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Major, trace element and stable isotope composition of water and muds precipitated from the hot springs of Bolivia: Are the waters of the spring's potential ore forming fluids?

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ABSTRACT

The deposition of metal-rich black or reddish muds by many thermal springs in the Cordilleras and the Altiplano of Bolivia suggest that these geothermal waters may be related to those that once formed the world-class Bolivian tin, silver and gold mineralisation. The discharge temperatures of these springs are as high as 70 °C. According to $\delta^{18}O$, δD, tritium data and Ar/N_2 ratios these waters are predominantly of meteoric origin. Less than 10% of the discharging thermal water represents deep-seated metal-rich thermal brines of at least 530 °C according to carbon exchange between CO_2 and CH_4. These brines ascend along tectonic faults and mix with low-temperature meteoric water in surface-near aquifers. The meteoric component of the thermal water is recharged in the high Cordilleras with residence times exceeding 50 years. The chemical composition of the thermal water is dominated by the rather inefficient low-temperature leaching of the surface-near aquifer rocks by meteoric water. The small fraction of metal-rich hot deep-seated water is not able to increase the metal content of the water mix to a level sufficient to classify these thermal waters as ore-bearing. Surface-near leaching is supported, e.g., by the B/Li ratios of the spring water of the Western Cordillera and Caleras/Pulacayo in the Eastern Cordillera that correspond very closely to that of the easily leachable glassy inclusions of the outcropping andesitic lavas. The often remarkable metal content of the muds deposited by the springs originate from efficient scavenging of heavy metals by ferric oxyhydroxides. Under the given arid to semi-arid climate the muds are additionally enriched in metals by wind-transported dust. The present study does support a relation of the actual thermal waters with neither the classical subduction-related Upper Tertiary tin, silver and gold mineralisation nor the supposed younger Sb mineralisation of Bolivia.

1. Introduction and problem

The still debated relation between the actual geothermal water and those that once formed the Bolivian ore deposits is addressed by Barnes (1979) in his text book "Geochemistry of hydrothermal ore deposits" with the statement that: "*Unfortunately, the composition of the Bolivian hot springs is not available*". The assumption that the chemical and isotopic composition of the water of the Bolivian thermal springs and their hydrogeological setting resembles those that produced the world-class Bolivian tin, lead, zinc, antimony, silver and gold mineralisations is supported by the following observations:

(i) the thermal springs of Bolivia occur in the tin, lead/silver and antimony ore belts;
(ii) the deposition of black or reddish mud suggests the ongoing precipitation of sulphides and hydroxides from the thermal water of the springs (Lehrberger and Morteani, 1989);
(iii) the country rocks of some of the springs host veinlets of stibnite, cinnabarite, psilomelane, jarosite, opal, barite and sulphur (Ahlfeld, 1974);
(iv) the thermal water of the springs shows in some cases a remarkable As and W content (Risacher et al., 1984; Risacher and Fritz, 1991).

The classification of the Bolivian geothermal waters as potential ore-forming fluids is not questioned a priori by the fact that the discharge temperature of the Bolivian thermal springs seldom reach more than 70 °C and such low temperatures are rarely capable to leach and transport the necessary amounts of metals for significant

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ore deposition. In contrast, the equilibration of CO_2 and CH_4 with $\delta^{13}C_{CO2}$ values between −4‰ and −8‰ (PDB) and $\delta^{13}C_{CH4}$ values between −20.9‰ and −12.3‰ (PDB), respectively, indicates that some waters experienced temperatures of at least 530 °C at depth (Spiro et al., 1997). Geothermal drillings near the Laguna Colorada (Western Cordillera) revealed temperatures up to 260 °C at a depth of only 1800 m (Carrasco, 1977) 0.5–44% of He in the thermal waters of the Altiplano originates from the mantle. In the Eastern Cordillera the mantle He contribution goes up to 14% (Hoke et al., 1994) with the highest mantle He contents found in the area between Oruro and Potosí, i.e., in the central part of the tin–silver belt as defined by Ahlfeld (1967).

In the present paper the chemical and isotopic composition of the water, gases and deposited mud of selected thermal springs of the Cordillera Oriental, the Cordillera Occidental (Eastern and Western Cordillera) and the Altiplano is presented and the origin and ore-forming potential of the geothermal springs in the context of the regional hydrogeological setting is discussed. The importance of understanding the hydrogeology driving ore-forming processes is highlighted.

2. Geological setting

The Bolivian Andes consist of three contiguous N–S trending morphotectonic units which are, from west to east, the mountain range of the Cordillera Occidental, the flat Altiplano and the mountain range of the Cordillera Oriental. Fig. 1 shows a satellite image of the study area and the sampling locations of Ludington et al. (1975) by squares and ours by dots with attached sampling numbers.

The high mountain range of the Cordillera Occidental with elevations up to 6500 m is built by Late Miocene to Quaternary andesitic to dacitic lavas, ignimbrites and ash-flow tuffs that erupted in the course of underthrusting of the south American continental plate by the oceanic Nazca plate. The volcanic rocks overlay a thick sequence of Early Tertiary clastic sediments and evaporites (Margaritz et al., 1989; Mortimer and Rendic, 1975). No report of historic eruptive activity is known, although many of the stratovolcanos show active fumaroles.

The Cordillera Oriental is a polygenetic fold and thrust belt built of Paleozoic and Mesozoic marine shales and sandstones deposited on a basement of predominantly Precambrian age and intruded by Paleozoic to Miocene intrusives. Locally it is covered by Upper Miocene to Quaternary ignimbrites (Turner, 1972; Jezek et al., 1985; Strecker et al., 2007).

The volcanic rocks of the Cordillera Occidental and Cordillera Oriental build the western and eastern branch of the N–S trending Central Volcanic Zone (CVZ) (Thorpe, 1984; Thorpe et al., 1979). The two volcanic arcs converge in Bolivia at the southern end of the Altiplano and continue into Chile and Argentina. The CVZ is part of the Altiplano-Puna Volcanic Complex (APVC) (De Silva, 1989; De Silva et al., 2006). Geophysical data suggest the existence of a large magma body below the APVC at a depth of 10–20 km (Chmielowski and Zandt, 1999).

The Altiplano consists of a series of intramontaneous basins formed primarily during the Andean orogeny and containing a more than 15 km thick layer of clastic sediments intercalated by volcanic rocks and salt layers. The great salares (alkaline lakes) of Uyuni and Coipasa are Holocene remnants of large glacial lakes that covered the Altiplano during the Pleistocene. Besides the Salares de Uyuni and Coipasa more than 200 salares are known in the Altiplano (Ludington et al., 1975). Some of them are of actual or potential economic interest for their lithium and boron contents (Alonso and Viramonte, 1990). The Salar de Uyuni is one of the largest resources of lithium brines in the world. Boron and lithium contents in the rivers and thermal springs feeding the alkaline lakes can be as high as 244 and 105 mg/L, respectively (Ludington et al., 1975, Table B-8). Risacher et al. (1984) report 2300 ppm As and 20 ppm W in the Salar de Cachi that is found at the border of the Altiplano and the Cordillera Occidental.

The whole study area is characterised by a remarkable high heat flow. The Altiplano shows a variable heat flow ranging between 60 and 180 mW/m^2 and a temperature of about 200 °C at a depth of 10 km. Values ranging up to 180 mW/m^2 are either related to ascending fluids or to a shallow magma chamber (Hamza and Munoz, 1996; Myers et al., 1998; Springer and Förster, 1998). In the Cordillera Oriental and Occidental the heat flow is about 110 and 150 mW/m^2, respectively (Springer, 1999; Springer and Förster, 1998).

The Andes of Bolivia are one of the most famous metallogenetic areas of the world that offered many historical world-class Sn and Ag deposits such as those of the Cerro Rico de Potosí, Llallagua, Huanuni and Chojlla and offers now superb mining opportunities such as the San Bartolome and San Vincente silver–zinc mines and the San Cristobal silver–lead–zinc mine. The tin, gold, lead/zinc, antimony and copper ore belts are shown in Fig. 2. In the last years the economic interest in the ore deposits of Bolivia increased due to their enhanced governmental support.

In Bolivia the mineralisation started at the end of the Oligocene at around 26 Ma ago and continued into the Quaternary (Evernden et al., 1977). The subdivision of the Bolivian mineralisation into three different periods of 19–26 Ma, 9.7–12.5 Ma and <6.5 Ma by Evernden et al. (1977) is still debated. The actual stibnite deposition by thermal springs led Ahlfeld (1974) to the hypothesis that the stibnite mineralisation is younger and not cogenetic with the tin, gold and lead/zinc mineralisation. He considered the stibnite mineralisation as a late metallogenetic event of its own produced by magmatic fluids ascending at the end of the Andean orogenesis along deep faults.

According to Sillitoe (1972, 1976) the zonal distribution of metals in the Andes is related to a selective mobilisation of metals from the subducting oceanic slab. Lehmann (1990), Tistl (1985) and Schneider and Lehmann (1977) derived the mineralisation from metal-enriched crustal rocks. Lehrberger and Morteani (1989) and Lehrberger (1992) explained the Sb (Au, Ag, Sn) mineralisation of the Cordillera Oriental by mobilisation of metals from the black shales during the Hercynian and Andean tectonic–orogenic cycles.

The thermal springs of Bolivia occur predominantly in valleys which mostly coincide with tectonic lineaments along the border of the Cordillera Oriental and the Cordillera Occidental to the Altiplano. Reddish to black sediments precipitate in the vicinity the spring's quietly bubbling outlets due to the exsolution of CO_2. Only in the area of the Laguna Colorada (Cordillera Occidental) a forceful ejection of steam and water as geysers occurs. In some cases travertine deposits are found close to the geothermal springs.

3. Sampling

The locations of the sampled rivers, springs, sinters and muds found at the outlet of the springs are given in Figs. 1 and 2. Sample numbers and coordinates of the sampled thermal springs are given in Table 1.

Measurements of pH and Eh and water sampling were done as close as possible to the outlet of the thermal water. The colour of the associated muds varies from black to reddish over some dm distance from the outlet indicating a rapid change in the chemical composition of the water and mud in contact with air. Algae mats are either floating on the surface of the ponds or covering the muds. Consequently most mud samples contain variable amounts of organic substance.