CHEMICAL VARIATIONS IN THE ROCKS OF LA PRIMAVERA GEOTHERMAL FIELD (MEXICO) RELATED WITH HYDROTHERMAL ALTERATION

R.M. PROL-LEDESMA[1], S.I. HERNANDEZ-LOMBARDINI[2] AND
R.LOZANO-SANTA CRUZ[3]

[1] Instituto de Geofiscia, UNAM. Mexico, D.F. [2] Facultad de Ingenieria, UNAM. Mexico, D.F.
[3] Instituto de Geologia, UNAM. Mexico, D.F.

SUMMARY - The origin and fate of the components dissolved in the geothermal fluids are of great importance in the study of epithermal deposits, and in the environmental considerations for exploitation of geothermal fields. The chemical study of La Primavera geothermal field in Mexico has environmental importance due to the high arsenic concentration observed in the thermal water and the possible contamination of aquifers in the area. The variations in the chemistry of all altered samples with respect to unaltered samples indicates depletion of manganese, and the alkalis; and enrichment in iron and magnesium. Most samples show an enrichment in aluminum and titanium, and depletion in silica and calcium. Trace elements follow different trends at various depths; shallow depths are more favorable for deposition of the analyzed trace elements than the surface or the deep part of the reservoir.

1. INTRODUCTION

The water-rock interactions that take place in hydrothermal systems cause chemical changes in the fluid and in the reservoir rocks; in some systems they are related to the attainment of chemical equilibrium. In a general model there is chemical and mass transfer from the magma bodies that play the role of energy sources of the hydrothermal system in addition to the chemical transfer between the geothermal fluid and the reservoir rocks (Ellis and Malion, 1977; Giggenbach, 1981; 1984).

The typical constituents that can be leached from the rocks are silica, sodium, potassium, calcium, magnesium, aluminum, iron and manganese; however, their concentrations are determined by the solubilities of the minerals in which are contained. Experiments have shown that important quantities of chloride, boron, fluoride and arsenic are dissolved from the host rocks (Ellis and Mahon, 1963; 1967). Hot dry rock development has provided important results about the chemical changes due to water-rock interactions at high and moderate temperatures (Duchane, 1994; Kiho and Mambo, 1995). The data available indicate,, that in most cases volatiles are contributed by the intrusive bodies that act as heat source, and the rest of the components come mostly from the rocks in contact with the fluids (Ramos-Candelaria et al., 1995). Chemical data froni epithermal deposits show erratic trends that probably reflect the influence of the various stages of hydrothermal activity (Kerrich, 1983).

Interaction of thermal water with shallow aquifers is a very widespread phenomenon in countries like Mexico with abundant hydrothermal systems. The mixing of thermal and groundwater favours the diffusion of some environmentally hazardous elements in groundwater used for domestic consumption; hence the importance of studying the sources of some trace elements. In La Primavera geothermal field, which is located in the vicinity of Guadalajara the second largest city in Mexico, the arsenic concentration is high in the water discharged by the hot springs, and hydrologic studies have shown that mixing processes affect the chemical composition of some shallow aquifers used for domestic and agricultural use (Cerriteño, 1991). The concern about the growing needs of groundwater for Guadalajara supported the proposal of a study to determine the sources and deposition conditions of some trace elements dissolved in the thermal water; this work reports the preliminary studies about the changes induced by hydrothermal activity in the reservoir rocks of La Primavera.

2. LOCAL GEOLOGY.

La PrimaVera geothermal field is located in the western section of the Mexican Volcanic Belt (Fig. 1). It is contained within a volcanic center that is formed by a caldera structure, pyroclastic and lava flows, rhyolitic domes, ash flows, air-fall pumice and lake sediments in the inner part of the caldera are present. The geology (Fig. 2) and eruptive history of La Primavera has been reported by Mahood (1980). The first volcanic activity took place 120,000 years ago; the strongest eruption occurred 95,000 years ago and corresponds to the Tala Tuff that has a volume of 20 km3. After this eruption the roof of the magma chamber collapsed and formed a 11 km diameter caldera. A lake was formed where sediments of volcanogenic origin collected. Volcanic activity resumed 75,000 years ago with the eruption of rhyolitic domes in the southern caldera margin. Eruption of lava flows of rhyolitic composition continued in the southern margin from 60,000 to about 20,000 years ago approximately. The lithologic column of the area is based on data from exploration wells (Fig. 3), it is dominated by rocks of rhyolitic composition: however, the reservoir is mostly contained in the andesitic strata (Gutiérrez-Negrín, 1991).

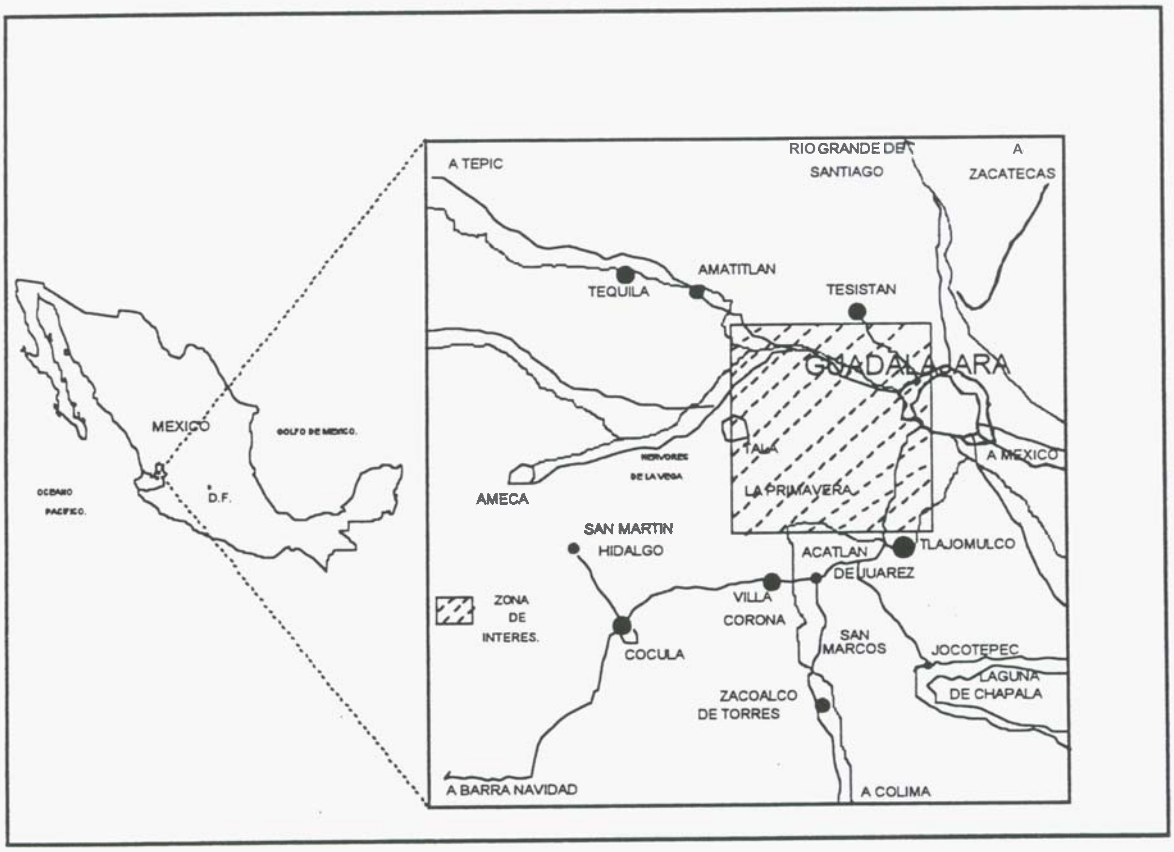
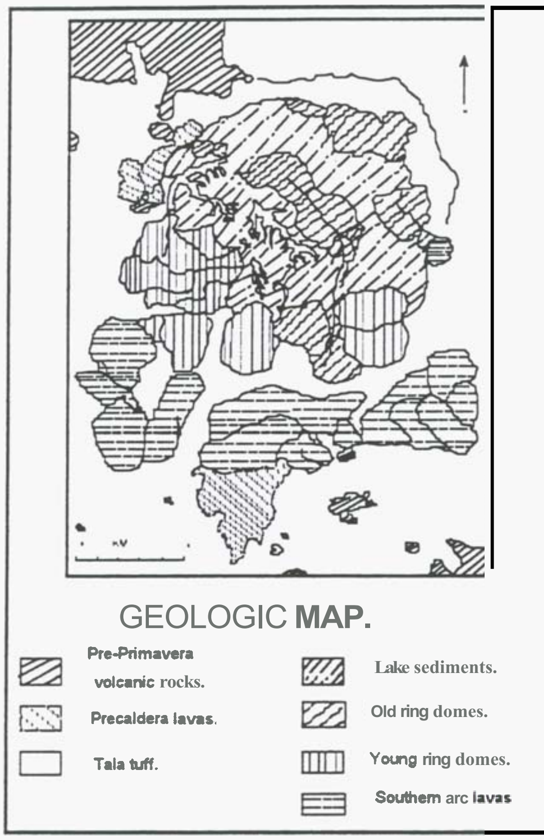


Fig. 1 Location of La Primavera geothermal field.

3. WATER COMPOSITION OF LA PRIMAVERA SURFACE MANIFESTATIONS AND EXPLORATION WELLS.

Discharge features in La Primavera geothermal field include hot springs and fumaroles, their location has a close relation with the main fault systems in the area (*Mahood* et al., 1983). Exploration work of the geothermal field for electricity production included chemical and isotopic analyses of water from the springs, fumaroles and wells in La Primavera Geothermal Field, major dissolved ions and some trace elements of environmental importance as arsenic have been analyzed determined in order to understand the reservoir conditions and the hydrologic processes that take place in the shallow aquifers (*Mahood* et al., 1983; Gutiérrez-Negrín, 1991). Waters discharged by the exploration wells are classified as sodium-chloride. Hot springs discharge in the surface a mixture of sodium-chloride and bicarbonate waters rich in calcium and magnesium. The isotopic data yield similar hydrogen isotopic composition for deep and surface samples, and they correlate well with a sample from a cold well (Y.T.P.) taken as reference, the condensates from fumaroles seem to be in equilibrium at 170°C with an isotopically similar water. Tritium values for the water indicate a residence time of more than **50** years (Mahood et **al.,** 1983). The chemical and isotopic characteristics of the water and vapor, and the temperatures obtained with the chemical and isotopic geothermometers can be interpreted as the result of conductive cooling of the reservoir water during its flow to the springs (Mahood et **al.,** 1983).



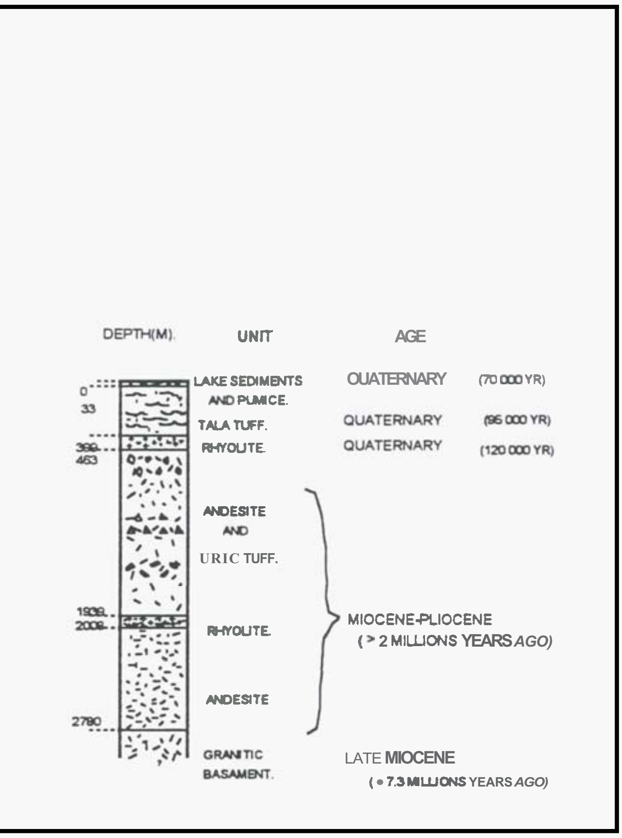


Fig. 2 Surface geology of La Primavera Geothermal field (After Mahood, 1980).

Fig. 3 Stratigraphic column in the area of La PrimaVera geothermal field (After JICA, 1989).

Table 1. Chemical analyses of spring waters in La Primavera (From Mahood et **al.,** 1983).

LOC.	T°C	pH	Li	K	Na	Ca	Mg	Rb	Cs	Mn	SO_4	Cl	F	HCO_3	Si02	B
ORF.	58	7,2	0,88	11,0	267	5,4	0,81	0,05	0,04	0,15	43	112	18	452	218	12
RC .	67	7,0	0,92	11,0	280	3,5	0,40	0,09	0,08	0,05	43	106	17	487	227	9,7
A. BRAVA	67	7,0	0,90	12,5	268	3,8	0,46	0,08	0,06	0,07	31	94	16	495	207	10
A. **VERDE**	68	6,9	0,87	11,0	268	4,1	0,46	0,08	0,06	0,08	30	94	17	487	215	9,1
A. CAL.E	63	7,6	1,05	9,5	275	1,5	0,35	0,03	0,04	0,01	5	155	29	377	177	9,1
C. FLORES	35	6,8	0,04	2,8	35	2,3	0,86	0,01	0,01	0,01	6	5,4	1,8	90	123	0,2
Y. T. P.	15	n.d.	0,05	5,0	31	1	0,85	0,11	0,01	0,01	3	1,6	1,6	81	12,2	0,15

Table **2.** Chemical analyses of water discharged **by** exploration wells in La Primavera (From **Mahood** et al., **1983;** and Gutiérrez-Negrín, 1991).

Well	pH	Na	K	Li	Ca	Mg	Rb	Cs	As	Cl	B	HCO_3	SO_4	SiO_2	DTS
PR-1	8.2	730	170	8,1	1,2	0,01	1,3	1	18	1100	150	11	40	1280	3614
PR-8	8.6	810	130	8	1,4	0,02	1	1	12	870	100	420	110	1040	3783
PR-9	8.3	650	145	6	1,8	0,01	0,5	0,6	15	1030	130	200	54	1200	3273
PR-12	7.9	810	214	9,3	3,2	0,06	1,7	1,1	20	1300	155	61	22	1320	4065
PR-13	8.5	778	128	6,7	1	0,02	1,1	1,2	16	865	103	229	92	1056	3277

4. GEOCHEMISTRY AND PETROLOGY OF UNALTERED SAMPLES.

Petrological and geochemical data for the main outcropping rocks were described by Mahood **(1980).** Phenocrysts content in the porphyritic eruptive units varies between 1 and **5%** by volume. Quartz and sodic sanidine comprise about **97%** of the phenocrysts, being the rest hedenbergite, fayalite, and ilmenite.

Deep samples from exploration wells show the presence of some units that do not outcrop in the area. From petrographic analysis andesitic lava flows and lithic tuffs were identified. Primary minerals in these units are: a labradorite and andesine matriz with augite phenocrysts in the andesites; and the lithic tuffs show a mixture of andesitic and rhyolitic mineralogic compositions.

The chemistry of the surface samples do not show significant variations in the major elements concentrations, silica content is commonly higher than **75%;** however, variations in the trace elements concentration are large.

5. GEOCHEMISTRY AND HYDROTHERMAL MINERALOGY OF ALTERED SAMPLES.

Alteration minerals were identified in the petrographic microscope and some data were taken from the JICA report (1989). At depth the most common secondary minerals are quartz, albite, adularia, calcite, sericite, chlorite, and pyrite. At shallower depths montmorillonite, kaolinite and microcrystalline quartz predominate. Deposition of sulfur is observed in the fumarole vents. Samples from the surface manifestations were collected in order to determine their chemical changes with respect to unaltered rocks of the same stratigraphic unit and to reservoir rocks; they correspond to samples: PR951 to PR957.

The characteristic feature of altered rocks is the increase in iron, magnesium, titanium and aluminum concentra with respect to fresh rocks. Most altered rocks are dep in silica, calcium, sodium, manganese and potasium (3 and Fig. 4).

Core and cuttings samples were analyzed to determine their chemical composition; the results are shown in Table **4.** In figures **5** and **6** the concentrations of trace elements is plotted normalized to deep altered samples, shallow and surface samples are depleted in most analyzed trace elements.

Analysis of trace elements in cuttings (JICA 1989) sho enrichment in mercury and arsenic in the reservoir concentrations of more than 1 and 50 ppm respec were measured.

Table 3. Major elements concentration in altered well samples normalized to unaltered rock average **(U.R.A.)from** the analyses reported **by** Mahood (1981)

U.R.A.	Elements	PR951	PR952	PR953	PR954	PR955	PR956	PR957
75,43	SiO2.	0,67	0,60	1,00	1,12	0,49	0,96	1,02
0,12	Ti02	3,31	3,01	1,22	1,30	2,06	1,37	0,78
11,52	Al2O3	2,51	3,18	1,00	0,59	3,12	1,22	1,03
0,84	Fe2O3	6,45	6,03	3,02	1,48	4,85	3,27	2,71
0,05	MnO	0,85	0,47	0,71	0,26	0,08	0,69	0,83
0,04	MgO	4,82	1,86	3,62	1,98	3,23	2,20	1,81
0,24	CaO	0,43	0,52	1,20	0,72	0,03	1,30	1,28
4,43	Na2O	0,05	0,06	0,28	0	0	0	1,01
4,61	K2O	0,18	0.01	0,92	0,30	0,34	0,77	1,00

Table **4.** Trace elements concentration in altered shallow well samples normalized **to** deep **well** samples

D.W.S.A.	Elements	PR442	PR1192	PR1400
77,71	Rb	2,05	2,37	2,82
109,00	Zn	1,17	1,15	1,02
647,43	Ba	0,34	0,34	0,34
22,71	cu	1,01	0,97	0,75
55,86	Cr	0,63	1,02	0,55
25,71	Ni	0,74	0,89	0,74
9,57	co	0,00	0,00	0,00
505,43	Sr	0,00	0,00	0,02

Table **4.** Trace elements concentration in altered surface samples normalized to deep well samples

D.W.S.A.	Elements	PR951	PR952	PR953	PR954	PR955	PR956	PR957
77,71	Rb	0,50	0,03	2,15	0,55	0,03	1,74	2,25
109,00	Zn	0,61	3,20	1,29	0,53	0,21	1,28	1,26
647,43	Ba	0,36	0,34	0,43	0,34	0,41	0,34	0,32
22,71	CU	1,32	0,53	0,53	0,70	0,48	0,57	0,66
55,86	Cr	2,02	0	0	0,29	0	0,14	0,27
25,71	Ni	2,33	0,43	0,51	0,66	0,47	0,54	0,62
9,57	co	2,61	0	0	0	0	0	0
505,43	Sr	0	0,01	0,03	0	0,02	0,00	0

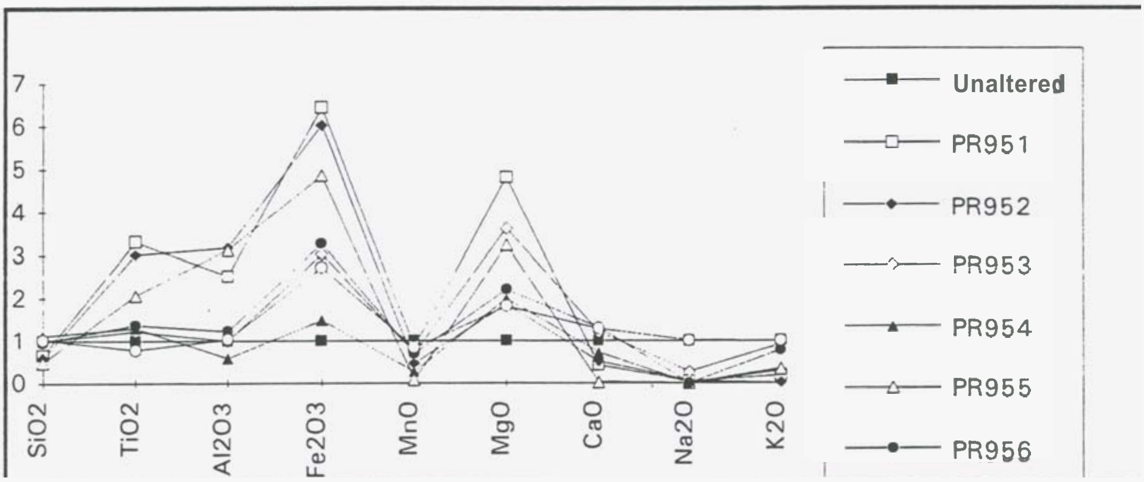


Fig. 4 Major elements concentration in altered surface samples normalized to an average composition of unaltered rocks **from data by** Mahood (1 981).

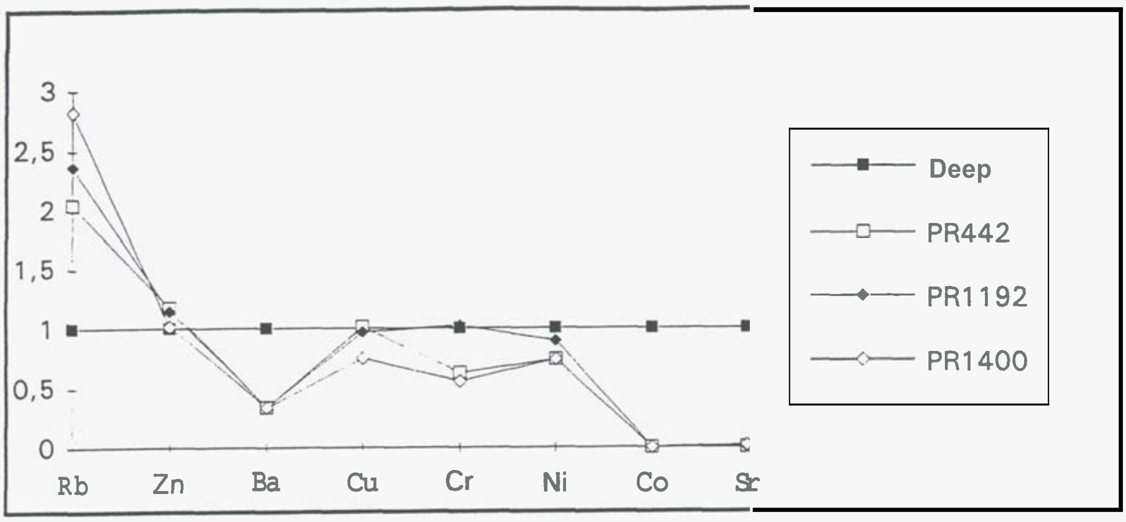


Fig. 5 Trace elements concentrations in shallow samples (<500m) normalized to deep samples.

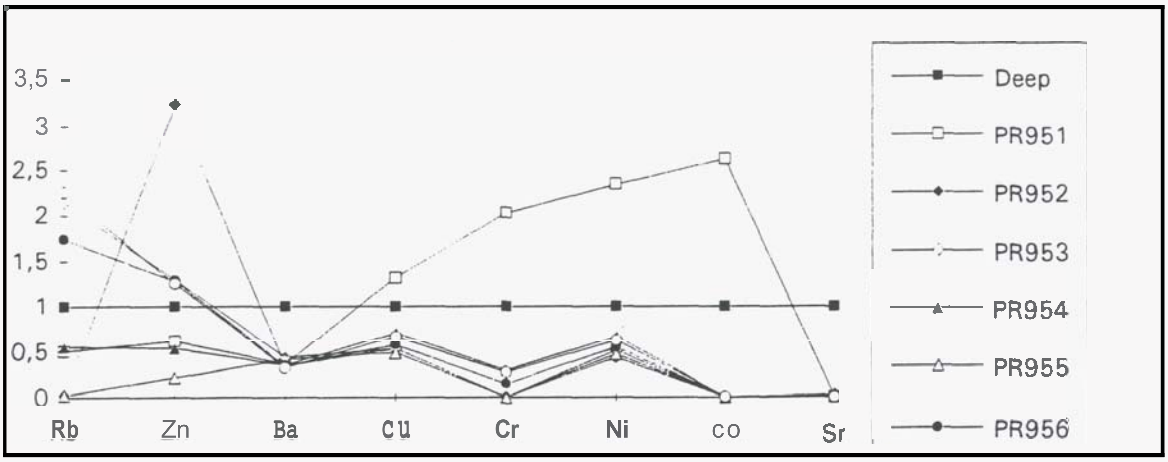


Fig. 6 Trace elements concentrations in surface samples normalized to deep samples (<500m).

6. RESULTS

Major element concentrations show that thermal fluid leaches a significant percentage of the main cations, and the enrichment shown by altered surface samples in iron, magnesium and titanium may be a result of this leaching.

Deep samples show an enrichment in barium, cobalt and strontium with respect to shallow samples, and in all trace elements except rubidium with respect to surface samples. Only one surface Sample presents enrichment in Cu, Cr, Ni and Co with respect to deep samples, the Same sample has the largest enrichment with respect to unaltered samples in Ti, Fe, and Mg. This sample comes from a fumarola vent where sulphur deposition takes place.

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