

Element Mobility Due to Hydrothermal Alteration in Los Azufres Geothermal Field, Mexico

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ABSTRACT

We report the chemical composition (major and trace elements, including REE) of a drill well core sample from the Los Azufres geothermal field, Mexico, which presented a hydrothermally altered section and an almost fresh part. This special sample allowed us to study the mineralogical and chemical effects imposed by hydrothermal alteration on the mm scale in this important geothermal system. The altered part of the sample shows intense silicification, hematization, and dissolution boundaries. Most major and trace elements were mobilized from the original rock. Major element composition reflects the silicification, chloritization, and epidotization processes taking place in the geothermal system. High-field strength elements such as Zr, Ti, and P show a significant concentration decrease in the highly-altered rock. The rare-earth elements La and Ce, as well as Yb and Lu were probably partially re-deposited during alteration. The positive anomaly of Eu in the altered section may suggest that Eu is being concentrated in hydrothermal epidote after its release from plagioclase to the geothermal fluid. The geothermal fluid responsible for this hydrothermal alteration was probably oxidizing, of high temperature (> 250°C), and enriched in REE and other trace elements.

1. INTRODUCTION

The Los Azufres geothermal field (LAGF) is located in the central part of the Mexican Volcanic Belt (MVB; Figure 1), approximately 200 km northwest of Mexico City. LAGF represents the second most important geothermal field in Mexico, with a total installed capacity for electricity production of 188 MW (Gutiérrez-Negrín, 2007).

This work presents a comparative mineralogical and geochemical study of a core sample which shows two distinct parts, a nearly fresh (or less-altered) rock section and its highly altered equivalent. This special rock sample from well Az-48 at 2678 m depth (Fig. 1) allowed us, for the first time in LAGF, to observe at mm scale the mineralogical changes caused by hydrothermal alteration and to quantify the chemical changes imposed to this single volcanic rock after alteration. Petrographic studies and geochemical analyses (major and trace elements, including REE and HFSE) of this rock sample helped us to obtain a better understanding of the water/rock interaction processes occurring in this active hydrothermal system.

2. GEOLOGICAL SETTING

Los Azufres is one of several Pleistocene silicic volcanic centres with active geothermal systems in the Mexican

Volcanic Belt (MVB, Aguilar y Vargas and Verma, 1987). Geologically, two principal units can be distinguished at the LAGF (Dobson and Mahood, 1985; Fig. 1): (1) a silicic sequence of rhyodacites, rhyolites and dacites with ages between 1.0 and 0.15 m.y. and a thickness up to 1000 m; (2) a 2700 m thick interstratification of lava flows and pyroclastic rocks, of andesitic to basaltic composition with ages between 18 and 1 m.y., forming the local basement. This unit provides the main aquifer with fluid flow through fractures and faults (most importantly E-W oriented; Garduño Monroy, 1988), sometimes reaching the surface forming fumaroles, solfataras and mudpits.

Hydrothermal alteration has affected most rocks in the geothermal field to varying extent. Hydrothermal alteration at LAGF has been described, among others, by Cathelineau et al., (1985), Torres-Alvarado, (2000 and 2002) and more recently by Pandarinath et al. (2006). These studies have shown that partial to complete hydrothermal metamorphism has occurred. Most important alteration assemblages with increasing depth are: argillitization/silicification, zeolite/calcite formation, sericitization/chloritization, and chloritization/epidotization. For a complete description of alteration characteristics see Torres-Alvarado (2000 and 2002, and references therein).

Geochemical studies of the rocks from the LAGF have been reported since 1985 (see Torres-Alvarado and Satir, 1998, and references therein). Cathelineau et al. (1985), Torres-Alvarado and Satir (1998), and Verma et al. (2005) have discussed in detail the hydrothermal alteration effects in the chemical composition of the volcanic rocks from LAGF.

3. SAMPLES AND ANALYTICAL DETAILS

The studied sample was carefully divided into two pieces avoiding contamination between the highly-altered portions of the core from the less-altered rock. All handpicked pieces were cleaned, oven dried at about 60°C, and pulverized for geochemical analyses. A standard thin section was carefully prepared for petrographic purposes.

Major elements were analyzed by X-ray fluorescence spectrometry (XRF) on duplicate lithium metaborate fused discs, using a Philips MAGIX PRO spectrometer at the Centro de Investigación en Energía, Universidad Nacional Autónoma de México (procedure similar to the one reported by Verma et al., 1992). The rare earth elements (REE) and other trace elements were measured by inductively-coupled plasma mass spectrometry (ICP-MS) at GeoForschungsZentrum Potsdam, Germany (for details about the analytical procedure see Dulski, 2001).

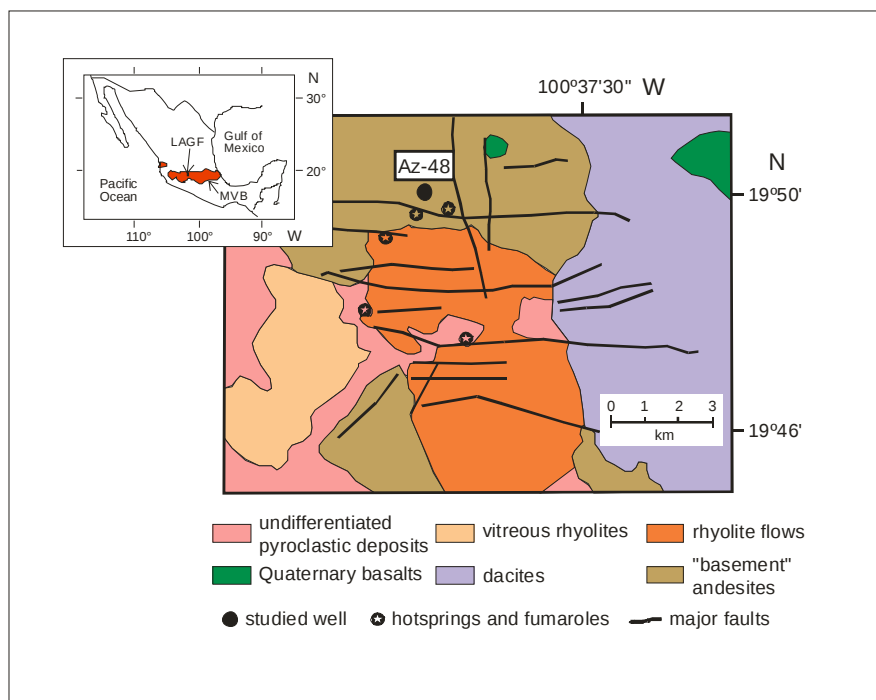


Figure 1. Simplified geologic map of the Los Azufres geothermal field (LAGF; modified after Dobson and Mahood, 1985). MVB = Mexican Volcanic Belt.

4. RESULTS AND DISCUSSION

4.1. Petrography

The relatively fresh rock sample in hand specimen is an aphanitic volcanic rock, dark gray in color. Under the microscope it shows a pilotaxitic to porphyritic texture. Phenocrysts of olivine and pyroxene are embedded in a matrix of microlitic plagioclase, zircon, apatite, and magnetite (the last mostly altered to hematite). Olivine and pyroxene phenocrysts are totally altered to chlorite and hematite. Microlitic plagioclase is only partially altered to clay minerals, allowing us to estimate, for this sample, a degree of alteration of about 30%. Several chlorite and quartz veins cut the sample; additionally, a chlorite vein was cut by a vein of cryptocrystalline quartz, providing evidence for the existence of at least two fluid flow events during hydrothermal alteration precipitation.

The highly-altered section of the sample (altered to nearly 100%) is aphanitic as well, showing a light greenish gray color. Under the microscope, this rock section is built up by banded chlorite, clay minerals, and cryptocrystalline to microcrystalline anhedral quartz. Hydrothermal plagioclase and K-feldspars are also present, the first showing an albitic composition, as indicated by X-ray diffraction analyses. They all may contain anhedral to subhedral epidote crystals and rarely some small amphibole crystals of acicular texture (probably tremolite as indicated by X-ray diffraction analyses). Opaque minerals (mainly hematite) are also present. Close to the quartz or chlorite veins, the rock shows intense silicification along with dissolution, showing that chlorite and clay minerals contribute to the complete replacement of the original volcanic rock.

4.2. Chemical Composition

According to the TAS classification (Le Bas et al., 1986; Le Bas, 2000) the less-altered rock shows a basaltic

composition. Most elements show a general decrease in the altered sample compared to the less-altered rock (Fig. 2). Exceptions to this are SiO₂, MgO, and MnO, which are important elements incorporated into the highly-altered rock due to silicification, chloritization, and epidotization, respectively (Torres-Alvarado, 2000), in agreement with the importance of these alteration processes in the LAGF (Torres-Alvarado, 2002).

About 75% of the alkalis were removed from the fresh rock by means of hydrothermal alteration (Fig. 2). Loss of alkalis seems to be an important alteration effect for the LAGF, as already pointed out by Torres-Alvarado and Satir (1998) and Verma et al. (2005). Al and Fe presented a decrease of about 34 and 79%, respectively. The highest concentration changes were interestingly observed for the high-field strength elements (HFSE), considered to be immobile during hydrothermal alteration process (e.g., Rollinson, 1993). Ti, Nb, Zr, Hf, P, and Th concentrations decreased to about 100%. This observation is noteworthy because these elements, especially the HFSE, are widely used for petrogenetic studies. Caution must be therefore exercised studying rock samples which are hydrothermally-altered, such as in older metamorphic terranes.

All REE are present at lower concentrations in the highly-altered rock compared to the less-altered one (Fig. 3). They behaved as a relatively consistent group presenting a decrease (from 50 to 83%; Fig. 2) in their concentrations, with the exception of Eu whose decrement reached only about 14%. Whereas the original rock shows a smooth, light REE (LREE)-enriched pattern with no Eu anomaly (typical of surface basaltic rocks from the LAGF; Verma et al., 2005), the highly-altered rock shows lower rock/chondrite concentration ratios for all elements, with a remarkably positive Eu anomaly. Heavy REE (HREE) presented the lowest concentration changes within the REE group.

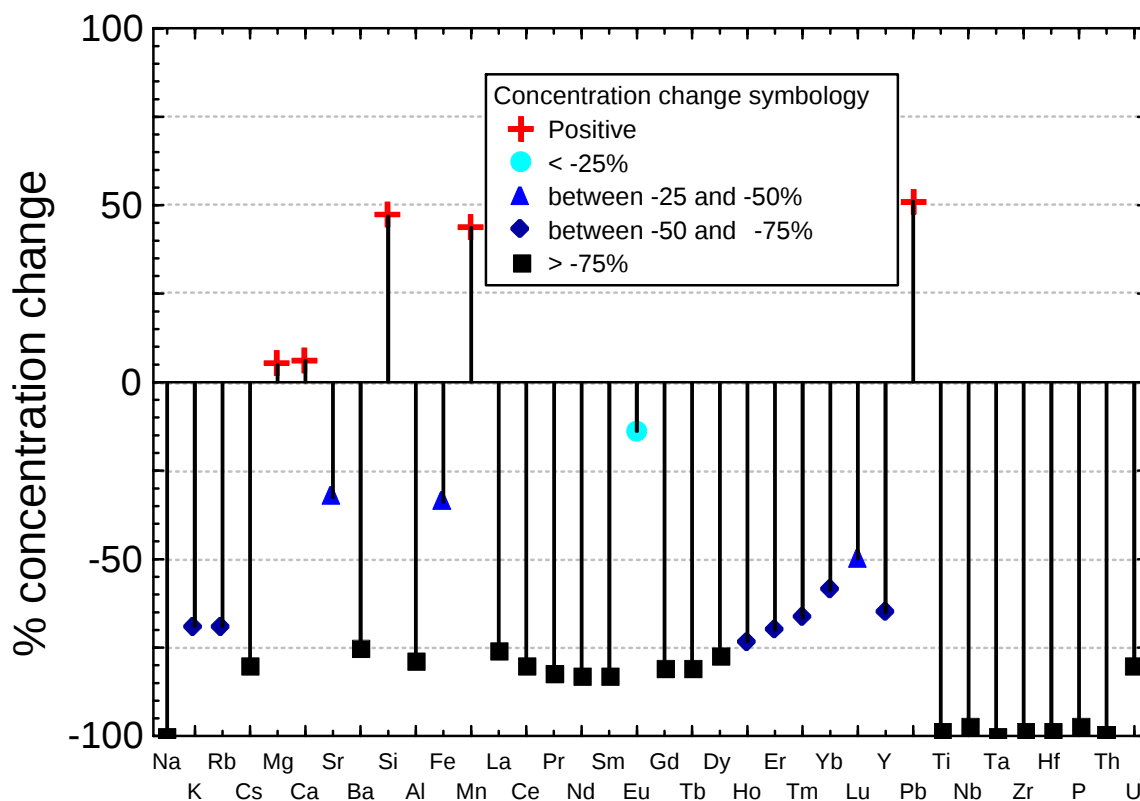


Figure 2. Elemental changes between the highly-altered and the less-altered sample for all analyzed elements. Concentration changes were calculated using the relation $100 \cdot (CA_i - CFI) / CFI$, where CA_i is the concentration of element i in the highly-altered sample, and CFI is the concentration of the same element in the less-altered sample. Different symbols shown as inset indicate different ranges of concentration change. Note that elements were arranged principally according to their atomic number, rather than their petrogenetic behavior.

The positive Eu anomaly present in the highly-altered sample has been also observed in some hydrothermal ore deposits (e.g., Palacios et al., 1986) and in hydrothermal fluids from mid-ocean ridges (e.g., Klinkhammer et al., 1994). Klinkhammer et al. (1994) suggested that the partition of REE^{3+} and Eu^{2+} is dominated by chemical substitution for Ca^{2+} and Sr^{2+} in plagioclase, respectively, during the transition from An-rich plagioclase to Ab-rich hydrothermal plagioclase. Furthermore, Palacios et al. (1986) considered epidote as the principal hydrothermal mineral containing REE and pointed out that its REE concentration is controlled by the REE content in the hydrothermal fluid with probably oxidizing characteristics.

Both previous statements agree with our results, suggesting a predominant role for epidote allocating REE which have been perhaps mobilized from plagioclase by hydrothermal alteration processes. According to Palacios et al. (1986) this could suggest an oxidizing, REE-enriched geothermal fluid, which could be the source for the precipitation of hydrothermal assemblages at LAGF. Abundant hydrothermal hematite supports this hypothesis.

These observations stress the caution that has to be taken when assuming REE as relatively immobile under hydrothermal conditions and emphasizes the necessity of determining REE concentrations for the geothermal fluids at the LAGF for a better understanding of the alteration processes.

CONCLUSIONS

A core sample from well Az-48 at 2678 m depth allowed us to study the mineralogical and chemical variations imposed by hydrothermal alteration processes to a basaltic rock sample in Los Azufres geothermal field.

Most major and trace elements were mobilized from the original rock. Silicification, chloritization, and epidotization processes account for the major-element composition of highly-altered rock. Most REE were probably mobilized by hydrothermal processes. La and Ce, as well as Yb and Lu probably mobilized from the original volcanic rock were partially re-deposited from the geothermal fluids during deposition of hydrothermal minerals, as well as during the alteration of the sample. A remarkable positive anomaly of Eu suggests that Eu is being concentrated in hydrothermal epidote after being released from plagioclase to the geothermal fluid. High-field strength elements were mobilized as well during hydrothermal alteration, stressing the necessity of caution using these trace elements for petrogenetic studies of igneous and metamorphic rocks.

The geothermal fluids responsible for this alteration may have been characterized by a high temperature (>250 °C, as evidenced by the presence of hydrothermal epidote and amphibole), oxidizing conditions (as suggested by significant amounts of hematite), and enrichment of both REE and HFSE.

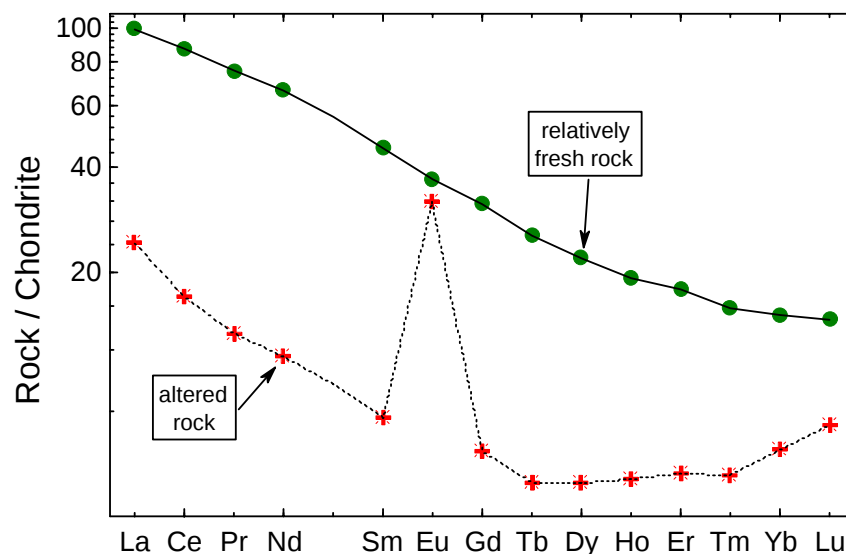


Figure 3. Rare earth elements chemical composition of the analyzed samples, normalized to the chondritic abundances (values from McDonough and Sun, 1995).

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