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CHEMICAL REACTION PATH MODELLING OF VEIN MINERALIZATION IN THE TONGONAN GEOTHERMAL FIELD, LEYTE

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ABSTRACT

Using chemical speciation and reaction path calculations, boiling and mixing of the recalculated “primary” geothermal water of the Tongonan geothermal system (Leyte, Philippines) were simulated. The main purpose of the computer simulation was to ascertain which of these two processes would be the better precipitating mechanism for ore minerals. Primary water was assumed to be represented by the least diluted well discharge (Well 410) as suggested by chloride-enthalpy diagram.

Adiabatic boiling done from 300 to 100ºC resulted in the precipitation of a sequence containing paragenetically early traces of gold with quartz; followed by quartz, acanthite, chalcocite and late quartz, sphalerite, galena, acanthite, bornite. Interestingly, the pH of the residual boiled solution decreased instead of increased contrary to the commonly accepted increase with the release of volatiles in the steam phase.

Steam-heated end-member used for mixing was generated by titrating the vapor phase at 100ºC which resulted from boiling of primary water and mixing with a sample of the groundwater. Mixing of this steam-heated water with the boiled primary water at 300ºC resulted to the formation of the ore minerals: acanthite, bornite, chalcocite, covellite, galena, pyrite, and sphalerite. Gangue minerals include anhydrite, Mg-chlorite, alunite, kaolinite, muscovite, and quartz.

Observed vein minerals in cores and well cuttings include base metals (sphalerite, galena, chalcopyrite), pyrite, anhydrite, quartz, calcite, epidote-clinozoisite, chlorite with minute specks of Au-Ag electrum,

The results of the chemical modelling suggest that both boiling and mixing processes or a combination of these processes could have precipitated the ore minerals in the Tongonan geothermal system. However, the absence of some minerals predicted by the simulation (e.g. acanthite), likewise, the presence of other minerals in the veins (e.g., chalcopyrite) suggest that physico-chemical conditions other than those assumed in the simulations are prevailing in the system.

1. Introduction

Precipitation of hydrothermal minerals is in response to any one or combination of factors. These include changes in temperature, pressure and composition of the solution through boiling, dilution or water-rock interactions.

Numerical chemical models using chemical speciation and reaction path calculations for different hydrothermal mineral depositional mechanisms, namely boiling, mixing and water-rock interactions are presented in this paper. The objective is to determine what processes are most likely to have caused the precipitation of the hydrothermal minerals in the field. Emphasis is placed on modelling the mass transfer of the relevant components in the geothermal system.

2. The Study Area

The area considered in this study is part of the Greater Tongonan Geothermal Field (TGF) in Leyte Island, central Philippines. The Greater Tongonan Geothermal Field is one of four areas developed for electric power generation in the Philippines. Exploration of the Tongonan Geothermal Field started in the early 1970's.

Detailed surface geological investigations and well logging, together with gravity measurements, show that the TGF is underlain by an Early Miocene basement made up of granodiorite and diorite intrusives. Overlying this intrusive basement is a thick sequence of Tertiary andesitic lava flows with associated pyroclastics and intercalated marine sedimentary rocks (Pagado and Salonga, 1990). The youngest volcanic unit in the area consists of Quaternary andesitic lava flows erupted from different volcanic centres in the field. Several faults intersect the TGF, and the most prominent of these structures are three branches of the Philippine Fault: the West Fault Line, the Central Fault Line, and the East Fault Line.

Fluid chemistry and stable isotope data suggest that the neutral chloride water circulating in the present-day system originated primarily from local meteoric water with a very minimal magmatic contribution (Alvis-Isidro et al., 1993). The parent water for the present-day system had a temperature of about 340°C and a chloride concentration of 13400 mg/kg (Balangue, 1999). The composition of the parent water has been modified to varying extents and this is indicated by the different chemical compositions of geothermal water discharged by springs and wells. Processes which have resulted in these changes are primarily boiling and dilution by a steam-heated water with a temperature in the vicinity of 89°C and "zero" chloride content (Balangue, 1999)

3. Geochemical Modelling

The calculations were performed using the programs GEOCAL, SOLVEQ and CHILLER (Reed, 1989) and the thermodynamic database SOLTHERM (1989 edition). The program GEOCAL was used to convert the concentrations of the components into molalities. SOLVEQ calculated the saturation concentrations of the various component species while CHILLER calculated the reaction paths and chemical speciation for the various processes simulated.

Calculations of the reaction paths resulting from geological processes were performed using the reconstructed primary waters. The processes modeled include 1) adiabatic boiling, and 2) mixing of steam-heated water and boiled primary water.

The selection of the well discharge for the starting fluid composition is based on the Cl_{res}-enthalpy diagram. The closest well discharge to the inferred primary water is from well 410. The shift from the primary water position is mainly by slight vapor loss rather than by dilution. Moreover, the high chloride content (>16000ppm) of the discharge indicates it has undergone relatively limited dilution. The composition of well 410 discharge is given in Table 1 and this is taken from Lovelock et al. (1983).

4. Results

4.1 Boiling with Mineral Fractionation

In this model calculation, one kilogram of the primary water was isoenthalpically boiling from 300°C to 100°C. Mineral phases precipitated are removed from the system as soon as they formed, therefore not allowing the component to back react with the solution. The gases evolved are assumed to remain in contact with the boiling solution. In addition, the boiling solution is assumed to be isolated from the wall rock. These assumptions provide a reasonable simulation of what might happen to a fluid ascending along an open conduit towards the surface leaving behind minerals precipitated from the fluid onto the conduit walls.

Significant changes in the solution composition occur during boiling. Most of the aqueous components steadily decrease in concentration. These include HCO_3, HS, SiO_2, Fe^{2+} (as total iron), Pb^{2+}, Ag^+ and $CuCl_2^-$ (Figure 1A) which decrease in abundance as a result of loss to the gas phases or mineral precipitation.

Sulphate and chloride concentrations, together with Na^+, K^+, Mg^{2+}, Ca^{2+} and Al^{3+} slightly increase with boiling. This is due to their enrichment in the residual solution as other components are consumed by precipitating minerals. The increase in Cl concentration results from the breakdown of the chloride complexes of base metals as well as from the dissociation of HCl with the accompanying lowering of temperature.

Although the simulation predicts mineralization composed dominantly of quartz, small quantities of sphalerite, galena, bornite, acanthite, gold and chalcocite are also produced (Figure 1B). The calculations suggest that a sequence containing paragenetically early traces of gold with quartz would be precipitated. This would be followed by quartz + acanthite + chalcocite and late quartz + sphalerite + galena + acanthite + bornite.

There is also rapid degassing at the onset of boiling (Figure 1C). The gas composition is dominantly H_2O, H_2S and CO_2, with traces of H_2, HCl, SO_2, S_2 and CH_4. The amount of H_2O in the gas increases as the temperature decreases. Since the gases are not fractionated, the relative amount of H_2S and CO_2 in the gas becomes reasonably invariant with boiling. However, the concentrations of other gases like H_2, HCl, SO_2, S_2 and CH_4 steadily decrease with boiling.

High chloride concentration in the solution makes chloride complexes dominant for all ore metals except Au, for which the chloride complex is secondary to bisulfide (Figure 1D). For the bisulfide complex of gold, precipitation of gold is a consequence of pH.

All of the complexes remain stable until the sulfides start to precipitate. As the chloride complexes become less stable metals are released to form sulfide minerals. In neutral to weakly acidic solutions, the cooling of the solution due to boiling is particularly effective in depositing metals transported as chloride complexes. This is due to the strong temperature control on solubilities of these complexes (Seward and Barnes, 1997). The precipitation of base metals yields hydrogen ion to the solution thereby further lowering the pH.

The pH of the solution slightly increases in the first 5° of boiling after which hydrogen ion concentration steadily increases with boiling. The predicted lowering of pH with boiling is opposite to the normally observed increase in pH with boiling resulting from separation of acidic components into the vapor phase (Drummond and Ohmoto, 1985). However, if the solution is acidic enough (i.e. contains significant concentrations of associated HCl and HSO_4^-), boiling may cause a decrease in pH because these two acidic components will dissociate during cooling so that H^+ concentrations rise in the aqueous phase (Figure 1E). These effects offset the consumption of H^+ in the aqueous phase caused by CO_2 degassing (Reed, 1992).

4.2 Mixing Steam-Heated Water and Primary Water

A steam-heated water was generated by titrating meteoric water (HC-1, Tansinsin and Fajardo, 1972) with the vapor phase left over from the boiling run at 100°C and 1 bar. The ground water composition used is given in Table 1.

The condensation of the vapor phase into the meteoric water produced an acid (pH = 4.69)-sulfate-chloride water, with a temperature of 89.1°C that is at equilibrium with pyrite, gibbsite and kaolinite.

The aqueous phase of the recalculated primary water at a temperature of 300°C (pH = 5.12) was numerically titrated with the steam-heated water (temperature = 89.1°C and pH = 4.69). Pressure was kept slightly above the boiling saturation pressure to avoid boiling of the solution. For this calculation, gases were not allowed to escape and minerals formed were removed from the system. This would closely approximate the mixing of two solutions along an open fracture but isolated from the wall rock.

The composition of the resulting solution changes as mixing progresses. Aqueous components that decrease in total concentration with mixing include Cl^-. Na^+, K^+, $SiO_{2(aq)}$ and HCO_3. On the other hand, Mg^{2+} concentration shows an increase in the solution (Figure 2A).

The pH of the resulting solution decreases with mixing from a starting pH of 5.12 down to 3.6.

Acidification of the primary water by the steam-heated water results in the formation of silicates, sulfates and ore minerals (Figure 2B). The "ore" produced includes early quartz, anhydrite, sphalerite, galena, Mg-chlorite, chalcocite, and bornite. In the middle stages of the titration, veins are predicted to consist of quartz, anhydrite, muscovite, sphalerite, covellite, and pyrite. Near the end of the mixing, quartz, alunite, galena and pyrite are the minerals present.

The absence of gold in the assemblages predicted by the simulated mixing may be due to the increase in sulfate activity overriding the effect of acidification, thus keeping the Au-complex in solution.

For Ag and base metals, the dominant complexes transporting these metals are the chloride species. But as mixing progresses (or at about 240°C), there is a predicted change in complexes from chloride to bisulfide (Figure 2C).

5. Discussion

5.1 Comparison of the results

Modelling of the two depositional processes can be used to predict the precipitation and dissolution of hydrothermal minerals. The calculations show that these two processes are effective in precipitating the sulfides of Fe, Ag, Cu, Pb and Zn, as well as silicate minerals. However the results for each process modeled show differences in terms of paragenesis or sequence of mineral precipitation, amounts of minerals formed, and change in the composition of the resulting solutions (e.g. pH change).

Comparisons of vein deposition sequences predicted by the boiling and the mixing calculations, show that precipitation of base metals sulfide and gold occurs at different stages and to different extents in each case.

Boiling of parent waters precipitates early gold, middle acanthite and chalcocite and late sphalerite-galena-bornite together with quartz as the gangue mineral. Mixing of the steam-heated water and parent water leads to the early formation of base metal sulfides with the appearance of covellite at the expense of bornite and chalcocite.

Aside from the sequence of precipitation, the relative amounts of sulfides also differ. Of the two vein forming processes, mixing appears to be the most effective in depositing base metals. However, gold is not predicted to precipitate in any of these processes. Boiling results in saturation of the solution with Au resulting in deposition of this metal. Once precipitated, gold persists throughout the process of solution evolution.

Deposition of some minerals, particularly silicates, sulfates and oxides, is predicted in only one or two models. For example, a distinctive feature of models involving mixing of steam-heated and parent waters is the appearance of kaolinite, covellite, anhydrite and alunite.

5.2 Comparison with observed vein mineralization

The objective of using the reaction path and chemical speciation calculations was to determine the effectiveness of the different depositional mechanisms in precipitating hydrothermal minerals both as vein filling and as replacement of primary minerals in the wall rocks.

Boiling of "inferred" parent w solutions and mixing results in the precipitation of minerals that match the observed vein in the TGF, e.g. silicate and sulfate minerals, base metals and silver sulfides and native gold (as electrum). Marked differences, however, are observed in terms of relative proportions of individual minerals. Silver and base metal sulfides only occur in the TGF as trace minerals subordinate to pyrite and silicates. However, in the calculations, the former predominates over the latter. This may be a consequence of forcing equilibration with the sulfide minerals to obtain the saturation concentration for the dissolved metals.

The fact that the present-day solution in the TGF is saturated with Ag, Au and base metals is consistent with the presence of sulfides in well precipitates, blockages and ejecta as reported by Arevalo (1985).

The appearance of particular hydrothermal alteration minerals in the TGF has been observed to be temperature-dependent and key minerals are used as geothermometers.

The calculations failed to predict the formation of a number of hydrothermal minerals which have been reported in the TGF. A mineral commonly observed in TGF is calcite. Its absence in the mineral assemblages predicted using the calculations may be consequence of low solution pH and/or low f_{CO2} in the reconstructed parent water.

Among the ore minerals, the observed Cu-sulfide in the TGF is chalcopyrite. None of the calculations predict the occurrence of this mineral. In most cases, chalcocite and bornite, with covellite are predicted by the numerical modelling.

In conclusion, although the calculations lead to a close approximation of the observed mineralogy, there are inconsistencies between the models and the observed mineralogy and mineral parageneses. These may be explained by the fact that the models are based on assumptions that represent an oversimplification of the real processes. In the calculations there was a lack of consideration between the hydrothermal solutions and previously formed minerals for the boiling and mixing runs> Progressive changes in the permeability and porosity of the wall rock and the fracture system were also not considered. These parameters would affect the flux rate for the solution thereby affecting the amount of fresh solution circulating in the system.

6. Acknowledgements

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TABLE 1 Water compositions used in chemical reaction path and chemical speciation calculations

	Well 410 discharge[1]	Calculated primary water	Cold ground water	Steam-heated water
PH	6.6	5.1	6.6	4.7
Component	molality	molality	molality	molality
Cl^-	5.04E-01	4.69E-01	1.41E-04	6.44E-04
SO_4^{2-}	3.65E-04	3.53E-04	8.54E-04	2.76E-04
HCO_3^-		1.29E-03	3.44E-05	1.10E-05
HS^-		6.32E-03	2.99E-05	1.68E-04
$SiO_{2(AQ)}$	2.32E-02	8.29E-03	8.99E-04	2.80E-04
Al^{3+}		9.29E-07	4.78E-05	9.38E-07
Ca^{2+}	6.10E-03	5.90E-03	1.03E-03	3.39E-04
Mg^{2+}		2.35E-04	6.99E-04	2.30E-04
Fe^{2+}		6.56E-08	4.84E-05	2.30E-10
K^+	28E-02	6.07E-02	4.60E-05	1.51E-05
Na^+	4.10E-01	3.96E-01	6.09E-05	2.00E-05
Zn^{2+}		1.39E-04		
Cu^+		4.33E-06		
Pb^{2+}		1.26E-05		
Ag^+		3.87E-06		
$AuCl^{2-}$		6.67E-07		
Gas in mole %				
H_2O	9.95E+01			
CO_2	5.04E-01			
H_2S	2.08E-02			

[1] Lovelock and Baltazar, 1983

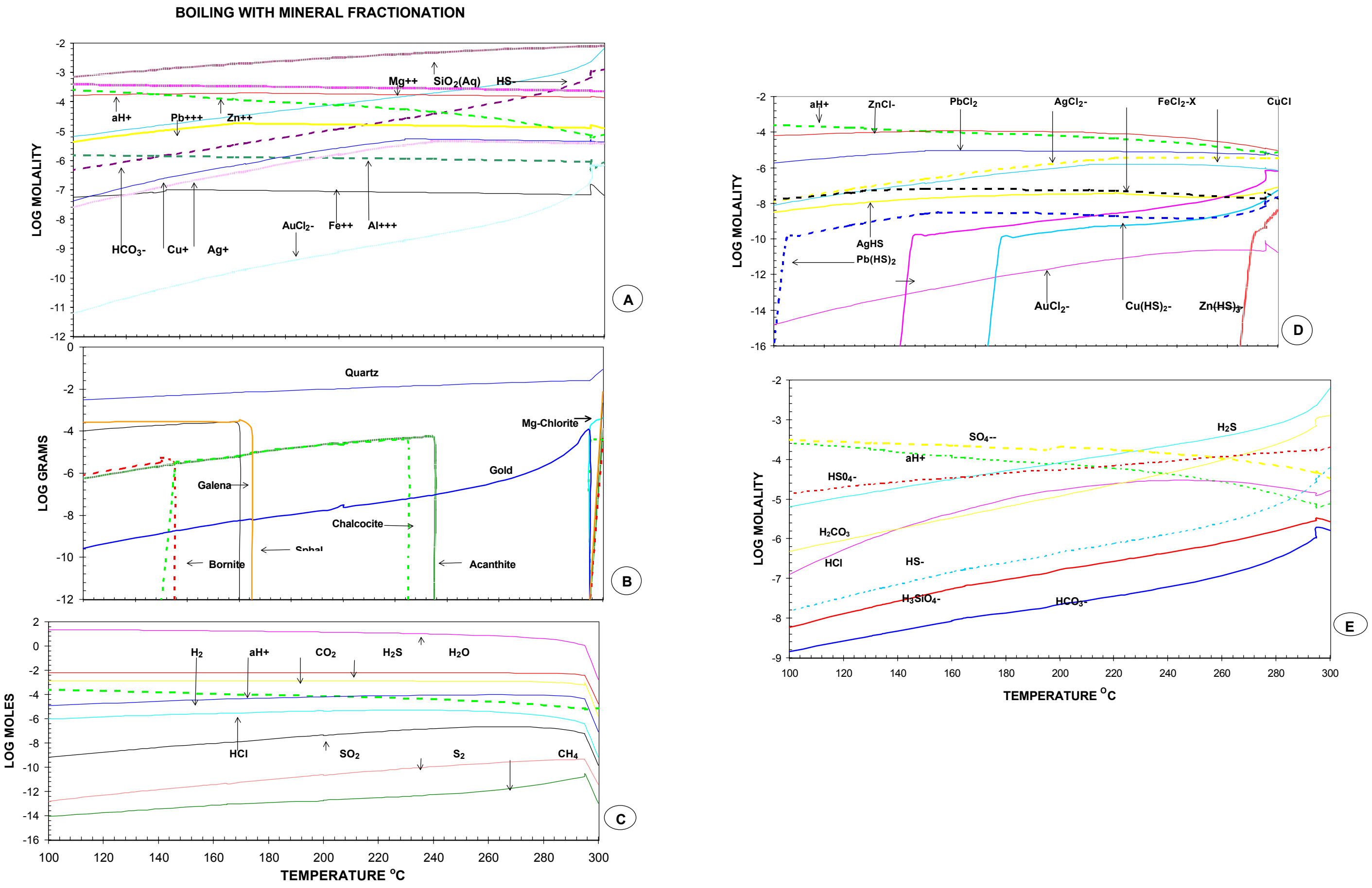

Figure 1 Results of isoenthalpic boiling of 1 kg of reconstructed primary water from 300□C to 100□C.
A. Total molality of a portion of the aqueous component species. Activity of H+ is shown for which the scale refers to –log activity.
B. Rate of precipitation of minerals per degree of temperature change.
C. Moles of species in the gas phase, continuously in equilibrium with the minerals and the aqueous phase.
D. Individual species of the principal ore metal complexes.
E. Molality of inividual species of acidic components.

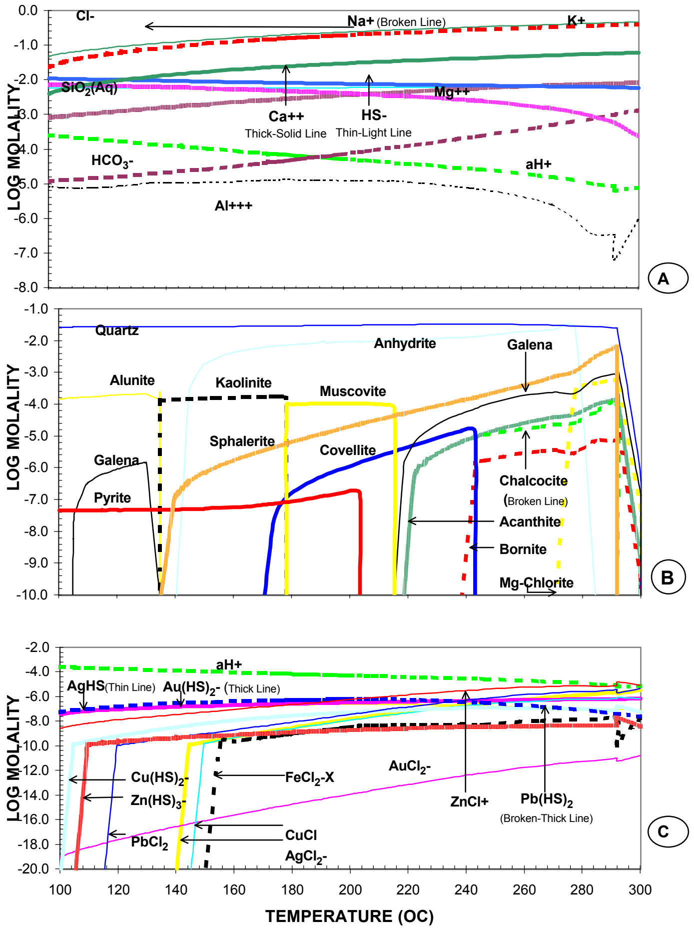

Figure 2 Results of calculations of mixing of steam-heated water and primary solution with mineral fractionation.

A. Total molality of a portion of the aqueous component species. Activity of H+ is shown for which the scale refers to –log activity.

B. Rate of precipitation of minerals per degree of temperature change.

C. Individual species of the principal ore metal complexes.