

THE MINERALOGIC CONSEQUENCES AND BEHAVIOR OF DESCENDING ACID-SULFATE WATERS: AN EXAMPLE FROM THE KARAHA-TELAGA BODAS GEOTHERMAL SYSTEM, INDONESIA

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ABSTRACT

Acidified steam condensates that are enriched in SO₄ but poor in Cl are found in the upper parts of many geothermal systems occurring in steep terrains. In this paper, we characterize the chemical evolution of these acid-sulfate fluids by combining mineral and fluid inclusion relationships from Karaha-Telaga Bodas with numerical simulations of water-rock interactions.

These interactions were modeled at temperatures up to 250°C, using the compositions of the lake water from Telaga Bodas and a typical andesite. The simulations predict mineral distributions consistent with the observed alteration patterns and a decrease in the freezing point depression of the fluid with increasing temperature. Fluids trapped in anhydrite, calcite, and fluorite at temperatures of 160°-205°C display a similar decrease in their freezing point depressions. This change is due mainly to the incorporation of SO₄ into the newly formed hydrothermal minerals. Between 205° and 235°C, the freezing point depressions remain at their minimum values. These values represent the residual salinity of the fluid, which is controlled primarily by Cl and unreacted CO₂.

The salinities of fluid inclusions containing Cl poor steam condensate are better expressed in terms of H₂SO₄ equivalents than the commonly used NaCl equivalents. At solute concentrations >1.5 molal, freezing point depressions represented as NaCl equivalents overestimate the salinity of Cl poor waters. At lower concentrations, differences between apparent salinities calculated as NaCl and H₂SO₄ equivalents are negligible.

INTRODUCTION

Waters that circulate within the upper kilometer of active geothermal systems in steep terrains are frequently dominated by steam condensates. These waters contain SO₄ as their dominant anion and H as

the main cation. Condensates produced by the boiling of deeper hydrothermal waters are characterized by negligible Cl and their SO₄ is derived from the oxidation of ascending H₂S (e.g. Ellis and Mahon, 1979). Condensates and crater lakes associated with actively degassing magmas, on the other hand, usually contain SO₄ derived from the disproportionation of magmatic SO₂, and/or oxidation of H₂S and intermediate oxi-anions of S (Kusakabe et al., 2000; Christenson, 2000). In addition, variable concentrations of Cl, F, and B are introduced through dissolution of magmatic gas species (HCl, HF, and H₃BO₃, respectively) and by dissolution of the host rocks (Hedenquist, 1995; Christenson et al., 2002).

The development of acidic steam condensates is common above vapor-dominated geothermal regimes, and in those systems that have a deeper liquid-dominated zone and a shallower vapor or two-phase zone. Hydrothermal minerals that typically form during interactions with these acid-sulfate waters include kaolinite, dickite, pyrophyllite, illite, sulfur, natroalunite, alunite, jarosite, anhydrite, andalusite, tourmaline, diaspore, pyrite, marcasite, and enargite (Reyes, 1990, 1991). Advanced argillic alteration assemblages (Hemley et al., 1969) thought to be produced by the descent of acid-sulfate waters occur as deep as 2500 m in the Philippines, although depths of 1600-1800 m are more typical (Reyes, 1991). However, similar assemblages form when high-temperature magmatic volatiles condense into the surrounding reservoir fluids at depth (Christenson and Wood, 1993).

Despite the ubiquitous occurrence of advanced argillic alteration assemblages and acidic steam condensates in many geothermal fields, the thermal and chemical evolution of these fluids is only partially understood. In this paper, we first describe mineralogic and fluid inclusion data from the active geothermal system at Karaha-Telaga Bodas where advanced argillic alteration assemblages related to descending acid-sulfate waters are well developed.

We then present the results of numerical simulations that were conducted to characterize the interactions occurring between the steam condensates and wall rocks. Finally, we combine the results of the simulations with the petrologic data to develop the most appropriate methodologies for interpreting fluid inclusion freezing temperatures in this environment.

THE KARAHA-TELAGA BODAS GEOTHERMAL SYSTEM

Geologic and Mineralogic Relationships

Karaha-Telaga Bodas is a recently discovered partially vapor-dominated system in western Java, Indonesia. The field is associated with Galunggung

Volcano, which erupted most recently in 1984. Allis et al. (2000) presented a conceptual model of the geothermal system (Fig. 1). Powell et al. (2001) described the chemical characteristics of the fluids. These studies show that the system consists of a deep liquid-dominated reservoir with low-salinities (1-2 weight percent) and temperatures up to 350°C, an extensive vapor-dominated regime, and an overlying cap rock with fluids dominated by steam condensates. Surface discharges occur at the southern and northern ends of the explored portions of the prospect, approximately 10 km apart. At the southern end, the thermal features include the fumaroles at Kawah Saat, an acidic lake (Telaga Bodas), and chloride-sulfate-bicarbonate springs that discharge neutral to acidic waters. Kawah Karaha, a smaller fumarole field, is located at the

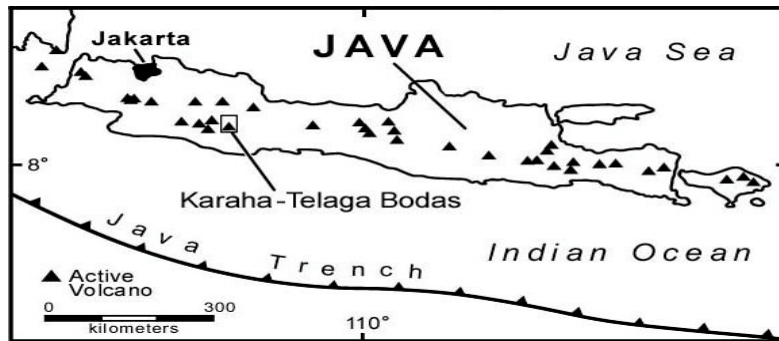
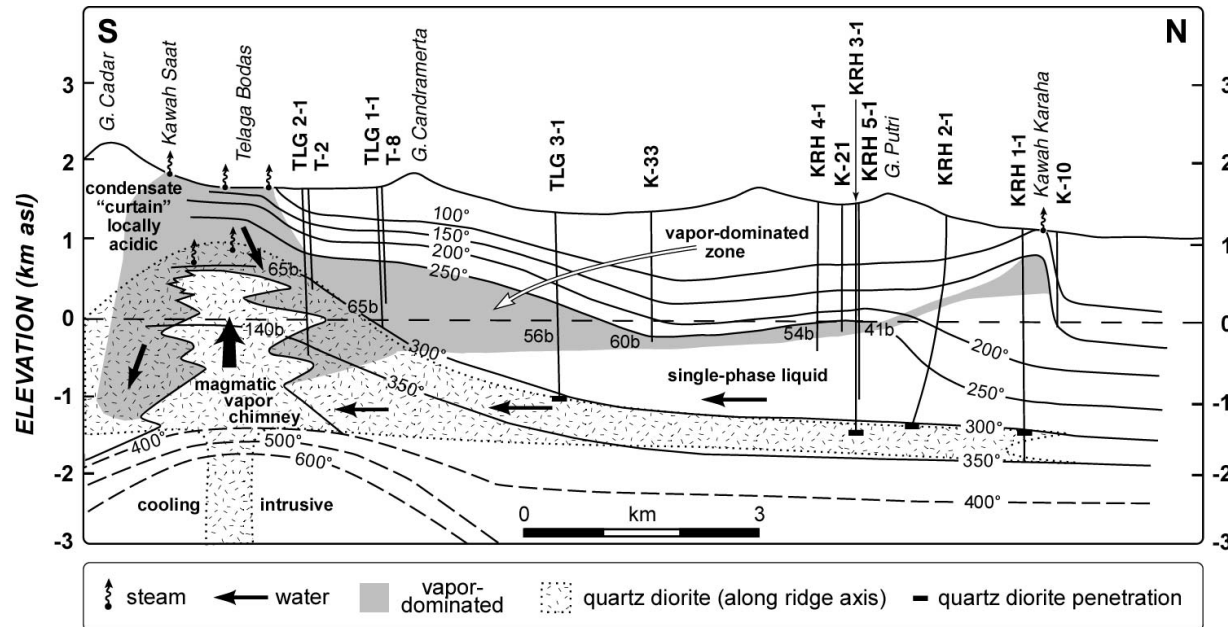


Fig. 1. Location map and north-south cross section through the geothermal system. Modified from Allis et al. (2000) and Tripp et al. (2002). The main vent of Galunggung Volcano lies ~5 km south of Telaga Bodas.

northern end. High $^3\text{He}/^4\text{He}$ ratios of 5-7.7 Ra throughout the field, and the presence of elevated F and Cl in the lake water and nearby wells suggest that magmatic gases influence the fluid compositions.

Moore et al. (2000, 2002) described the general features of the hydrothermal alteration at Karaha-Telagas Bodas. They distinguished alteration assemblages produced by an early liquid-dominated system from assemblages that formed after catastrophic depressurization and boiling led to the development of vapor-dominated conditions. The liquid dominated system produced successive episodes of argillic alteration, silicification, and propylitic/potassic alteration (chlorite, epidote, actinolite, biotite, clinopyroxene, plagioclase, pyrite, and Fe-Cu sulfides). The transition to vapor-dominated conditions was marked by the precipitation of chalcedony and quartz. Subsequent hydrothermal fluids deposited anhydrite, pyrite, carbonates (calcite, dolomite, and siderite), fluorite, wairakite, chlorite, and native sulfur. Anhydrite, the carbonates, and fluorite have retrograde solubilities. The occurrence of veins dominated by these minerals suggests that they were deposited by descending waters. Overlying near-surface rocks contain advanced argillic alteration assemblages. Crosscutting relationships suggest the advanced argillic alteration assemblages predate the deposition of anhydrite and later carbonates. These argillic assemblages document interactions with aggressive, descending acid-sulfate waters.

Assemblages produced by steam condensates are best developed in core hole T-2, located ~1 km from Telaga Bodas. This well reached a temperature of 321°C at 1383 m. The distribution of mineral assemblages in the upper 900 m of the well, where measured temperatures reach 250°C, is shown in Figure 2. Advanced argillic alteration assemblages characterized by alunite, dickite, kaolin, natroalunite, pyrophyllite, sepiolite, and smectite are present to depths of 340 m. At greater depths, alunite is absent and anhydrite becomes an important phase. Anhydrite is ubiquitous to a depth of 750 m but is present only sporadically in the deeper parts of the well. Kaolin and smectite persist to 600 m. Tourmaline occurs in trace amounts between 340 and 725 m. Electron microprobe analyses of samples from 634 m indicates that it is Mg-rich, with a composition close to dravite ($\text{NaMg}_3\text{Al}_6(\text{BO}_3)_3\text{Si}_3\text{O}_{18}(\text{OH})_4$). Native sulfur is found in Telaga Bodas and occurs in fractures between depths of 390 and 440 m. At depths greater than 650 m, calcite, fluorite, chlorite, and wairakite are found. Pyrite and quartz occur throughout the well. The clay minerals occur primarily as alteration products of the host rocks; other minerals are disseminated in the host rocks and occur in veins.

The vein assemblages display relatively simple parageneses. Veins are only sporadically developed above depths of 305 m. These veins cut advanced argillic alteration assemblages and consist mainly of alunite \pm natroalunite, quartz, and pyrite. Veins are more abundant below 305 m, with many being essentially monomineralic. Six major pulses of vein mineralization that postdate both the advanced argillic alteration assemblages and the boiling event that produced chalcedony are recognized. These veins are represented by the successive deposition of: 1) chlorite; 2) anhydrite \pm tourmaline \pm quartz; 3) pyrite; 4) wairakite; 5) calcite; and 6) fluorite. Chlorite and wairakite are found mainly in the deeper parts of the wells. Chlorite occurs below 680 m and wairakite is found primarily below 850 m.

There are a few significant deviations from the generalized paragenetic sequence. Alternating veins of pyrite and anhydrite are the most common. At 441 m in T-2, dolomite, and then native sulfur postdate anhydrite. In addition, fluorite is absent in T-8 and anhydrite is much less abundant in this well than it is in T-2. Core hole T-8 is located .75 km further from Telaga Bodas than T-2, suggesting that the differences in the mineral assemblages are related to interactions with acid-sulfate waters.

Fluid Inclusion Systematics

Fluid inclusions trapped in anhydrite, calcite, and fluorite were measured. The distribution of fluid inclusion homogenization temperatures with respect to depth and the downhole measured temperatures are shown in Figure 3. Fluid inclusions trapped in veins from T-2 record temperatures that are similar to the measured temperatures. In contrast, inclusions in T-8 record a wider range of temperatures, documenting cooling to the present downhole values.

Comparison of Figures 3 and 4 indicates that there is a progressive change in the chemistry of the fluids with both depth and temperature. The freezing temperatures of the inclusions vary markedly but progressively with depth, the measured downhole temperatures, and also the homogenization temperatures of the inclusions. At depths less than 800 m, the freezing point depressions decrease from 2.8° to 1.5°C as homogenization temperatures increase from ~160° to 205°C, and then remain nearly constant as temperatures increase to 235°C. Although freezing temperatures are normally expressed as NaCl equivalents, apparent salinities represented in this way are not appropriate for steam condensates containing only negligible Cl. Instead, the salinities are better expressed as H_2SO_4 equivalents. As discussed below, salinities calculated as H_2SO_4 equivalents are substantially different than those based on NaCl equivalents for solutions with solute concentrations >1.5 molal.

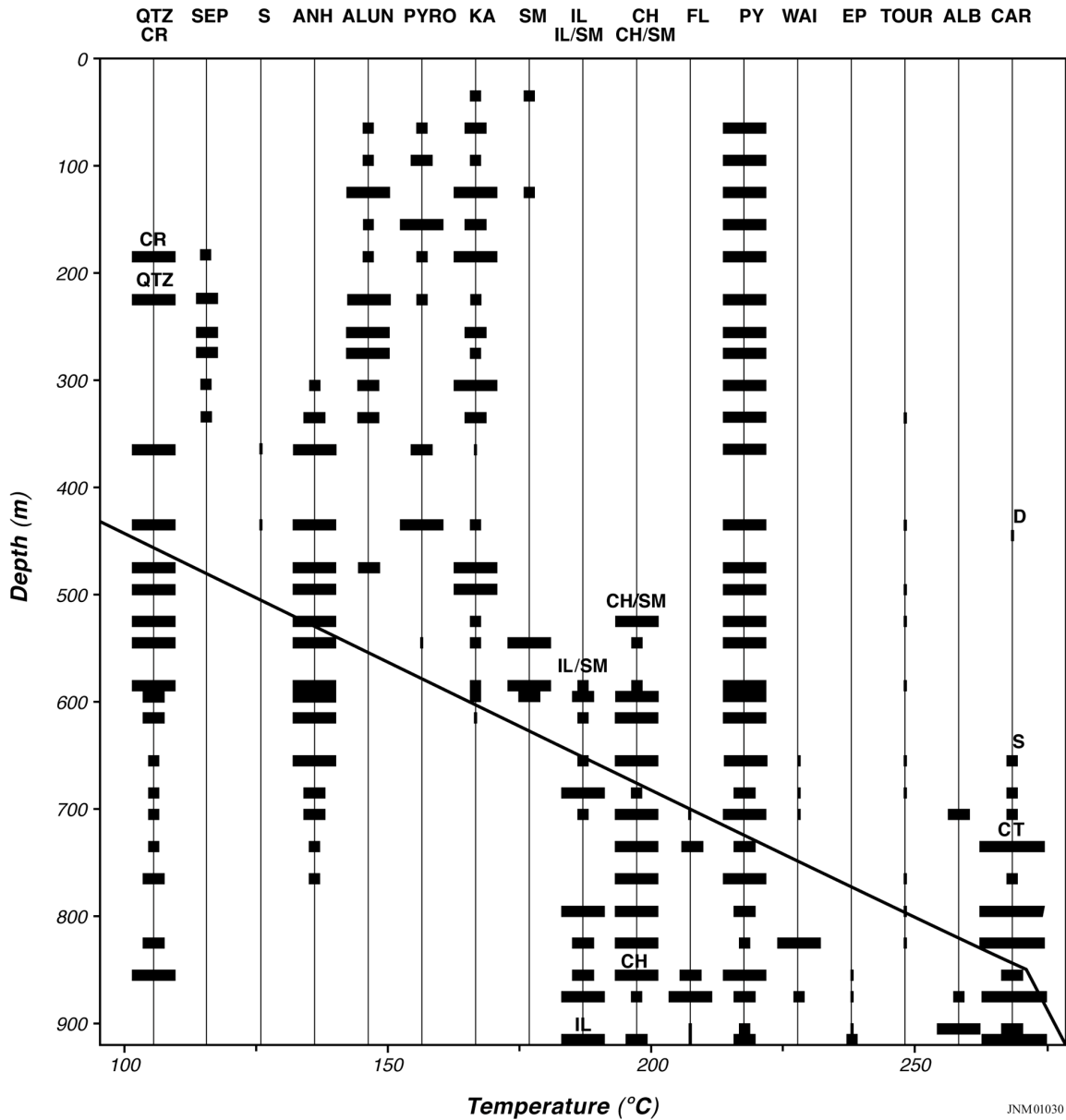


Fig. 2. Distribution of mineral assemblages associated with descending steam condensate and downhole temperatures in T-2. Abbreviations: alun=alunite and natroalunite; anh = anhydrite; car = carbonates (includes dolomite (d), siderite (sid), and calcite (ct)); ch = chlorite; ch/sm = interlayered chlorite/smectite; cr = cristobalite; fl = fluorite; ka = kaolinite and dickite; il = illite; il/sm = interlayered illite-smectite; py = pyrite; pyro = pyrophyllite; qtz = quartz; s = sulfur; sep = sepiolite; sm = smectite. The relative abundance of each mineral is given by the bar width (trace, minor, common, or major). Present-day temperatures are shown by the solid line.

At depths greater than 800 m, where inclusions gave homogenization temperatures hotter than 235°C, the direction of the freezing trend reverses (Fig. 4). Here the freezing point depressions increase with depth and increasing temperature. Inclusions trapped in anhydrite from 1044.9 m in T-8 contain halite-saturated fluids with salinities of 31 weight percent NaCl equivalent. The presence of halite suggests that

salinities of inclusions from depths >800 m are better expressed in the usual way, as NaCl equivalents. Furthermore, the occurrence of chemical precipitates on anhydrite containing hypersaline fluids indicates that boiling towards dryness caused the salinities to increase (Moore et al., 2000, 2002). Boiling, or combinations of boiling and mixing, however, will not explain the progressive decrease in

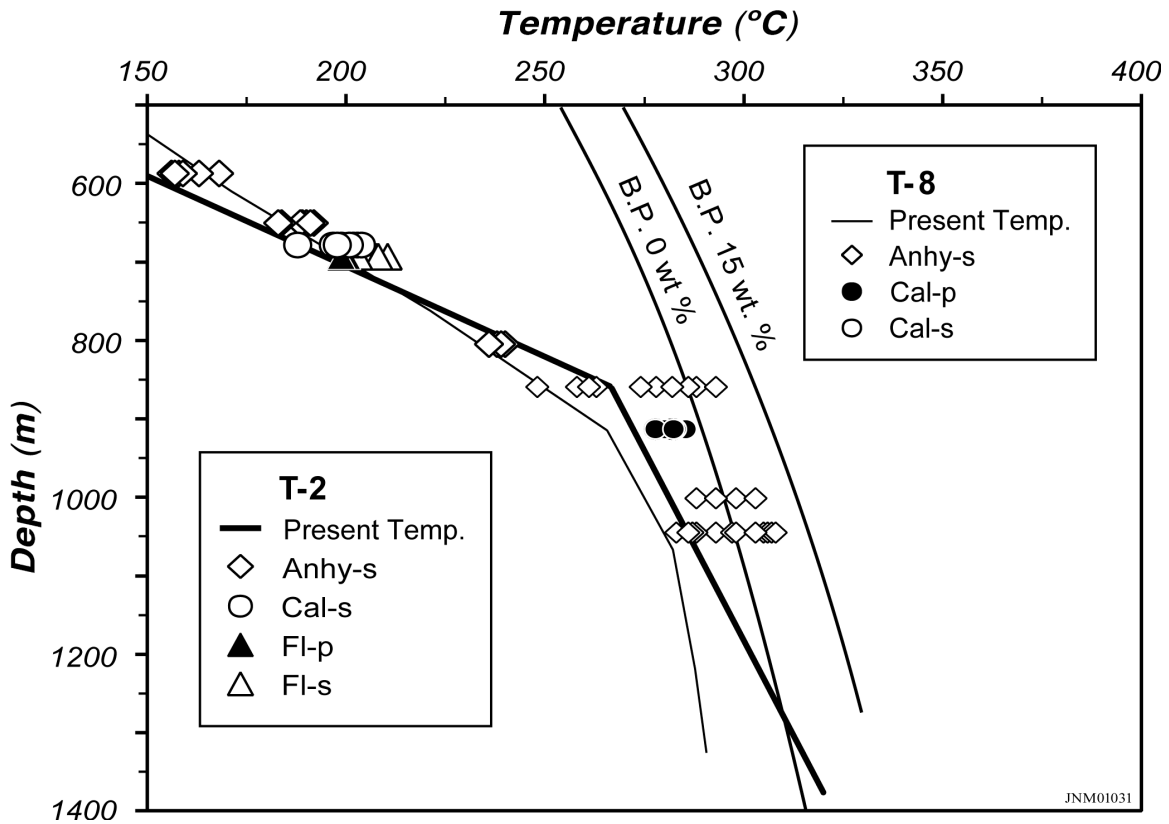


Fig. 3. Homogenization temperatures of fluid inclusions from T-2 and T-8. For reference, the measured downhole temperatures are also shown. Abbreviations: anhy= anhydrite; cal = calcite; fl = fluorite; p = primary; s = secondary.

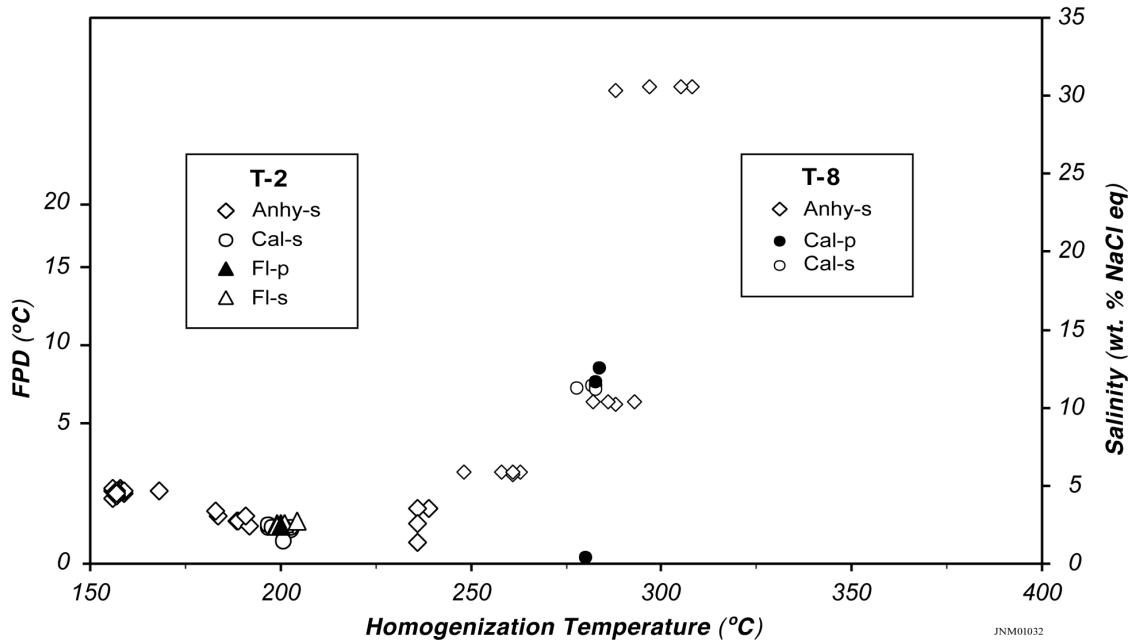


Fig. 4. Homogenization temperatures and freezing point depressions (FPD) of individual fluid inclusions shown in Salinities, expressed as weight percent NaCl equivalent are shown on the right. Abbreviations as in Fig. 3.

the freezing point depression of the fluids at shallower depths. Instead, the temperature-depth-composition relationships suggest that this must be the result of mineral precipitation. In the following section, the effects of water-rock interactions on the composition of the fluids are described.

WATER-ROCK INTERACTIONS

Reaction path simulations of volcanic gas condensation and subsequent water-rock interactions have been treated in detail elsewhere (Christenson and Wood, 1993; Symonds, 1998). Volcanic fumarole condensates are typically hyper-acidic (pH <1) consisting of dilute mixtures of H₂SO₄ and HCl. At temperatures <250°C they generally precipitate elemental sulfur. The condensates aggressively attack unaltered reservoir lithologies, and the ensuing hydrolysis reactions consume hydrogen ions, leading to both the re-dissolution of the elemental sulfur and an overall reduction in the oxidation state of the fluid.

To simulate these processes in the Karaha-Telaga Bodas system, we have selected lake water from Telaga Bodas (Table 1; unpublished data) as representative of the acid-sulfate condensate component in the system, and have numerically reacted these fluids with rock of andesitic composition (Christenson and Wood, 1993) using the reaction path simulator REACT (Bethke, 1992). The initial lake water is assumed to be in equilibrium with elemental sulfur, which is present on the lake floor and in fractures to depths of 440 m. The calculations show that pyrite is also saturated in the lake at 20°C. The CO₂ concentration in the condensate has been set at 0.16 molal, which is typical of arc-type systems (Christenson et al., 2002).

To model descent of the condensate into the system, the temperature of the fluid was incrementally increased from 20° to 250°C, thus simulating conductive heating of the fluids. In addition, the model runs on a “flow-through” basis, where 1 kg of

condensate equilibrates with a total of 200 g of andesite in 100 steps (i.e. 2 g per step), with reacting fluids being isolated from solid reaction products after each progress step. This best simulates the early development of the magmatic-hydrothermal vapor system.

The resulting alteration mineral assemblages and solution pH are portrayed as functions of temperature in Figure 5. The solution pH increases from ~0.4 to 6 over the reaction sequence, with quartz and sulfate minerals predominating at low pH. As the pH increases to 5-6 (neutral), sheet silicates and clays and then calcite become stable.

The relationship between time and space with respect to hydrothermal alteration in volcanic-hydrothermal systems is often difficult to resolve. Indeed, recent transport modeling by White and Christenson (2001) shows that a wide range of alteration minerals may form in environments where both fracture and intergranular permeability affect the processes controlling fluid migration (e.g. convection vs. diffusion). The results presented here are broadly representative of a fluid dominated environment, which occurs in fracture channels, but it should be stressed that near-neutral pH conditions and alteration assemblages may coexist within the lower permeability reservoir rocks nearby.

EFFECTS OF WATER-ROCK INTERACTIONS ON FLUID INCLUSION SALINITIES

The freezing point depression is a colligative property, which, under ideal conditions, is dependent only on the concentration and not the nature of the solute (Atkins, 1978). For aqueous solutions, the ideal relationship is:

$$\text{Freezing Point Depression} = 1.86 \cdot \sum m_i$$

where m_i is molality of the i th species.

| Lake Telagabodas (in mg/l) | lab pH | Ca | Mg | Na | K | SO ₄ | Cl | B | SiO ₂ | As | Fe | Sr | NH ₄ |
|----------------------------|--------|-----|-----|-----|------|-----------------|------|------|------------------|-------|------|------|-----------------|
| 97.10.22 | 0.4 | 394 | 206 | 122 | 30.1 | 30500 | 8850 | 1.31 | 348 | 0.098 | 2320 | 1.38 | 13.9 |

Table 1. All analytical values are listed as mg/l. The pH was calculated for 20°C from ion balance criteria.

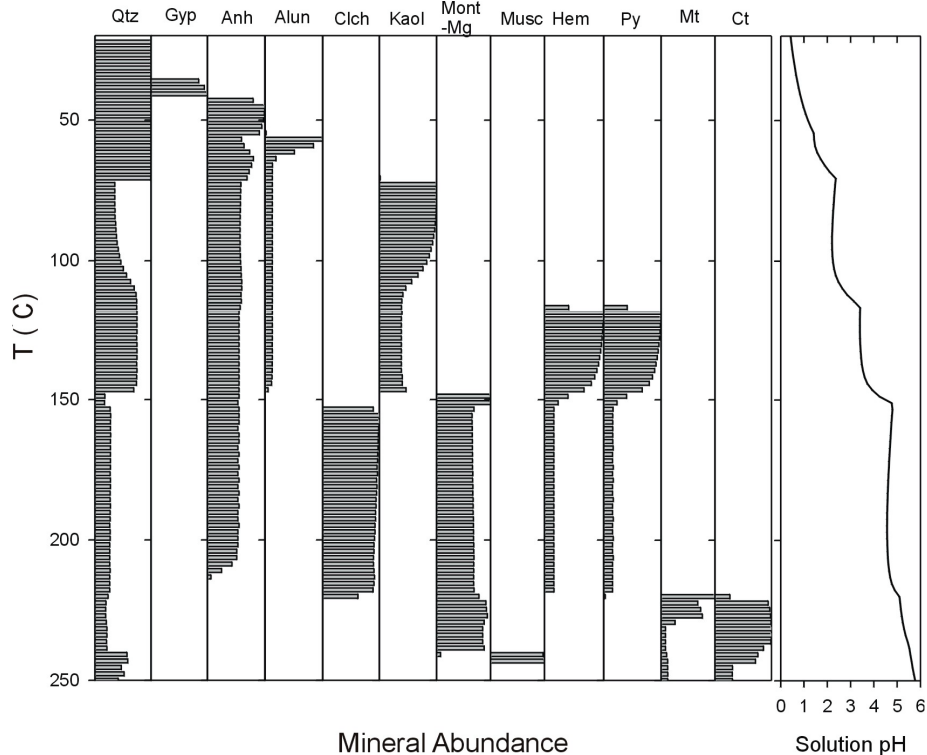


Fig. 5. Simulated mineral assemblages resulting from the reaction of 1 kg of modified Telaga Bodas lake water with 200 g of andesite. Abbreviations: anh = anhydrite; alun = alunite; clch = clinocllore; ct = calcite; gyp = gypsum; hem = hematite; kaol = kaolinite; mt = magnetite; mont-Mg = Mg montmorillonite; musc = muscovite; py = pyrite; qtz = quartz.

The effect of NaCl solutions on the freezing point depression remains close to ideal for concentrations up to 5 molal (Fig. 6). The effects of H₂SO₄, on the other hand, depart strongly from ideal behavior at concentrations above ~1.5 molal, suggesting that this non-ideality should be accounted for in the highly concentrated H₂SO₄ solutions that could be encountered in magmatic hydrothermal systems. For concentrations above 1.5 molal, calculation of salinities on a NaCl equivalents basis will yield higher values. The measured concentrations of SO₄ in Karaha-Telaga Bodas reservoir fluids, however, suggest that the non-ideality contribution to the freezing point depression in the shallower, lower temperature environments is probably not significant.

The reaction path modeling suggests that the inverse correlation between fluid inclusion salinity and homogenization temperature can be explained, at least in part, by uptake of SO₄ and acid neutralization of descending acid-sulfate condensate. As shown in Figure 7, the simulated fluid freezing point depressions decrease from ~2.1 to 0.9°C (a decrease from ~6.4 to 2.7 weight percent NaCl equivalent) as

of the acid neutralized fluid can, in this case, be attributed largely to the combined effects of Cl (which behaves conservatively) and unreacted CO₂.

CONCLUSIONS

The downward percolation of acid-sulfate waters is a common feature of many geothermal systems. Condensates associated with boiling hydrothermal fluids are characteristically SO₄ rich but Cl poor. These fluids aggressively react with the host rocks, leaving a distinctive mineralogic signature characterized by a variety of clays that are stable in low pH environments and alunite. At Karaha-Telaga Bodas, descending steam condensates have produced advanced argillic alteration assemblages that are superseded at depth by veins dominated by anhydrite, pyrite, calcite, fluorite, and chlorite. Fluid inclusions trapped in anhydrite, calcite, and fluorite provide a unique record of the chemical and thermal changes that have affected the fluids. The data indicate that the freezing point depressions and hence, the apparent salinities of the fluids, first decrease as the homogenization temperatures increase from ~160° to 205°C, then remain approximately constant to 235°C, and finally increase, becoming hypersaline as temperatures reach 300°C. Moore et al. (2002) attributed the increase in salinity above 235°C to the boiling off of the condensate within the vapor-dominated portion of the reservoir.

The evolution of the descending steam condensates between temperatures of 20° and 250°C has been simulated using the compositions of water from Telaga Bodas and a typical andesite. These simulations have yielded mineral assemblages and fluid freezing temperatures that are consistent with the observed relationships. They show that quartz, anhydrite, alunite, and kaolin predominate at temperatures <100°C and a pH <2. Anhydrite, clinocllore, Mg montmorillonite, pyrite, and hematite are the major phases at temperatures of 100°-225°C and a pH of 2-5. At higher temperatures (225°-250°C) and a pH of 5-6, calcite and magnetite become stable.

The simulations indicate that the freezing point depression of the descending steam condensate initially decreases as the fluids are heated from 20°-220°C and SO₄ is removed by the alteration minerals. At higher temperatures, between ~220° and 250°C, the freezing point depressions of the modeled fluids remain nearly constant, as do those trapped in the fluid inclusions at these temperatures. Based on the modeling results, the freezing point depressions of the inclusion fluids are interpreted as representing the residual salinity, consisting mainly of Cl and CO₂.

The compositions of steam condensates trapped in fluid inclusions can be better represented in terms of

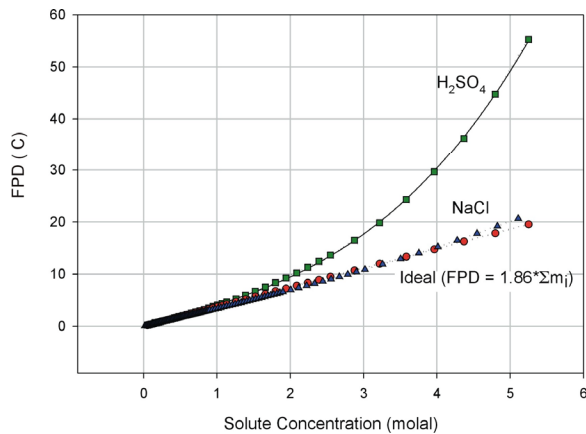


Fig. 6. Freezing point depression effects due to non-ideal behavior in NaCl and H₂SO₄ solutions. Experimental data for NaCl and H₂SO₄ are from CRC Handbook of Chemistry and Physics (1976 ed).

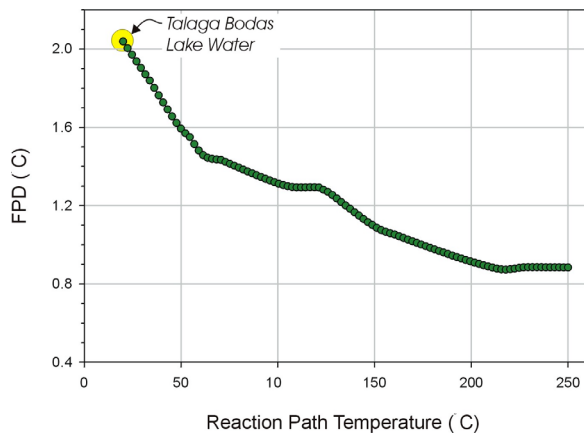


Fig. 7. Simulated effect of water-rock interactions on the salinity of acid condensate.

SO₄ concentrations decrease from >30,000 mg/l (lake water composition) to <1 mg/l in the acid neutralized fluid at 250°C. The relatively high residual salinity

H₂SO₄ equivalents than the more commonly used NaCl equivalents. Compilations of freezing point depressions for NaCl and H₂SO₄ solutions indicate that there are substantial differences in the behavior of these fluids at moderate to high solute concentrations. At concentrations >1.5 molal, freezing point depressions expressed as NaCl equivalents will overestimate the salinity of a Cl poor steam condensate. However, at lower concentrations between 0 and 1.5 molal, the differences in the calculated salinities are insignificant.

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