

Experimental and Modeling Study of Water-Rock Interaction in Active Geothermal Fields: Los Azufres, Mexico

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ABSTRACT

The Los Azufres Geothermal Field in Mexico is a typical high temperature hydrothermal system along convergent plate boundaries. Models of high-temperature-pressure experiments and geochemical simulation calculations have been performed. Natural rock samples which had been cut and polished into small rock cylinders with a diameter around 4.0 mm were used as the solid phase in experimental study. Mineral alteration and the evolution of the equilibrium solution composition due to water-rock interaction processes were explored in this study. A conceptual model of the origin and evolution of the fluids in Los Azufres hydrothermal system is presented. These achievements may have significance to the study of moderate temperature mineralization, exploitation of geothermal fields and the study of the migration of radionuclides in High Level Waste Repositories.

1. INTRODUCTION

Los Azufres geothermal field is located in central Mexico, approximately 200 km Northwest of Mexico City. It was one of the several Pleistocene silicic volcanic centers with active geothermal systems in the Mexico Volcanic Belt (MVB). It was the first geothermal field in Mexico to generate electricity from fluids in volcanic rocks, and represents the second most important geothermal field in Mexico after Cerro Prieto (Tello, 1997). Geologically, the volcanic rock at Los Azufres can be divided into two principal units (Torres, 2000). (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 provided the main aquifer with flow through fractures and faults. So andesite was selected as the solid sample in our study.

2. METHODOLOGY

2.1 Experimental Study

The experiment was designed to simulate water-rock interaction and chemical evolution of thermal fluids in geothermal systems. The distinguishing feature of the experimental study was that rock samples cut and polished into small rock cylinders of about 4 mm diameter were used rather than the rock powders used in most experiments (Xiong, 1998, Zhou and Zhang, 2000). The advantage of this method was that water-rock interactions took place on the mineral surface especially at the interface of different minerals, which was helpful in the study of surface interactions and alteration of minerals. At the same time it had the disadvantage that it was difficult to interpret the

chemical composition of the resulting fluid, as the rocks were usually heterogeneous materials (Zhang, 2000). The experiments were carried out in the National Key Laboratory on Mineral Deposit Research, Nanjing University. Detailed experimental procedures were similar to those performed by Zhou and Zhang (Zhou and Zhang, 2000).

The compositions of rocks were measured in the analysis center in ECIT. The Elan 6000 ICP-MS in Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, measured the solution compositions from the experiments. The JEOL JXA-8800M Electronic Probe X-Ray Micro-analyzer (EPMA) in the National Key Laboratory on Mineral Deposit Research, Nanjing University, measured the mineral compositions before and after experiments. The measured conditions of the EPMA included accelerating voltage 12~15KV, beam current 2×10^{-8} A, and beam spot 0~2 μ m, ZAF correction was employed.

2.2 Modeling Study

The exact samples (solution and rock) in the experimental study were used in the modeling in order to verify the experimental results. The EQ3/6 geochemical software package was run on a SUN Sparc 20 workstation in ECIT to simulate the interaction under different conditions. The calculation models were the reaction path calculation in a closed system.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

The rock cylinders of andesite-M2 (Table 1) from Los Azufres geothermal field were selected as the solid phase of the reaction. The liquid phases MF prepared according to the composition of waters from well in Los Azufres. The Water/Rock ratio (W/R) was determined to be around 1, the temperature varied between 350°C to 150°C, and the pressure was fixed at 50 MPa, the duration of the reaction was designed from 48 to 720 hours (Table 2).

Table. 1. Chemical composition of rocks

Sample	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	MgO
M2	59.8	16.73	0.8	6.69	0.15	3.72
M3	55.92	17.96	0.88	6.81	0.15	3.32
M2		CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
M3		7.2	3.38	1.16	0.38	100.01
		6	5.66	2.54	0.36	99.6

Measured by East China Institute of Technology

3.1 The characteristic of solid phase before and after experiment

After slicing, the solid phase (rock cylinder) before and after experimentation was studied by means of microscope and electron microprobe analysis. Using a microscope, an

obvious discoloured alteration of feldspar and lots of little secondary crystals around the porphyritic crystals of pyroxene were observed in the rock slice after the experiment. More detailed electron microprobe analysis results are described below.

Table 2. Parameters for the experiments

No:	Rock	Fluid	W/R	T (°C)	P (Mpa)	Duration (hours)
SY-02	M2	MF	1	350	50	144
SY-04	M2	MF	1	350	50	720
SY-08	M2	MF	1	350	50	48
SY-09	M2	MF	1	250	50	48
SY-10	M2	MF	1	150	50	48
SY-12	M2	pure water	1	350	50	48
SY-17	M2	MF	1	350	50	480

Note: M2: rock sample; MF = 0.1M NaCl + 0.02M KCl

3.1.1 Feldspar before and after experiment

In M2 rock cylinder, two kinds of feldspar, porphyritic crystal and micro-crystal in matrix, could be distinguished. The component of An in feldspar in the matrix varied from 48.5 to 51.9%, and from 36 to 42% in the porphyritic crystal, showing andesine to labradorite and andesine respectively. Both feldspars had normal girdle banding. In M3 natural altered rock sample, there were two kinds of feldspars, K-feldspar and albite, which were the products of water-rock interaction of andesine in the original rock with fluid enriched in Na and K. After the experiment, the secondary feldspar crystals around the porphyritic crystals were K-feldspar and albite, just like the natural altered rock sample. But in the leaked sample, the component of An in feldspar increased and the component of Ab decreased.

3.1.2 Pyroxene before and after experiment

In the M2 rock sample most pyroxenes were augite before the experiment, but during the experiment, most of them changed into diopside, actinolite and actinolite-Hb and epidote. In natural altered rock sample M3, all augite had changed into epidote and actinolite. Except that, electron microprobe analysis found some very little secondary minerals around the porphyritic crystal, there were hematite, chlorite, sphene, ilmenite, SiO₂ and calcite. The typical mineral paragenesis was actinolite + epidote + chlorite + albite.

3.2 Factors affecting the water-rock interaction

The analytical results of the solution after water-rock interaction experiment are listed in Table 3. Although it was affected by the heterogeneous of the rock cylinder, we could also get some knowledge from it.

3.2.1 Temperature

Temperature had an important effect on the water-rock interaction. The evolution of the elements when the interaction between MF and M2 andesite cylinder at different temperature might infer that high-temperature (350°C) was more favorable for the water-rock interaction. At 350°C, the content of the most major elements were lower than at 250°C and 150°C, except Mg and Ca; but minor-elements were inversed. That was because the

dominant process was the rock dissolving at low-temperature, but at high-temperature along the rock dissolving (which was more strong than low-temperature), some secondary minerals might precipitate.

3.2.2 The fluid composition

After the interaction with distilled water in the M2 andesite cylinder, a Na, K, Si, Al, Ca, Fe enriched solution was formed, which was similar to the thermal fluid from the studied geothermal field. Those indicated that the local meteoric water had added into the fluid after water-rock interaction when infiltration into the andesite rocks zone.

Table 3. Chemical composition of solution after experiment

Elem- ent	Sy-9	Sy-10	Sy-12	Sy-17	Elem- ent	Sy-9	Sy-10	Sy-12	Sy-17
Li	2.403	1.114	1.422	18.124	Mn	0.164	0.286	0.353	0.717
Na	2887.89	2958.96	71.07	2425.37	Fe	0.395	1.541	16.939	1.272
Mg	0.571	1.22	23.155	3.643	Co	0.005	0.007	0.018	0.004
Al	0.234	0.949	23.633	0.497	Ni	0.212	0.385	0.246	0.469
Si	3.005	7.133	29.449	3.809	Cu	0.475	0.186	0.136	0.169
P	0.114	0.237	1.457	0.321	Zn	0.146	0.062	0.31	0.246
K	789.78	736.48	30.767	624.48	Rb	0.154	0.252	0.052	0.704
Ca	8.137	24.598	7.852	28.157	Sr	0.175	0.497	0.074	0.716
Ti	0.013	0.402	0.989	0.026	Mo	0.033	0.051	0.012	0.041
V	0.023	0.069	0.164	0.032	Sn	0.001	0	0.003	0.001
Cr	0.023	0.021	0.5	0.088	Pb	0.041	0.007	0.016	0.028

Measured by Elan 6000 ICP-MS in Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou;

4. MODELING RESULTS AND DISCUSSIONS

The MF solution shown in Table 2 was used as the water sample for the modeling study (except for K, Na, Cl, HCO₃, other element content as the pickup file required, such as Mg and Al, were 1.000E-12mol/L). M2 andesite was used as the solid sample. The rock-forming minerals settled according to the electron microprobe analysis and CIPW calculation were augite, pigeonite, orthoclase, plagioclase, quartz, magnetite and ilmenite. The interaction between MF and andesite under different temperature and pH value condition was performed.

4.1 The evolution of the solution

In the processes of water-rock interaction between MF and M2, the content of Na, Si, Ca in the solution increased continuously, Cl, B, C, Li, Ti were almost fixed, Mg, Fe decreased. The content of K and Al reached a peak during 1-10 days, and then declined 10 days later (Fig.1). The regular pattern of K, Na, and Ca was in accord with the experimental study. This regularity was due to the rock dissolving and secondary minerals precipitated in the processes of water-rock interaction. Fig.2 reveals the formation processes of the secondary minerals in the MF-M2 interaction. Only hematite precipitated throughout the reaction, epidote, hydroxyl-apatite, clinozoisite, mesolite, chlorite, amesite-14A, albite, diopside and muscovite precipitated from 1 day to the end of the reaction. The products of the modeling study were in accord with the experimental study and confirmed by the natural altered products in M3.

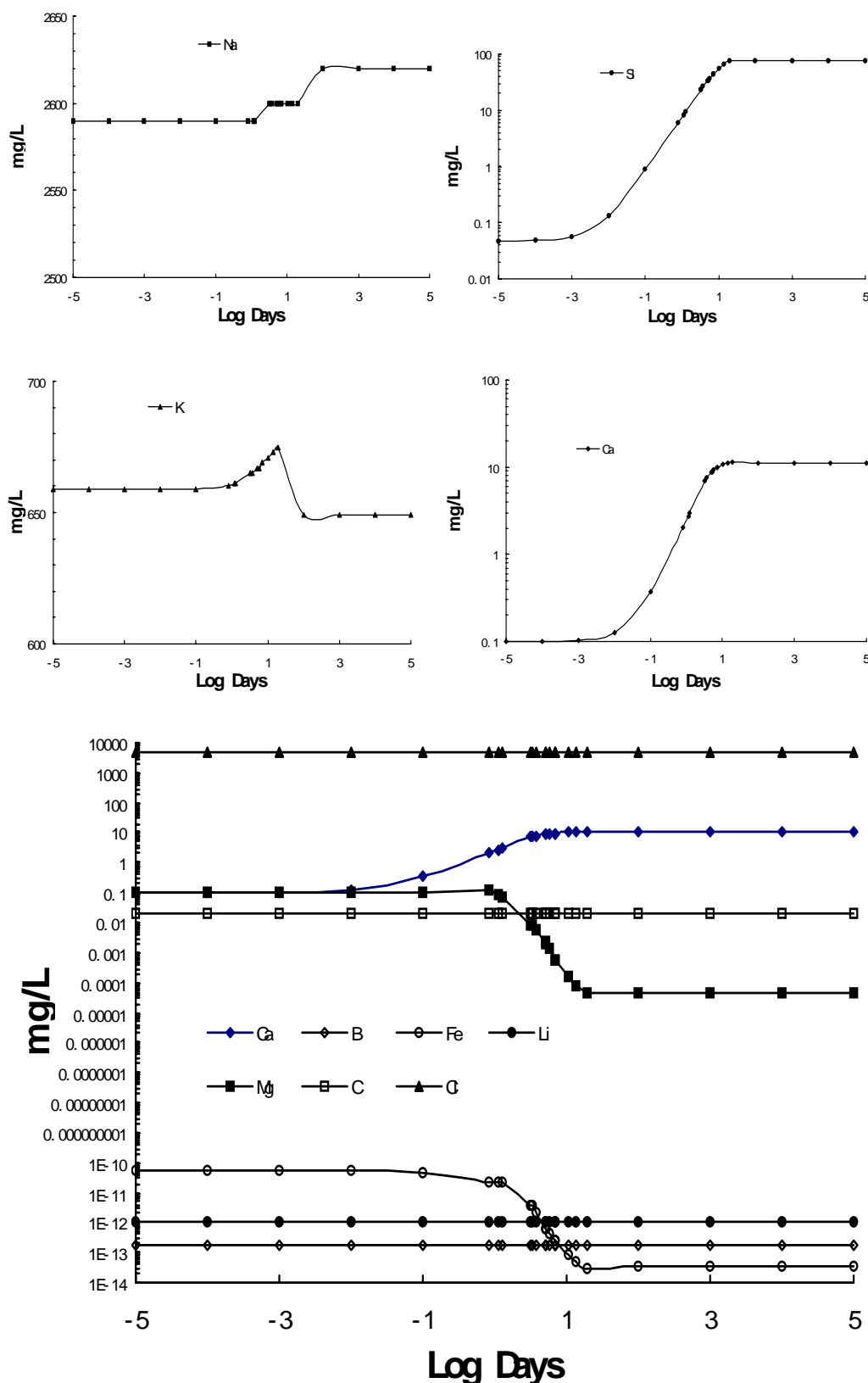


Fig. 1. Modeling study of MF-M2 interaction: Evolution of elements in the solution

4.2 Temperature

Temperature had a different effect on various elements in the MF-M2 interaction (Fig. 3). Temperature had no obvious influence on the content of the elements in the solution when temperature was higher than 250°C, while content of Fe, Mg, Ca, Ti, Al, Si were affected when

temperature was lower than 250°C. The content of Fe in the solution decreased with temperature between 200-150°C, but increased with temperature when temperature was lower than 150°C. The content of Mg and Ca increased when temperature declined, but Ti, Al, Si decreased with decline in temperature.

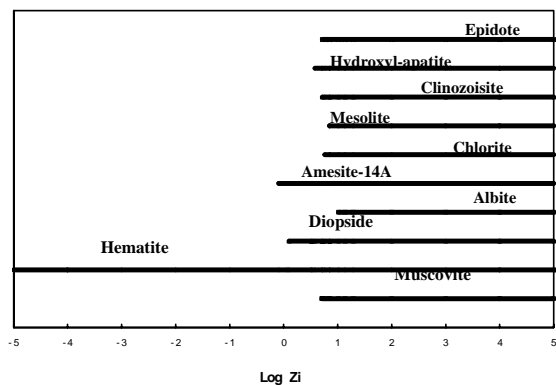


Fig. 2. Modeling study of MF-M2 interaction: Precipitated of the secondary minerals

4.3 Formation of the geothermal fluids

The fluid samples used in the modeling and experimental studies were the Na, Cl, K enriched fluid, which was the product of the long time water-rock interaction, not the original water. To verify if the local meteoric water could evolve into the geothermal fluid through the water-rock interaction, a modeling study of distilled water-andesite interaction was carried out. The evolution of elements and

precipitated of secondary minerals are shown in Fig.4. and Fig.5. At the early stage of the water-rock interaction, the element contents were very low and increased slowly. In the later stage, some elements had obviously changed. For instance the content of Si, K, Na and Al in the solution slowly increased at the early stage and then increased sharply. At the later stage of the water-rock interaction the content of Ca, Mg and Fe in the solution decreased sharply with the precipitation of the secondary minerals such as hydroxyl-apatite, amesite-14A, chlorite, muscovite, hematite, phlogopite, clinozoisite, biotite and epidote. But the content of Ti, C, B, Li, S, Cl were almost fixed throughout the water-rock interaction processes.

5. ORIGIN AND EVOLUTION OF THE GEOTHERMAL FLUID

5.1 Formation of the acid geothermal fluid

It was believed that water-rock interaction was one of the major factors in the formation of the acid geothermal fluid. In this section, we focus on the water-rock interaction in the studied hydrothermal system. Based on the field study, rock geochemistry study, experimental and modeling studies, water-rock interaction in Los Azufres could be divided into two stages: a deeper high-temperature stage and a near-surface low-temperature stage. They had different characteristics and different products.

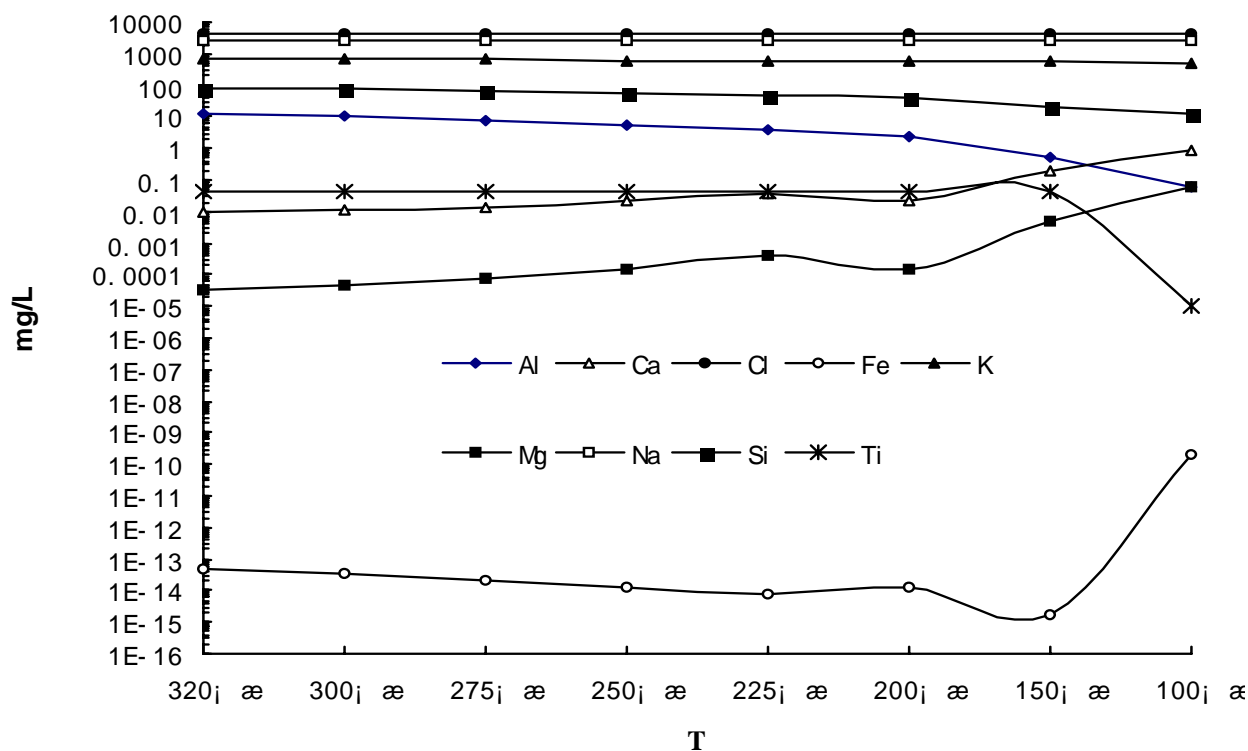


Fig. 3. Modeling study of MF-M2 Interaction: Temperature on the elements content

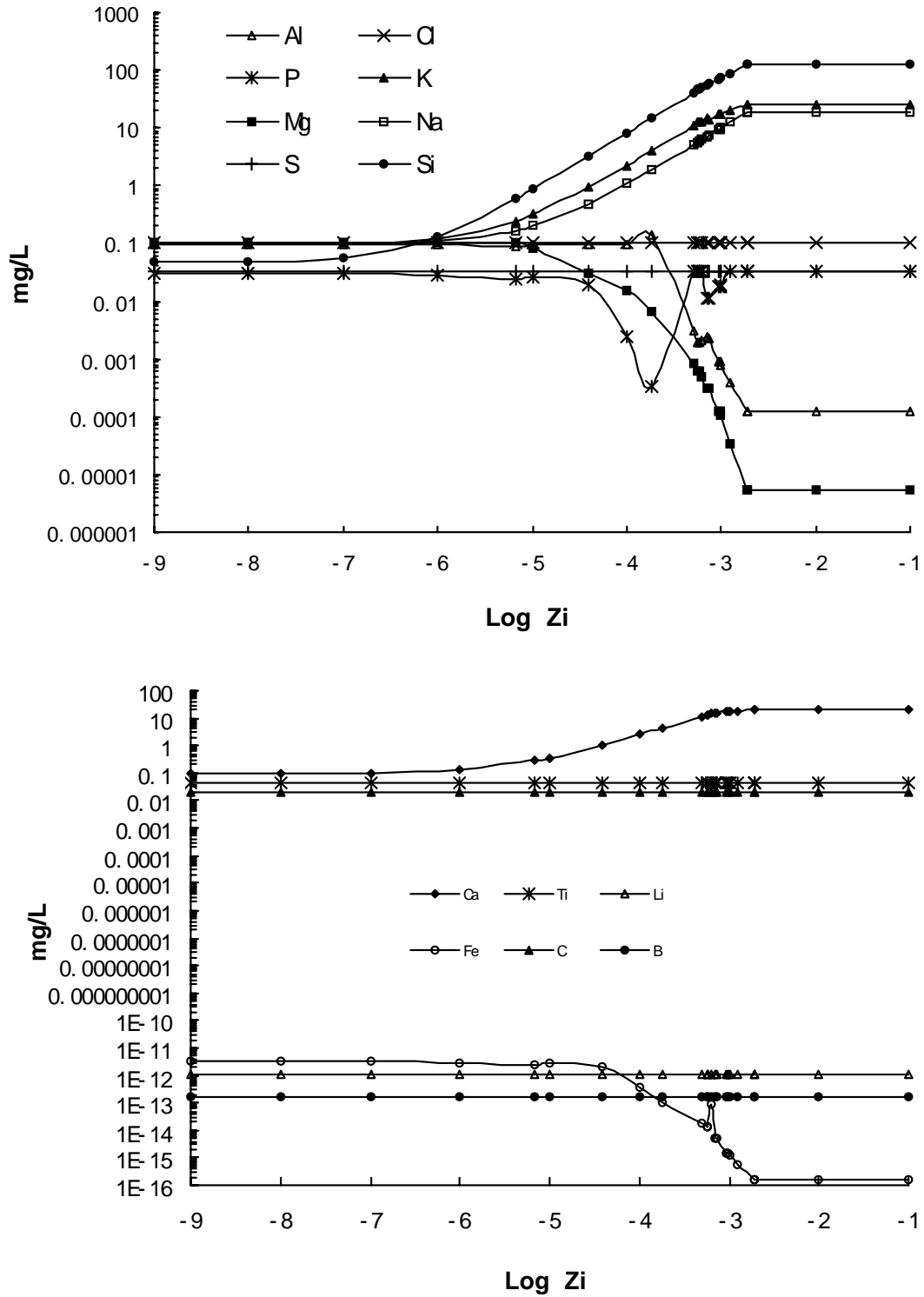


Fig. 4. Modeling study of distilled water-M2 interaction: The evolution of elements in the solution

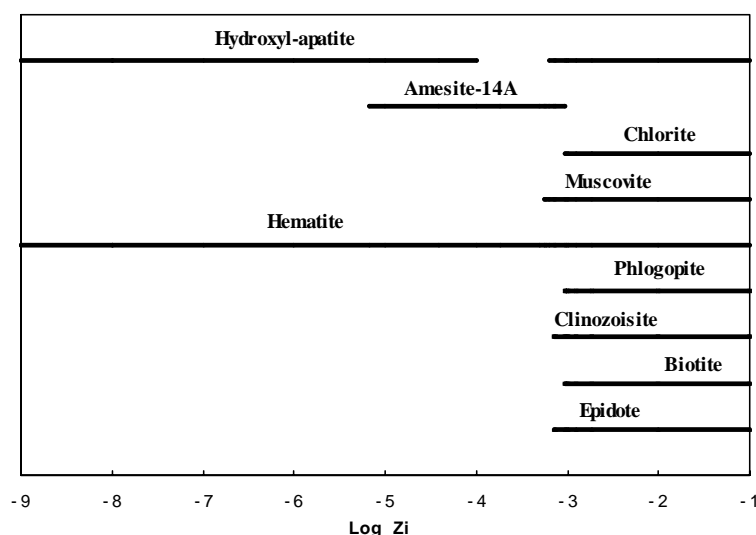
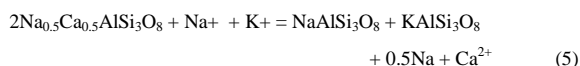
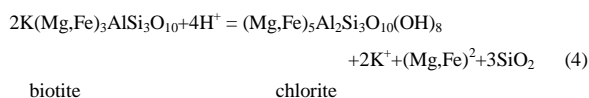
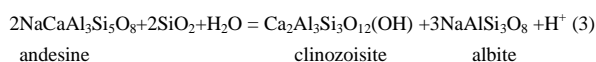
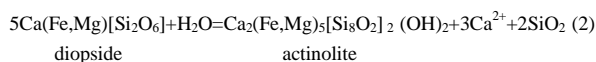
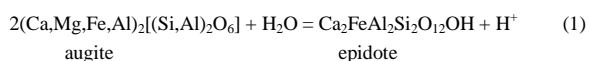


Fig. 5. Modeling study of distilled water-M2 interaction: Precipitated of the secondary minerals

5.1.1 Deeper high-temperature WRI

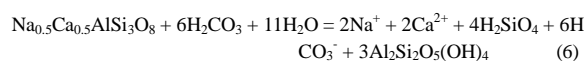
Microscope and electron microprobe analyses revealed that the rock-forming minerals in fresh M2 andesite included augite, andesine and labradorite, biotite and other minerals. The secondary minerals in naturally altered rock M3 and the experiment product formed by water-rock interaction were actinolite, diopside, epidote, chlorite, albite, hematite, muscovite, calcite and quartz. This data indicated that the following water-rock interaction took place in the K, Na, CO₂ enriched geothermal fluid at high-temperatures (250–350°C). The typical reactions were:



These reactions represented the typical reactions between andesite with K, Na, CO₂ enriched thermal fluid in Los Azufres, and formed the main paragenesis: actinolite + epidote + chlorite + albite; moreover, H⁺, Ca²⁺, CO₂ increased in the fluid. This H⁺, Ca²⁺, CO₂ enriched fluid flowed up and was involved in near-surface low-temperature interactions.

5.1.2 Near-surface low-temperature WRI

The main reactions were the incongruent reactions at low-temperature in Los Azufres. The minerals formed were calcite, kaolinite and amorphous silicoid. H_2S in the fluid changed into sulphur or SO_4^{2-} by the oxidation. The representative reactions were:



Thus cristobalite and well-crystallized kaolinite (in M8 rock sample) and CT-Opal (in M6 and M7 rock samples) were formed through the indicated water-rock interactions. At the same time some acid species such as H^+ , H_2SiO_4 , SO_4^{2-} , HCO_3^- were formed. This might be one of the major factors of the formation of acid fluid in the surface.

5.2 The origin and evolution of the geothermal fluid

The origin and evolution of the thermal fluid in a geothermal system was always one of the most important but also most disputed questions. Through the study of rock geochemistry along with experimental and model study, combined with the isotopic data, a conceptual model of the origin and evolution of the thermal fluid in Los Azufres geothermal system was set up as follows (Fig.6.). First heat, Na, Cl, H₂S, and CO₂, contained in andesitic water and magmatic water ascended from a magma chamber. Local meteoric water infiltrated through the faults in pyroclastic rock and mixed with the andesitic water flowing up in the andesitic rock zone, and formed the original thermal fluid. Then interaction between this original fluid and andesite took place, and oxygen isotopes exchanged between the water and rock, resulting in $\delta^{18}\text{O}$ decrease in rocks and $\delta^{18}\text{O}$ increase in water. At the same time the main paragenesis: actinolite + epidote + chlorite + albite formed in the altered rock, which made the contents of Si and Ca decrease in the altered rocks, but increase in the fluids. Silica precipitated in sequence as cristobalite and CT-opal as the temperature declined. H₂S in the fluid changed into sulfur or SO₄²⁻ by oxidation forming the acid fluid.

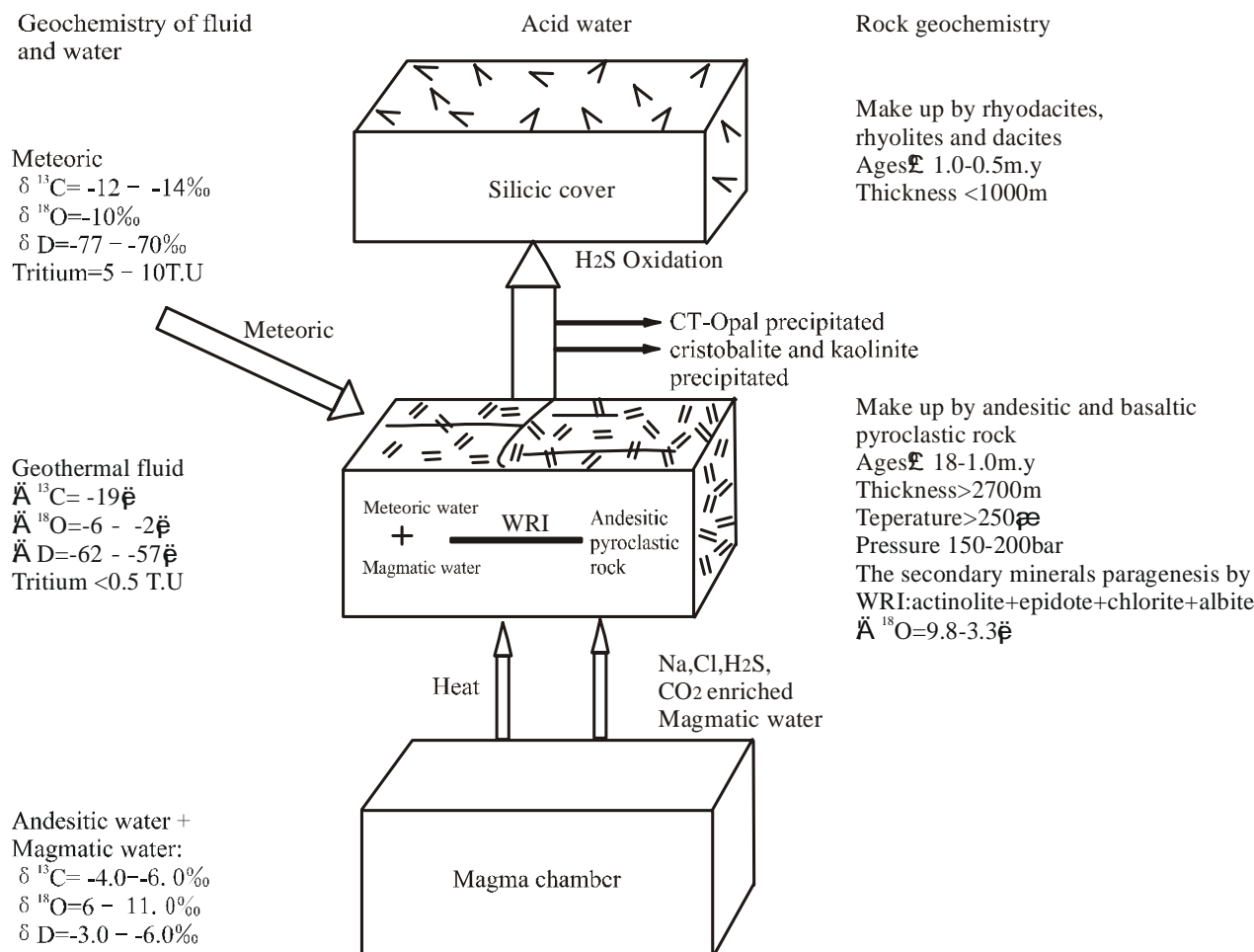


Fig. 6. Model of origin and evolution of the geothermal fluid in Los Azufres geothermal field

6. CONCLUSIONS

Electron microprobe analysis indicated that the main dark porphyritic crystals in the original experimental rock sample M2 were augite and hematite; light porphyritic crystals were andesine or andesine to labradorite having normal girdle banding. But in the rock cylinder after the experiment, the main very little altered minerals around the porphyritic crystals were diopside, actinolite, epidote, albite, K-feldspar, hematite, chlorite, sphene, SiO₂ and actinolite-Hb.

The modeling study of MF-M2 andesite interaction indicated that the evolutions of the elements in the solution were different. Contents of Na, Si, Ca increased continuously, Cl, B, C, Li, Ti were almost fixed, and Mg, Fe decreased. The contents of K and Al reached a peak during 1-10 days, and then declined 10 days later. The regular pattern of K, Na, Ca was in accord with the experimental study.

Water-rock interactions at Los Azufres could be divided into two stages: a deeper high-temperature stage and a near-surface low-temperature stage. These interactions have different characteristics and different products. During the deeper high-temperature stage, porphyritic crystals of pyroxene and feldspar were changed into diopside, actinolite, epidote, actinolite-Hb, K-feldspar and albite, the contents of SiO₂ and CaO in the altered rock decreased, and Al₂O₃, Fe₂O₃, K₂O, Na₂O, TiO₂ increased. In the near-surface stage, the influential factors may be more complex than those of the high-temperature ones, but the products

were simpler, these include complex mixtures of CT-opal and cristobalite, and well-crystallized kaolinite.

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