## COMPOSICION ISOTOPICA DEL OXIGENO Y AZUFRE EN ROCAS CON ALTERACION HIDROTERMAL Y DEPOSITOS DE YESO EN EL DISTRITO MINERO EL LACO, NORTE DE CHILE

# OXYGEN AND SULFUR ISOTOPES IN HYDROTHERMALLY ALTERED ROCKS AND GYPSUM DEPOSITS AT EL LACO MINING DISTRICT, NORTHERN CHILE

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#### ABSTRACT nonudinal being biw

El Laco iron district, located in the Andes of northern Chile, is spatially and genetically related to an andesitic strato-volcano, consisting of magmatic iron ore emplaced as intrusive (dyke, dome) and extrusive (magnetite flows, pyroclastic deposits) ore bodies. The iron ores were emplaced around the volcanic edifice during the volcanic evolution. At the waning stage of volcanic activity the district was affected by extensive hydrothermal alteration producing silicification, advanced argillic alteration, hydrothermal breccias and exhalative deposits of gypsum. The isotopic composition of sulfur in the gypsum is consistent with an hypogene origin and sulfur being derived from a magmatic source.

The isotopic composition of oxygen in magnetite, unaltered and altered rocks, and hydrothermal quartz, shows that, compared with the unaltered rock, magnetite is depleted in <sup>18</sup>O, whereas the altered rocks and hydrothermal quartz display <sup>18</sup>O enrichment. These results are interpreted as the product of a hydrothermal system dominated by magmatic water, which became progressively enriched in <sup>18</sup>O by initial interaction with magnetite, and subsequent boiling and decrease of temperature.

## **GEOLOGIC SETTING**

El Laco mining district is located in the Andean Cordillera at 23°48'S latitude and 4500 m above sea level. The district is emplaced on the flanks of a recent strato-volcano along the present magmatic arc in the Andes. This volcanic edifice, dated at 2 Ma. (Gardeweg and Ramírez, 1985), consists of andesitic lava flows, breccias, tuffs and minor flows of dacitic composition (Henríquez and Martin, 1978). Magnetite-apatite iron ores and areas with strong hydrothermal alteration are concentrically distributed on the flanks of the volcanic structure (Fig. 1).

The magnetite-apatite iron ore bodies were originated by the intrusion - extrusion of an iron-rich magma consisting of magnetite-rich flows (lava and pyroclastic), dykes and subvolcanic domes (Henríquez and Martin, 1978), and locally of minor quartz-magnetite hydrothermal breccias. Ore mineralogy consists mainly of magnetite and minor apatite, hematite and clinopyroxene. Fission track studies in apatite (Maksaev et al., 1988) indicate an age of about 2 Ma for the ore, coincident with the age of the spatially related volcanic rocks.

The hydrothermally altered areas have anomalous gold contents, and they display features similar to those observed in epithermal ore districts (e.g. quartz veins, hydrothermal breccias).

#### ALTERATION

Two types of alteration pattern are recognized in the district, the first restricted to the margins of the intrusive iron ore bodies, is overprinted by hydrothermal alteration affecting large areas in the district. The mineralogy of the altered rocks was determined by X-ray diffraction, microprobe analyses and standard microscopy techniques.

The iron ore related alteration occurs as halos around the intrusive ore bodies. and as single minerals deposited in open spaces in the extrusive ores. These halos are about 20 m wide and are hosted in the andesitic rocks. They display a reddish color and mineralogically consist of acicular crystals of clinopyroxene (diopside), quartz and magnetite. Plagioclase, sanidine, low tridymite, quartz, diopside, rutile, natro-alunite and alunite crystals were deposited in cavities of the ores or on the surfaces of magnetite crystals during cooling of the magnetite flows. Calcite and scapolite appear as very thin encrustations. Ouartz, rutile, and alunite are commonly associated with primary, hydrothermally formed hematite crystals.

Local hydrothermal alteration is of widespread distribution in the district and exhibits a characteristic light color of the altered rocks, which contrasts with the dark unaltered andesites. Silicified vein structures and hydrothermal breccias are often present within the zones of hydrothermally altered rocks. Locally, there are exhalative gypsum deposits accumulated on the surface.

The exhalative deposits are restricted in extent and thickness and were deposited around several discrete centers in the district. They consist mainly of gypsum accumulations with subordinated alunite,



Fig. 1: Geology of the El Laco iron district, modified from Alfaro et al, 1988 (Internal report, Compañía Minera del Pacífico).

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jarosite, sulfur, cristobalite, tridymite and calcite. Sulfur is often present as cross-cutting veinlets in the gypsum.

Hydrothermal alteration of the volcanic rocks consists of silicification and "bleaching", with destruction of the original textures, grading outward to rocks with moderate or weak alteration. The degree and extent of the hydrothermal alteration exhibits a good correlation with the lithology and permeability, being the pyroclastic rocks those most strongly affected. The silicification of the rocks was originated by leaching in combination with deposition of silica from the hydrothermal solutions. Mineralogically, silicified rocks are characterized by quartz, tridymite, cristobalite, alunite and jarosite, and minor amounts of K-feldspar, anatase and some non identified iron sulfates and phosfates. Gypsum and sulfur occur as veinlets in the hydrothermally altered rocks. Rocks affected by argillic alteration are characterized by quartz, alunite, kaolinite, gypsum, cristobalite, potash alum, smectite, bassanite, pyrite and pyrophyllite. In the less altered volcanic rocks replacement of the pyroxene by chlorite and of plagioclase by sericite and clay minerals is observed. A hematite-epidote association is also common in the less altered rocks. The isotopic composition of S was determined in eight samples of gypsum and one of alunite (Fig. 2). Its  $\delta^{34}$ S varies between +6.8‰ and +12.4‰, contrasting with the  $\delta^{34}$ S range of pyrite (-3.5+2.4‰) contained in the volcanic rocks (Nystrom and Henríquez, in Henríquez, 1991).

The isotopic composition of oxygen, determined in rocks and silica of veins and hydrothermal breccias, displays  $\delta^{18}$ 0 values in the range +7.9% to +35.3% (Fig. 2). The  $\delta^{18}$ O values have a good correlation with the degree of hydrothermal alteration in the volcanic rocks, increasing with more intense alteration. The lowest value was determined in the less altered andesite, whereas the largest are from a strongly leached and silicified andesite and a cristobalite-trydimite "veinlet" crosscutting the same rock. For comparison, the average  $\delta^{18}$  value (2.9‰) of the magnetite ores (Nystrom and Henríquez, in Henríquez, 1991) are also shown in Fig. 2. Similar isotopic compositions of oxygen have been reported by Larson and Oreskes (1993) for three samples of magnetite and three of hydrothermal quartz from two small magnetite ore-bodies at El Laco.

#### RESULTS

Samples for sulfur and oxygen isotopic studies were taken from unaltered and altered andesitic rocks, and hydrothermal quartz from veins, chert and breccias. The sulfur isotope composition is referred to Cañon Diablo troilite (CDT) standard and oxygen values have been normalized to SMOW standard. Reproducibility error is  $\pm 0.2\%$  at one sigma error level.

### DISCUSSION

The spatial and temporal relationships between the development of the volcanic edifice, iron ore emplacement and local hydrothermal alteration, is consistent with the interpretation of the area in terms of a magmatic-volcanic evolution producing both andesitic to dacitic volcanic rocks and magmatic iron ores (Vivallo et al., 1991). In this context, the pyroxenequartz-magnetite assemblage in the halos represents a high temperature association, directly related to the emplacement of



Fig. 2: The upper part of the figure shows the isotopic composition of oxygen in volcanic rocks, "hydrothermal quartz" (silica) and magnetite, and in the lower part the isotopic composition of the sulfur in pyrite and gypsum is shown. Data for magnetite and pyrite are from Henríquez (1991).

the iron rich magma and consequently considered as a "contact metamorphic event". The minerals or mineral associations deposited in open spaces within the extrusive ore bodies are the result of subsequent cooling-degassing, formed at lower temperatures than the mineral association in the halos, but higher than the temperature of the assemblages representing the local hydrothermal alteration event. The mineralogical associations of the local hydrothermal alteration are similar to a near-surface steam-heated environment in geothermal fields, suggesting temperatures lower than 300°C (Henley and Ellis 1983, and references therein). Silicified vein structures and hydrothermal breccia bodies. spatially related with the hydrothermally altered rocks, also support this interpretation.

The leached rocks and their secondary mineralogy along with the exhalative gypsum deposits suggest underground boiling in the hydrothermal system and generation of low pH and sulfur rich solutions that reached the surface. This interpretation is also supported by the isotopical composition of sulfur in gypsum and alunite from the exhalites. These are enriched in  $\delta^{34}$ S compared with the  $\delta^{34}$ S value of pyrite. Furthermore, the measured  $\delta^{34}$ S values are similar to values observed in epithermal deposits and geothermal systems, suggesting a magmatic source for sulfur and a hypogene origin for the gypsum and alunite in the exhalative deposits.

Compared with the unaltered andesite (Fig. 3), all the altered rocks and hydrothermal quartz become progressively enriched in <sup>18</sup>0. This is contrasting with the general trend mentioned by Field and Fifarek (1985), where the altered host rocks, of epithermal deposits or geothermal fields, are variably depleted in <sup>18</sup>O relative to their unaltered equivalents. These trends have commonly been interpreted as produced by the interaction between rocks and <sup>18</sup>O-depleted local meteoric waters, producing an <sup>18</sup>O enrichment in the water and the observed depletion in the rocks. The magnitude of the <sup>18</sup>O-shift in the fluids correlates directly with temperature and salinity of the hydrothermal solution, and inversely with the water/rock ratio of the system (Field and Fifarek, 1985).

The <sup>18</sup>0 enrichment observed in the volcanic rocks at El Laco requires, to be explained, the interaction of the andesitic rocks with an hydrothermal solution dominated by strongly <sup>18</sup>0-enriched water.

Magnetite, both magmatic and hydrothermal, is one of the most peculiar components of the El Laco system. This magnetite displays very low <sup>18</sup>0 values: it is well known that magnetite interacting with water produces a strong 180enrichment in the hydrothermal solution (Taylor, 1979). On the other hand, geological evidence such as presence of hydrothermal breccias, exhalative gypsum accumulation, along with the dispersal of  $\delta^{34}$ S values, suggest that boiling occurred during the evolution of the hydrothermal system. Combination of magmatic water. initially interacting with magnetite, and then moving to the surface to produce boiling and decrease in temperature can account for the <sup>18</sup>0-enrichment in the hydrothermal solution necessary to produce the observed values in the altered rocks and quartz.

The isotopic fractionation of oxygen in the magnetite-water and quartzmagnetite systems is strongly dependent upon the temperature, with the largest fractioning occuring below 300° C. This is consistent with the mineralogical composition of the altered rocks.

#### CONCLUSIONS

The geological setting of the El Laco district reveals the evolution of a mainly andesitic strato-volcano, producing flows and pyroclastic deposits. As a part of this evolution, magmatic iron deposits were formed, and emplaced as intrusive bodies, magnetite flows and pyroclastic deposits. High temperature alteration halos were formed around the intrusive ores, and at the waning stage of the volcanic evolution the district was affected by an extensive hydrothermal activity producing silicification and advanced argillic alteration in the volcanic rocks. and accumulation of exhalative gypsum deposits on the surface.

The mineralogy of the altered rocks around the magnetite ore-bodies and gypsum deposits are compatible with a steam-heated geothermal field environment. Sulfur isotopes suggest that the exhalative gypsum deposits are hypogene and the sulfur derived from a magmatic source.

Isotopic composition of oxygen in altered rocks, magnetite and hydrothermal quartz, is compatible with a hydrothermal system dominated by magmatic water, which becomes progressively enriched in <sup>18</sup>0, by initial interaction with magnetite, and subsequent boiling and decreasing temperature.

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