits range from 1208 to 1918 ppm (Glásby et al., 1997; Miura and Hariya, 1997; Nath et al., 1992; Nath et al., 1997; Usui and Someya, 1997; Wiltshire et al., 1999). The average of the total REE for the Boleo mantos ranges from 50 to 270 ppm and produce an average of 215 ppm. The average total REE for the manganese oxides from Neptuno area is around 560 ppm; sample LF-46 is characterized by a total REE around 1900 ppm, and excluding this particular sample, the average of total REE is 220 ppm. The average total REE for Lucifer and the deposits in Concepción Peninsula ranges from 25 to 37 ppm.

Figure 3e shows the NASC-normalized REE patterns for manganese oxides from hydrogenous and hydrothermal deposits from Usui and Someya (1997). The pattern for the hydrogenous deposits is enriched relative to the NASC values, whereas the pattern for the hydrothermal deposits is either depleted or slightly enriched than NASC values. This figure also shows the spectrum for the average modern and fossil hydrothermal deposits from Usui and Someya (1997). In addition, this figure includes the average NASC-normalized REE spectra from the manganese deposits from the Boleo and adjacent areas, which are included within the hydrothermal field. The average REE patterns for the Lucifer and Santa Rosa deposits are the most depleted in REE and agree with the average modern hydrothermal deposits. The REE signature of the Gavilán deposit is located between the average modern and average fossil hydrothermal deposits. Finally, the REE signatures for the Boleo and Neptuno deposits are slightly more enriched in REE than the average fossil hydrothermal deposits, but still located within the hydrothermal field (Figure 3e).

In general, NASC-normalized REE patterns for the manganese mineralization around the Boleo district and Concepción Peninsula are relatively flat as noticed from the consistent normalized La/Sm, Gd/Yb, and La/Yb ratios. The REE patterns of the Boleo district and Neptuno area show middle REE enrichment (Figure 3a and 3b), which can be characteristic of hydrogenous manganese samples (Nath et al., 1992, 1997). Also, the REE patterns exhibit very distinctive positive Eu anomalies, which is a characteristic feature of modern hydrothermal deposits in the ocean (Hodkinson et al., 1994), as opposed to the REE signature of seawater, which exhibits a negative Ce anomaly and a slight enrichment of the HREE over the LREE (Douville et al., 1999). Although the mineralization in these deposits is not properly from hydrothermal activity in a marine environment, the Eu enrichment in the manganese ores can be explained by the presence of plagioclase in the fine-grained sediments derived from the ASL rocks. The mobility of Eu depends strongly on redox and temperature conditions (Michard et al., 1983), and Eu enrichment involves hot and reduced fluids, whereas Eu depletion involves cold and oxidizing fluids (Parr, 1992; Canet et al., 2005). Since each manto experienced such redox conditions, a positive Eu anomaly can be explained by the cyclical hydrothermal activity related to the formation of each manto. Moreover, these samples are located within the field of hydrothermal field deposits (Figure 3), and the hydrothermal nature is also confirmed by the total REE in Table 4.

The NASC-normalized REE patterns for the manganese ores from the Lucifer and the manganese deposits from Concepción Peninsula agree with the spectra of the average hydrothermal deposits (Usui and Someya 1997); only the average of total REE for the Gavilán deposit exhibits a subtle enrichment especially in the HREE relative to the average of modern hydrothermal deposits (Figure 3e). Hydrogenous manganese deposits are characterized by a positive Ce anomaly (Fleet, 1983), as a result of the oxidation of Ce3+ to Ce4+, which forms highly insoluble CeO2 in seawater (Elderfield and Greaves, 1981; Fleet, 1983; Nath et al., 1997; Canet et al., 2008). Conversely a negative Ce anomaly is characteristic of hydrothermal Fe-Mn deposits (Fleet, 1983). The slightly negative Eu could be explained by cold and oxidizing fluids (Parr, 1992), as previously reported for the recent Mn mineralization in Concepción Bay (Canet et al., 2005). Furthermore, the total REE content of these deposits confirms their hydrothermal nature when compared to other hydrothermal deposits in Table 4.

In summary, trace element and REE geochemistry in the manganese oxides from the Boleo district and Concepción peninsula, demonstrates the hydrothermal nature of the ores (Figures 3 and 4). The REE enrichments for the Boleo mantos and Neptuno mineralization can be explained by mixing of hydrothermal and hydrogenous sources or by supergene processes.

**Metal sources**

Lead and strontium isotope data for the Peninsular Ranges batholith and the volcanic rocks in Santa Rosalía
region, the Boleo conglomerate, and the sulfide and manganese oxide mineralization have been reported previously by Conly (2003) and Conly et al. (2005, 2006, and 2011). The present study contributes with Pb and Sr isotope data for the lithologic units and the manganese oxide mineralization have been reported previously by Conly (2003) and Conly (2005, 2006, and 2011). The lead isotope data for the manganese oxides from the Boleo district are located within the field of the ASL rocks; however there is a trend towards the Peninsular Ranges batholith rocks. This interpretation is supported by field observations along the Arroyo del Infierno in Lucifer area, where the Peninsular Ranges batholith is found underlying the ASL rocks; also, some ASL rocks contain xenoliths of the Peninsular Ranges batholith. In contrast, lead isotope data for the Boleo manganese oxides suggest negligible mixing processes between the ASL and batholith rocks, basically because the ASL rocks act as the basement in the Boleo district.

Lead isotope measurement of a single sample from the Gavilán deposit in Concepción Peninsula, indicate that the ASL rocks in that area are less radiogenic that those from the Santa Rosalia region (Figure 5a), suggesting slight isotopic differences for the sources involved in the genesis of the ASL rocks trend along Baja California (Figure 1). An alternative explanation for the less radiogenic nature of the ASL rocks in the Gavilán deposit is the possibility of the continuation of the regional isotope trend of the ASL rocks from the Boleo district; this is probably reflecting the less radiogenic nature of the underlying rocks along this seg-

### Table 4. Rare earth element average concentrations from hydrothermal and hydrogenous manganese oxide deposits, including those from Baja California.

<table>
<thead>
<tr>
<th>Locality</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
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<td>4.1</td>
<td>0.6</td>
<td>2.9</td>
<td>0.2</td>
<td>3.0</td>
<td>0.2</td>
<td>234.6</td>
<td>9</td>
</tr>
<tr>
<td>Boleo district - manto 4</td>
<td>87.5</td>
<td>129.1</td>
<td>6.2</td>
<td>27.8</td>
<td>5.2</td>
<td>2.5</td>
<td>4.4</td>
<td>0.7</td>
<td>5.1</td>
<td>1.1</td>
<td>3.9</td>
<td>0.5</td>
<td>3.8</td>
<td>0.5</td>
<td>278.4</td>
<td>9</td>
</tr>
<tr>
<td>Boleo district - Gloria Fm</td>
<td>63.4</td>
<td>99.9</td>
<td>10.1</td>
<td>34.5</td>
<td>6.1</td>
<td>3.6</td>
<td>7.9</td>
<td>0.4</td>
<td>6.8</td>
<td>0.6</td>
<td>5.0</td>
<td>0.3</td>
<td>5.0</td>
<td>0.3</td>
<td>243.8</td>
<td>9</td>
</tr>
</tbody>
</table>
The similarity of the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the manganese oxides and manto sulfides demonstrate that the fluids responsible for the Cu-Co-Zn mineralization are similar to those that precipitated the Mn oxides of the Boleo district, although significant differences are noted in the $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios suggesting a more radiogenic lead in the manganese oxides than in the manto sulfides (Conly et al. 2011). The slight shift to higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the Boleo manto sulfides is interpreted as the result of the interaction of Pb from basin seawater with ferromagnesian minerals from the arc-to-rift volcanic rocks and $^{206}\text{Pb}/^{207}\text{Pb}$-enriched seawater fluids that interacted with the Cretaceous quartz-monzonite basement (Conly et al. 2011). The higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the Boleo manganese mineralization...
suggest diagenetic alteration by sedimentary pore waters due to the interaction with Th-rich fluids (Conly et al., 2011). However, the new lead isotope data of the Boleo manganese oxides from the different mineralized mantos overlap the isotope fields for the ASL and Boleo Formation rocks, suggesting similarities in the lead isotope ratios, and therefore an alternative explanation is that the metals involved in the manganese oxide mineralization in the Boleo mantos were leached from the ASL and Boleo Formation rocks (Figures 5a and 5b). The lead isotope field for the Boleo manto sulfides partially overlaps those of the Boleo manganese oxides, the ALS, and the Boleo Formation rocks, which suggests a source with similar isotopic composition for the metals. The isotopic shift can be explained by modifications in the isotopic signature due to interactions with post-depositional fluids, which can be easily explained by the fine-grained nature (<50 μm) of the sulfide mineralization (Conly et al., 2006).

Figure 6 shows the strontium and lead isotope compositions of the lithologic units and manganese oxides. In general the 87Sr/86Sr and 206Pb/204Pb isotope ratios for the ASL rocks and the Peninsular Ranges batholith have a constrained range and form a restricted field, as oppose to the rift-related rocks, which are characterized by lower 87Sr/86Sr ratios and less radiogenic lead. The most elevated 87Sr/86Sr ratios belong to the gypsum member of the Boleo Formation, which clearly has an important component of seawater as indicated by the Sr isotope composition of seawater at the time of deposition around 7 Ma (Figure 6) (McArthur et al., 2001; Conly et al., 2011).

The manganese oxide mineralization from the Boleo district and surrounding areas is clearly located on a mixing trend between the high 87Sr/86Sr and low 206Pb/204Pb end-member and the low 87Sr/86Sr ASL and Peninsular Ranges batholith end-member (Figure 6). The elevated 87Sr/86Sr ratios in the manganese oxides from Boleo district indicate the incorporation of more radiogenic strontium in the mineralizing fluids, and could suggest an important involvement of seawater fluids during the formation of the mantos. The most probable explanation for the 87Sr/86Sr ratios is the interaction of the ascending fluids with the gypsum member located stratigraphically below the clastic sequence that hosts the mineralized mantos (Figure 2). The isotope field for the manganese oxides from Lucifer deposit is closer to the more radiogenic members of the ASL rocks and Peninsular Ranges batholith, suggesting that the involvement of seawater fluids during the mineralization processes was minimal.

The manganese oxides from the Gavilán deposit in Concepción Peninsula show 87Sr/86Sr similar to those from Lucifer deposit and a 206Pb/204Pb isotope ratio within the range of ASL rocks (Conly, 2003; Conly et al. 2005, 2006, and 2011) and the more radiogenic end-member of the rift-related rocks (Conly, 2003; Conly et al. 2005, 2006, and 2011) (Figure 6). The Sr isotope signature of the ASL rocks in Conception Peninsula is similar to that of the manganese oxide from Lucifer deposit; therefore, a minimal interaction with seawater is interpreted for the manganese oxide mineralizing fluids. The lead and strontium isotope signatures of the manganese oxides clearly shows that the rift-related volcanics are not the source of metals for the manganese mineralization, and that the ASL rocks undoubtedly act as the most important source, with a minor role of the Peninsular Ranges batholith rocks.

Manganese oxide mineralization and regional implication

The constraints on the genesis of the manganese oxides along the eastern coast of Baja California contributes to the understanding of metallogenetic processes during the proto-rift to rifting tectonics of the Gulf of Baja California. Hydrothermal activity and manganese oxide mineralization is recorded along a stretch of 200 km on the eastern coast from Lucifer deposit, located in the northwestern portion, to the Cerro Mencenares volcanic field, located in the southeastern portion (Figure 1).

The most reliable age for the manganese oxides from the Boleo district is obtained from a hydrothermal manganese-oxide-quartz vein hosted in manto 4, constrained to 7 Ma, which is within the range of the Boleo Formation deposition age (Conly et al., 2011). Lucifer deposit correlates with manto 4 of the Boleo district, and is considered to have been located within the margin zones of the basin when the Boleo Formation was deposited (Del Rio Salas et al., 2008). Therefore, on the basis of geological correlation...
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and fieldwork observations, a similar manganese oxide age (~7 Ma) is interpreted for the Lucifer deposit. This age is also consistent with the geochronological constraints for the 24–13 Ma volcanic rocks of Andesita of Sierra Santa Lucía (Sawlan and Smith, 1984; Conly et al., 2005) that is hosting manganese oxide veins underlying the Lucifer deposit.

In contrast, the southern manganese mineralization, such as those in Santa Rosa and Juanico, is constrained to Pliocene structures (González-Reyna, 1956; Terán-Ortega and Avalos-Zermeno, 1993; Umhoefer et al., 2002), therefore, the hydrothermal activity responsible for the manganese mineralization in this area is younger than the geochronologic data reported for the Boleo district by Conly et al. (2011). In addition to this, volcanic activity such as the Pliocene Mencenares volcanic center is reported to be coeval with the manganese mineralization (Bigioggero et al., 2011). In addition to this, volcanic activity such as the Pliocene Mencenares volcanic center is reported to be coeval with the manganese mineralization (Bigioggero et al., 1995), which suggests the migration of the mineralization activity to the south of the Boleo district, as evidenced also by the present day hydrothermal activity reported in Concepcion Bay by Prol-Ledesma et al. (2004).

The geological context, the hydrothermal activity, and constructive comments.

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CONCLUSIONS

The geological context, the hydrothermal activity, and the Mn mineralization in the Boleo district, in conjunction with the manganese deposits of the eastern coast of Baja California, confirm the strong relationship between metallogenetic processes and the evolution of the proto-rift to rifting tectonics of the Gulf of Baja California. The trace element concentrations in the manganese oxides from the Boleo mantos, in conjunction with those for the manganese mineralization from Lucifer, Neptuno, and the manganese deposits from Concepción Peninsula, demonstrate the hydrothermal origin and the exhalative nature for all manganese deposits reported in the present study. The REE geochemistry in the manganese oxides supports the hydrothermal nature and excludes the hydrothermal nature for the manganese oxides.

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