

## GEOCHEMICAL ANALYSIS OF FLUID-MINERAL RELATIONS IN THE TIWI GEOTHERMAL FIELD, PHILIPPINES

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### ABSTRACT

Geochemical modeling simulations are being used to examine the source of the reservoir fluids in the Tiwi geothermal field and to evaluate the chemical and physical processes responsible for producing observed vein parageneses. Such information can be used to trace the evolution of the Tiwi geothermal field through time.

The React geochemical modeling code (Bethke, 1996) was used to simulate the effects of isothermal and isoenthalpic boiling, conductive cooling and heating, and incorporation of condensed steam, on fluids from the Matalibong area. Predicted mineral stabilities were used to identify mineral indicators for each process. Calcite and anhydrite precipitation were favored by conductive heating, while illite precipitation was favored when condensed steam was added to the reservoir fluid. Reconstructed downhole fluids from borehole Mat-25 are acidic, and are consistent with the presence of illite as the latest alteration mineral in veins.

The processes of isothermal and isoenthalpic boiling could be differentiated from conductive cooling by the presence of epidote and/or calcite during boiling, and illite during cooling. Both boiling and cooling favored precipitation of quartz, K-feldspar, wairakite and pyrite. Ratios of Na, Cl and Br in waters from the Matalibong area relative to seawater indicate a significant component of seawater in reservoir fluids.

### INTRODUCTION

Fluid chemistry and mineralogical relations are being used to help constrain the physical and chemical evolution of the Tiwi geothermal field. Tiwi is a large geothermal field located near the coast of

southern Luzon, Philippines (Figure ). Unocal completed Matalibong-25 (Mat-25) within the western part of the Matalibong sector as a deep corehole and observation well in 1993. Detailed mineralogical studies of this well have documented varied vein mineralogies, despite evidence that temperature variations were small during mineralization. This suggests that fluid-dominated processes such as boiling and mixing controlled the formation of different vein assemblages.

Vein assemblages mark the high permeability zones which channeled fluids in the past; the secondary minerals filling the veins reflect the chemistry of the fluids from which they precipitated. The purpose of this project is to use the secondary minerals to determine the physical and chemical processes that have impacted the Tiwi geothermal field in the past, and will probably continue to alter its character with time. The Tiwi field is especially well suited to this type of study because of the wealth of information that has been compiled on vein parageneses, fluid inclusions, and reservoir fluid chemistries. The vein mineralogy tends to be simple as well.

### VEIN MINERALOGY

Moore et al. (1997) are currently conducting detailed petrologic analyses of veins from the Mat-25 borehole. They have documented at least 8 stages of alteration and mineralization; a brief summary follows. The earliest stage is characterized by phyllic to propylitic alteration of the reservoir rocks (stage 1). Stages 2 through 8 produced veins characterized by quartz + epidote + pyrite (stage 2); anhydrite ± calcite (stage 3); epidote ± quartz ± adularia (stage 4); calcite ± anhydrite (stage 5); wairakite ± epidote ± quartz (stage 6); late calcite filling vugs in wairakite (stage 7); and illite (stage 8). Vein textures and minerals

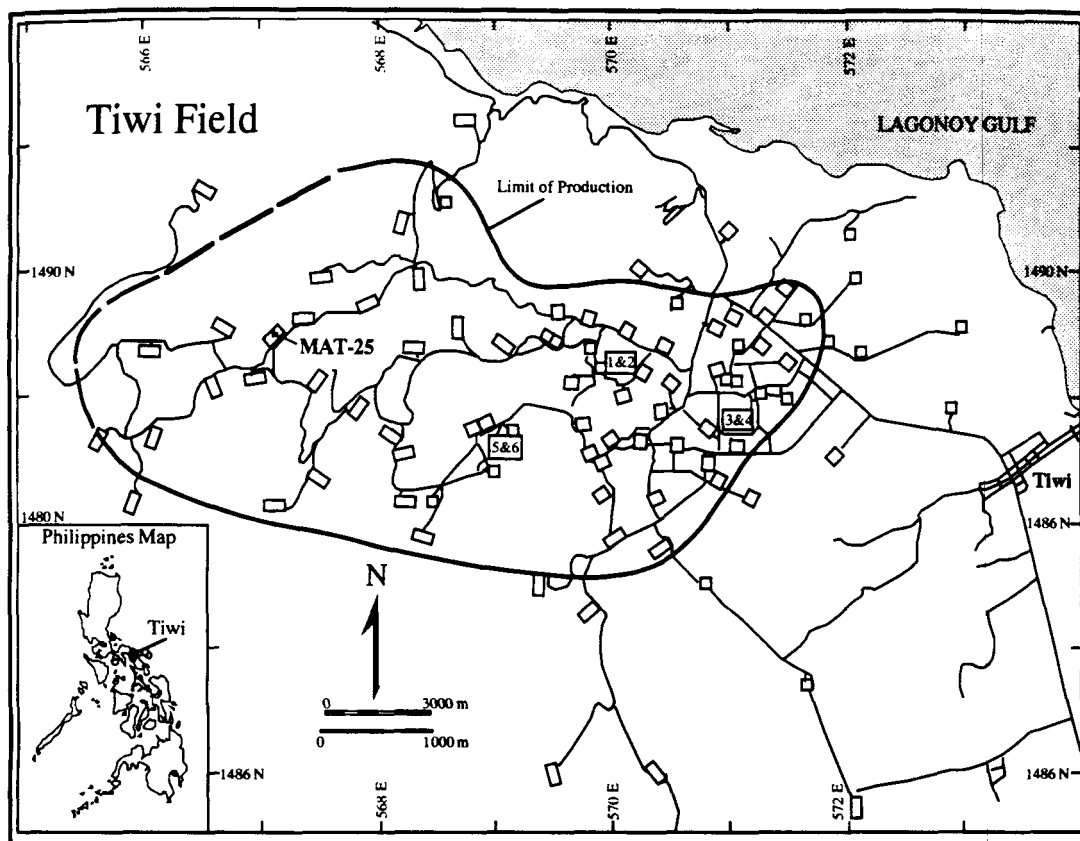


Figure 1. Map of the Tiwi geothermal system showing roads and well pads. Numbered boxes are power plants.

indicate that mineralization occurred mainly in response to boiling or the heating of the thermal waters as they migrated into hotter zones. Fluid-inclusion data demonstrate that the vein minerals were probably deposited from mixtures of fresh and sea water.

### FLUID CHEMISTRY

Relatively complete fluid analyses are available from Mat-25. A representative analysis for this well and its correction to reservoir conditions are given in Table 1. Partial fluid analyses from nearby producing boreholes Mat-11, 17, 20 and 26 are also available, although their overall salinities appear modified by production and are probably not representative of the initial state fluids at Tiwi. Nonetheless, the Na, Cl and Br contents of these waters seem to be directly related to the composition of seawater. Table 2 shows that the Na/Cl ratio of these downhole fluids approximate the Na/Cl ratio of seawater. In contrast, the Cl/Br ratios are higher than seawater, which indicates a consistent gain in Cl or a loss of Br. The ratio of the Cl concentration in the reconstructed downhole water of Mat-25 with that of Cl in seawater yields approximately 30 weight percent seawater in the reservoir fluid, assuming that seawater mixed with a low chloride fluid. Fluid inclusion evidence

suggests that such a low chloride end-member exists, and that it is probably a steam-heated water.

Downhole fluid compositions were reconstructed using the React geochemical modeling code in The Geochemist's Workbench software package (Bethke, 1996). Thermodynamic data were taken from the SUPCRT data base version V8.R5 of the GEMBOCHS data base (Johnson, Oelkers and Helgeson, 1982; Johnson and Lundeen, 1996)<sup>1</sup>. Fluid pressures were assumed to correspond to the liquid/vapor saturation curve for pure H<sub>2</sub>O.

The salinity in the reconstructed downhole Mat-25 water is equal to about 1.2 weight percent NaCl equivalent: carbonate is a major component. The pH of the downhole fluid is 5.3 at 270°C, as compared to the neutral pH of 5.6 at temperatures from 260 to

<sup>1</sup>The equilibrium constants for wairakite in the GEMBOCHS data base were reduced by 0.6 log units (based on a correction of -1500 cal/mole at 250°C) to better represent natural occurrences in the Kawerau (Christenson, 1987) and the Wairakei (Bruton, Christenson and Reyes, 1997) geothermal systems. This correction is thought to range from 0.4 to 0.6 log units; 0.6 was chosen for this study.

Table 1. Major constituents of discharge from well Matalibong-25, sampled on 26-Apr-1993.

	mg/L, as analyzed	mg/L, corrected*
pH	5.72	5.3
SiO <sub>2</sub>	662	512
B	72	55
Cl	6940	5371
SO <sub>4</sub> **	22	219
HCO <sub>3</sub> **		
		662
Ca	114	00
Mg	0.49	0.38

\* corrected for steam and gas loss during production. 22.61% steam, 2 wt.% NCG (97.2 mol% CO<sub>2</sub>, 2.2 mol% H<sub>2</sub>S, NH<sub>3</sub>, Ar, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> not considered).

\*\* SO<sub>4</sub> and HCO<sub>3</sub> represent total S and C; they do not refer to oxidation state or specific aqueous species.

Table 2. Compositions of Matalibong reservoir fluids compared to seawater. Ratios are on a weight basis.

Well	Na, mg/kg	Cl, mg/kg	Br, mg/kg	Na Cl	Cl Br
Mat-11	2519	4359	13.7	0.58	317
Mat-25	3115	5371	NA	0.58	-
Mat-17	4383	8235	24.8	0.53	332
Mat-26	6502	12348	38.6	0.53	320
Mat-20	7977	14639	NA	0.55	-
Seawater	10560	18980	65	0.56	292

NA = not available.

sw = seawater

280°C. The Mat-25 water is therefore slightly acidic, which correlates with the presence of illite as the latest vein mineral. The redox state of the water is characterized by approximately 10<sup>-33</sup> bars O<sub>2</sub>(g) fugacity at 270°C.

The quartz geothermometer based on quartz solubility data from Fournier (1983) yields a reservoir temperature of 261°C, and the discharge enthalpy suggests a temperature of 259°C, whereas the Na-K-Ca geothermometer yields a temperature of 278°C. Although the computed reservoir temperatures are in general agreement, they suggest that Mat-25 water may be a mixture resulting from production from multiple feed zones.

#### CALCULATED MINERAL STABILITY IN MAT-25 WATER

Figure 2 shows a saturation state-temperature diagram for Mat-25 which depicts the theoretical stability of minerals selected for their relevance to the Tiwi field and its operative processes. The Al concentration was required in order to calculate the relative stability of

aluminum-bearing secondary minerals, but was not available. Geothermal waters in New Zealand at 250°C to 270°C (e.g. Christenson, 1987) have measured Al concentrations of about 0.26 mg/kg after correction for steam loss. This value was used in the initial simulations for Mat-25 and yielded quite reasonable results. Fe concentrations were obtained by assuming concentrations consistent with the presence of pyrite, which is ubiquitous in the core samples.

Saturation state-temperature diagrams have been used to identify potential mineral assemblages and to estimate downhole temperature (Reed and Spycher, 1984; Kedaïd and Mesbah, 1996; Tole et al., 1993). The saturation state of a mineral is defined by the logarithm of the ratio of its ion activity product (Q) to its equilibrium constant (K) at the temperature and pressure of interest. A mineral is thermodynamically in equilibrium at a saturation state of 0, undersaturated when the saturation state is negative, and supersaturated when positive.

Although a mineral may be theoretically in equilibrium or even supersaturated, it may not be present in an actual phase assemblage owing to

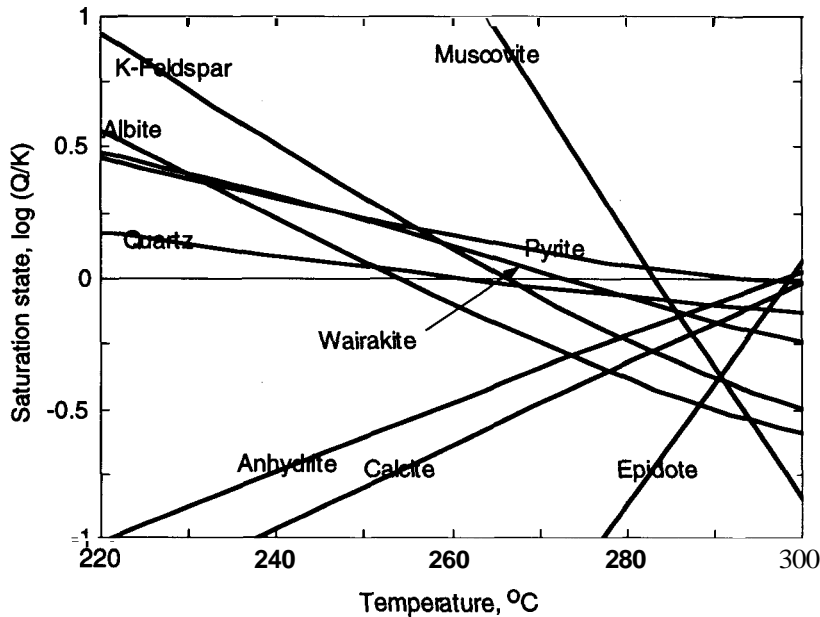


Figure 2. Saturation state of selected minerals as a function of temperature in Mat-25 water.

competition for common ions with other minerals, or kinetic constraints. The reliability of thermodynamic data is also a factor, as is the ability to adequately provide for the thermodynamic consequences of compositional variability, order/disorder, and so on. Nonetheless, saturation-temperature diagrams are a useful tool for delineating mineral-fluid relationships in systems of great chemical complexity. Activity diagrams, in contrast, are restricted to consideration of a limited number of compositional variables, and the solution composition rarely falls in the x-y plane of the diagram.

From the degrees of mineral saturation, Figure 2 suggests that: (a) muscovite would be actively precipitating from Mat-25 water; (b) K-feldspar, quartz and wairakite would be stable with respect to the fluid (i.e. unreactive if present); and (c) epidote<sup>2</sup>, calcite, anhydrite and albite would be unstable in contact with the fluid (i.e. dissolving if present).

Quartz equilibrium suggests a downhole temperature of 260°C, whereas K-feldspar (in this case, completely ordered with respect to Al and Si) equilibrium suggests a temperature of about 266°C. Pyrite is slightly supersaturated at these temperatures, keeping in mind that the Fe concentration was estimated.

<sup>2</sup>The epidote shown in Figure 2 represents a compositional end-member ( $\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}(\text{OH})$ ) of an epidote solid solution with an activity of 1. Future work will be directed at obtaining compositional data for vein minerals such as epidote which are characterized by significant compositional variability. Such data will better define the relationships between fluid and mineral chemistry.

These mineral relationships are consistent with the petrologic observation that illite, for which muscovite serves as a thermodynamic proxy in the above calculations, is the latest secondary mineral to form at Tiwi. However, the thermodynamic data for muscovite in the SUPCRT thermodynamic data base (Johnson, Oelkers and Helgeson, 1992) were obtained from high temperature phase equilibria, and may not adequately represent the illitic phases found in geothermal systems. Therefore, thermodynamic data for "mica-like" or illitic phases were derived from experimental data of Yates and Rosenberg (1996) at 200°C and 250°C. Yates and Rosenberg found that an illitic phase with a ratio of  $0.88\text{K}:\text{O}_{10}(\text{OH})_2$  formed at these temperatures. This illitic phase proved to be significantly more stable than muscovite under Mat-25 reservoir conditions, and thus the degree of supersaturation, or the tendency for precipitation of illite, is greater than that shown in Figure 2.

The proximity of a number of minerals to equilibrium in Figure 2 suggests that small variations in water chemistry, temperature or pressure could produce changes in the mineral assemblage. Therefore, limited degrees of boiling or cooling, for example (see below), could generate different phase assemblages.

The uncertainties and variabilities on produced fluid compositions over time, such as changing percentages of noncondensable gases which can affect pH, together with uncertainties in thermodynamic data and the common need to estimate the concentrations of some elements, dictate that saturation-temperature diagrams be used only as a guide along with other lines of information.

Nevertheless, they can be very useful for determining the potential mineralogical impacts of various chemical and physical processes.

Given our current state of knowledge regarding thermodynamic data and the kinetics of mineral precipitation and dissolution, saturation-temperature diagrams tend to be more useful in predicting mineralogical trends than using geochemical modeling codes to predict a specific subsurface mineral assemblage. Reed (1982) provides a good description of the advantages and disadvantages of the latter approach. A mineral whose thermodynamic data are suspect or which would be kinetically inhibited from precipitating in nature, might precipitate in the simulations and preclude the identification of more likely precipitates. Reaction path simulations providing explicitly for mineral precipitation require significant user intervention to ensure that calculational results reflect known natural constraints. At the same time, the user must be careful that he/she does not force the code into the answer he/she wants; sometimes the difference between simulation results and commonly-held beliefs yields valuable insight.

With saturation-temperature diagrams, the user can identify the tendency for mineral dissolution and precipitation to occur without explicitly modeling them. The drawback of this approach is that the impact of mineral dissolution and precipitation on the system's evolution is not considered. However, identification of appropriate mineralogical trends is the first step in designing more complicated simulations that provide explicitly for mineral precipitation and dissolution.

#### **IMPACT OF BOILING, COOLING, HEATING AND FLUID MIXING ON MINERAL STABILITY**

Even though the chemistry of Mat-25 water seems to be consistent with the most recent vein minerals, it does not directly shed light on the processes that resulted in the varied vein parageneses observed in Mat-25. We do not have compositional data on the fluids that precipitated these minerals, other than fluid inclusion data (Moore et al., 1997). However, we can use a geochemical reaction path modeling code to simulate the impact of changes in the chemical and physical environment on potential mineral precipitation from a representative water from the Tiwi geothermal system. We have selected the reconstructed Mat-25 water for our representative water. Although it may not be the parent fluid at Tiwi, it is adequate to identify the mineralogical indicators of operative physical and chemical processes.

In the following section, we will compute and briefly compare and contrast the mineralogical consequences of isenthalpic boiling, isothermal boiling,

conductive cooling, conductive heating, and the incorporation of condensed steam or acidic gases. Computer simulations were made of each process using the React geochemical modeling code<sup>3</sup> (Bethke, 1996). The systems were assumed to be either closed or open with respect to mass and heat<sup>4</sup>. Simulations explored the consequences of both allowing and suppressing mineral precipitation. Saturation state-temperature diagrams, in which temperature varied as a function of steam loss or gain and conductive cooling or heating, depending on the process under study, revealed trends of mineral saturation from which mineralogical indicators were obtained. The initial fluid composition for all simulations was reconstructed Mat-25 water at 270°C.

#### **Mineralogical effects and comparison with observed vein mineralogy**

Table 3 summarizes the tendency for precipitation of various secondary minerals during conductive cooling (cond. cool), isenthalpic boiling (isoH), isothermal boiling (isoT) and conductive heating (cond. heat) of Mat-25 water, and the effects of adding condensed steam (addtn. of gases). The minerals quartz, K-feldspar or albite, muscovite/illite, wairakite and pyrite have a tendency to form as pH decreases during conductive cooling. Isoenthalpic and isothermal boiling tend to favor quartz, K-feldspar or albite, wairakite and pyrite as well, but the boiling process is differentiated from conductive cooling by the potential formation of epidote and/or calcite, rather than muscovite/illite. The pH increases during boiling. Conductive heating is the only one of the four processes that favors calcite and anhydrite, along with epidote, as pH increases.

The simulations agree with the deduction of Moore et al. (1997) that vein assemblages in stages 3 and 5 composed of calcite and anhydrite seem to indicate heating, whereas the stage 4 quartz, K-feldspar and epidote assemblage forms in response to boiling. Although quartz can form in response to both conductive cooling and boiling, its association with epidote and wairakite in stage 6 would tend to suggest that this vein assemblage formed in response to boiling rather than cooling. The observed replacement

<sup>3</sup>Although React does not explicitly account for boiling and a separate gas phase, the liquid/gas partition calculations were first made independently and the resulting progressive gas losses were used to constrain a series of React simulations, with further corrections as necessary.

<sup>4</sup>The mineralogical consequences of open vs. closed systems were not pronounced in this study because the emphasis is on silicates rather than sulfides. Sulfide stability is sensitive to changes in oxidation state and total sulfide concentration, which evolve differently in open vs. closed systems.

Table 3. Summary of tendency for mineral precipitation from Mat-25 water accompanying boiling, cooling, heating and addition of condensed steam. "X" denotes a tendency for precipitation (*see* text); a blank denotes no impact or tendency for dissolution. "decr." and "incr." refer to decreasing and increasing, respectively; "neglig" denotes negligible.

Process	Calcite	Anhydrite	Quartz	Kspar/ Albite	Muscovite	Epidote	Wairakite	Pyrite	pH	fugacity O <sub>2</sub> (g)
Cond. cool			X	X	X		X	X	decr.	decr.
IsoH boil	X		X	X		X	X	X	incr.	decr.
IsoT boil	X		X	X		X	X	X	incr.	decr.
Addn. of gases					X				decr.	neglig. incr.
Cond. heat	X	X				X			incr.	incr.

f calcite and anhydrite by epidote in this stage might result from the cooling associated with boiling.

be mineralogical response of a system to which condensed steam is added is precipitation of muscovite/illite. The pH decrease caused by addition of acidic gases precludes precipitation of the other minerals listed in Table 3. The condensed steam was assumed to have a composition equivalent to that which would separate from Mat-25 water as it cooled from 270 to 265°C during isoenthalpic boiling. The combination of increasing acidity and the cooling effects of mixing with cooler condensed steam might result in the replacement of calcite and anhydrite by illite in stage 8.

be mineralogical consequences of seawater mixing and seawater heating must also be considered because of the important role that seawater plays in controlling the major element chemistry of Mat-25 waters (e.g. Table 2). Seawater provides a potential supply of sulfate that can lead to anhydrite precipitation. Simulations are being carried out to explore the implications of such mixing/boiling scenarios, and will be described in future publications.

### SUMMARY AND FUTURE WORK

Water from the Mat-25 borehole appears to be composed of about 30 wt. % seawater, as determined from relative ratios of Na and Cl. The Cl/Br ratios of the Matalibong sector waters are higher than seawater, but the Na/Cl ratios are about the same. Chemical geothermometers suggest that Mat-25 produces a mixed water, with the discharge enthalpy and quartz geothermometer yielding lower reservoir temperatures than the Na-K-Ca geothermometer. Produced waters from the Mat-25 borehole are slightly acidic under downhole conditions, and are consistent with the

presence of illite as the latest alteration mineral in veins.

Geochemical modeling simulations of isoenthalpic and isothermal boiling, conductive cooling and heating of Mat-25 water initially at 270°C, and the effects of mixing with condensed steam, illustrate the trends of mineral stability associated with each process. The minerals quartz, K-feldspar, wairakite and pyrite may be indicative of both boiling and conductive cooling. These minerals may be accompanied by illite during cooling, whereas epidote and calcite may form during boiling. The effects of isothermal and isoenthalpic boiling on silicate mineral stability are similar. Conductive heating is distinctive in that it favors calcite and anhydrite in addition to epidote. The incorporation of condensed steam produces illite in response to increasing acidity. Vein mineral assemblages from Mat-25 (Moore et al., 1997) are consistent with these trends.

Results of the above simulations should be considered as a general guide to the mineral assemblages indicative of each process, because differences in starting conditions and combinations of processes could produce different trends. However, these types of calculations can serve as a complementary tool for interpreting mineralogical observations, and serve as the starting point for continued simulations addressing more complex geologic scenarios.

Future modeling will explore more fully the relationships among fluid and mineral chemistry and the processes of boiling, heating, cooling and fluid mixing, especially with respect to seawater. Consideration must be made of variations in mineral composition (e.g. epidote), chlorite stability, and the stability of sulfides, which have been observed in the deeper portions of the Mat-25 core (Moore et al., 1997).

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