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Geothermal water-rock equilibria at Palinpinon, Philippines: insights from major reactive gas constituents

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Abstract

Eleven producing wells of the Palinpinon geothermal field have been monitored for major reactive gas components over the period 1998-2010. Based on H₂O, CO₂, H₂S, H₂, and CH₄ relative concentrations, we estimated redox conditions (controlled by the Fe(II)-Fe(III) buffer), a possible equilibrium mineralogical assemblage (made up by epidote-prehnite-quartz-calcite-pyrite-pyrrhotite), deep equilibration temperatures (up to 350°C), and CO₂ partial pressures (up to 12 bar) for the deepest, liquid-dominated portions of the reservoir.

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1. Introduction

The Palinpinon geothermal field has been supplying steam to the power plants of Palinpinon I (112 MWe) and Palinpinon II (80 MWe) since 1983 and 1993, respectively. Field exploitation and reinjection have been inducing large variations in chemical and physical properties of fluids since 1980’s (e.g. [1]). Steam production currently occurs from an expanded two-phase reservoir, although wells discharging single-phase vapor are also present. Eight of the eleven wells considered for this study were characterized by an excess enthalpy of +20 to +55% over the 1998-2010 monitoring period. The assessment and prediction of changes in non-condensable gas concentrations has become one of the aspects of greatest importance for the management of the field. A gas-geochemistry approach has been used to i) interpret geochemical changes in the geothermal reservoir, ii) define the sources of the gases, and iii) get a better understanding of the ongoing natural and exploitation-related processes controlling gas concentrations in...
the system. The present contribution is focused on major reactive components routinely analyzed at Palinpinon, i.e. $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{H}_2\text{S}$, $\text{H}_2$, and $\text{CH}_4$, and benefits from a large, high-quality database of 130 chemical analyses.

2. Materials and methods

Eleven producing wells, selected on the basis of geographical and reservoir engineering criteria, were sampled over the period 1998-2010. Chemical analyses are representative of the different sectors of the field: wells OK-5, OK-9D, BL-3D and LG-3D drain the main upflow zone; wells OK-2, PN-15D and PN-22D discharge from a two-phase zone in the central part of the field; wells NJ-5D, NJ-8D, SG-2 and SG-3D are representative of relatively peripheral sectors of the field. Steam samples were collected from the pipelines by means of a portable (Webre) separator. Geothermal gases were collected in pre-evacuated glass bottles containing alkaline solution (4N NaOH; [2]). Analyses of major gases where made by wet chemistry ($\text{CO}_2$ and $\text{H}_2\text{S}$), and gas chromatography ($\text{CH}_4$, $\text{H}_2$).

3. Results and discussion

Fluids discharged from the Palinpinon geothermal wells have low gas/steam ratios (generally below 1 mmol/mol). The non-condensable fraction of the gas phase is relatively uniform in composition, with $\text{CO}_2$ being the principal constituent, followed by $\text{H}_2\text{S}$ and $\text{N}_2$. Altogether, Palinpinon geothermal gases are interpreted to represent a mixture of deep-seated, hydrothermal-volcanic gases, and meteoric gases deriving from both the natural recharge of the system and reinjection. The input of volcanic gas from underlying magmatic system is demonstrated by high $\frac{^{3}\text{He}}{^{4}\text{He}}$ ratios in the range 7 to 7.9 RA [3].

Redox equilibria (Fig. 1A) have been investigated by comparing $\text{H}_2$ and $\text{H}_2\text{O}$ analytical data, expressed as iso-molar concentration ratios, with the corresponding equilibrium ratios calculated under liquid conditions at different temperatures (up to 350°C). The redox potential of the reservoir, here expressed in terms of the measurable $R_H$ parameter ($R_H = \log (X_{\text{H}_2}/X_{\text{H}_2\text{O}})$, appears to be best approximated by the Fe(II)-Fe(III) hydrothermal buffer [4]. Reasons for minor scattering of the representative points with respect to the reference equilibrium line, include: i) the use of bottom-well inferred temperatures not adequately representative of the effective temperature in the reservoir, ii) occurrence of secondary processes, e.g. phase segregation, which allow representative points to scatter in the diagram because of the low solubility of $\text{H}_2$ in aqueous solutions [4].

A set of compositional grids, based on iso-molar concentration ratios of other major gas constituents, has been calculated to investigate gas-water-rock equilibria at depth. The equilibrium theoretical curves have been computed under the assumption that the Fe(II)-Fe(III) buffer effectively controls redox conditions in the liquid-dominated portions of the geothermal reservoir. Fig. 1B shows that $\text{H}_2\text{S}/\text{CO}_2$ molar ratios plot within the equilibrium compositional grid when specific mineralogical assemblages are assumed to control the chemistry of circulating fluids. In particular, water-rock equilibration temperatures between 250 and 325°C, consistent with temperatures measured at bottom well and inferred by solute geothermometry, are obtained when $\text{CO}_2$ ($f_{\text{CO}_2}$) and $\text{H}_2\text{S}$ ($f_{\text{H}_2\text{S}}$) fugacities are assumed to be controlled by the clinozoisite-quartz-calcite-prehnite and pyrite-pyrrhotite-prehnite-epidote assemblages, respectively. Although no detailed information about the alteration mineralogy of the Palinpinon reservoir is currently available, all these minerals are considered ubiquitous, geochemically active rock constituents of high-temperature geothermal reservoirs. In the literature, several additional mineralogical assemblages have been proven to control $f_{\text{CO}_2}$ and $f_{\text{H}_2\text{S}}$ variations in hydrothermal systems (e.g. [5, 6]), but none of the equations developed for these assemblages produces reasonable results when applied to Palinpinon gases.
H₂S/CO₂ gas molar ratios provide consistent indication of possible attainment of water-rock equilibrium at depth, even though \( f_{\text{CO}_2} \) is often assumed to act as a temperature-independent, externally fixed parameter. By iteratively running the calculations with \( f_{\text{CO}_2} \) being the sole independent variable over the range 1-20 bars, we achieved best fitting conditions between analytical values and expected equilibrium temperatures for \( f_{\text{CO}_2} \) values between ~3 and ~13 bars. In particular, we obtained equilibration temperatures in the range 250-300°C and 270-325°C for \( f_{\text{CO}_2} = 5 \) and 12 bar, roughly consistent with present-day (P=5.5 MPa) and pre-exploitation (P=11 MPa) average total pressure (with \( P \approx P_{\text{H}_2\text{O}} + P_{\text{CO}_2} \)) conditions in the reservoir, respectively.

Fig. 1. \( \log (\text{H}_2/\text{H}_2\text{O}) \) vs. temperature (box A) and \( \log (\text{H}_2/\text{H}_2\text{O}) \) vs. \( \log (\text{H}_2\text{S}/\text{CO}_2) \) (box B) diagrams for Palinpinon geothermal gases. Box A: curves represent different redox buffers (mgt=magnetite; epid=epidote; prehn=prehnite; qtz=quartz; Fe(II)-Fe(III)) and ‘volcanic’ are typical hydrothermal and volcanic redox buffers, respectively [4]; D’Amore-Panichi is the empirical geothermal buffer by [7]. Box B: compositional grid computed under the assumption that CO₂ (\( f_{\text{CO}_2} \)) and H₂S (\( f_{\text{H}_2\text{S}} \)) fugacities are buffered by the clinozoisite-quartz-calcite-prehnite and pyrite-pyrrohotite-prehnite-epidote assemblages, respectively. Calculations account for different equilibrium temperatures (number above the line “vapor”) and gas fractions (y values) in the reservoir. Curves “vapor” and “res. liquid” represent maximum vapor gain and vapor loss, respectively, with respect to the composition expected for the discharge of a pure equilibrium liquid phase (“liquid”).

Fig. 2. \( \log (\text{H}_2/\text{H}_2\text{O}) \) vs. \( \log (\text{CH}_4/\text{CO}_2) \) diagram for Palinpinon geothermal gases.
Under redox conditions buffered by the Fe(II)-Fe(III) couple, we obtain CH$_4$/CO$_2$ equilibration temperatures in reasonable, but not complete, agreement with those estimated on the basis of the H$_2$S/CO$_2$ gas molar ratios. In fact, in the log H$_2$/H$_2$O vs. log CH$_4$/CO$_2$ space (Fig. 2), most of the samples still plot within the field of equilibrated hydrothermal fluids, but at slightly higher temperatures (between 275 and 360°C) compared to Fig. 1B, and negative y values (field of gas-depleted fluids). This feature is interpreted as a consequence of the fact that CH$_4$ is a slower-reacting species compared to H$_2$S. Two possible scenarios can be then envisaged: i) CH$_4$/CO$_2$ molar ratios reflect equilibrium conditions effectively attained at greater depth and higher temperature within the system (“roots of the geothermal system”), and do not re-equilibrate at shallower depths (“reservoir”) because of the rapid transfer of the gases between the two zones; ii) the higher apparent equilibration temperatures indicated by the couple CH$_4$/CO$_2$ are preserved despite relatively long residence times of the gases in the “reservoir”. In this case, CH$_4$ does not adjust to higher, “appropriate” concentrations due to the lack of suitable catalysts, able to enhance the inorganic reduction of CO$_2$ to CH$_4$.

4. Conclusions

Gas geochemistry of major reactive constituents has proved to be a successful tool in the assessment of physical processes and water-rock interactions occurring in the Palinpinon geothermal system. The principal conclusions of this work can be summarized as follows: i) H$_2$O, CO$_2$, H$_2$S, H$_2$, CH$_4$ relative concentrations reflect water-rock equilibria attained at temperatures between 250 and 320°C in the deepest, liquid-dominated portions of the geothermal system; ii) redox conditions are buffered in the system by the Fe(II)-Fe(III) couple; iii) $f_{\text{CO}_2}$ (up to 12 bar) and $f_{\text{H}_2S}$ values are likely controlled by an assemblage composed of epidote-prehnite-quartz-calcite-pyrite-pyrrhotite.

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References