Geochemical modeling of water-rock interaction processes in the geothermal systems of the continental rift zone of East Africa and related implications

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ABSTRACT

Reaction path modeling of the dissolution of an average pantellerite from Menengai volcano in pure water and in diluted magmatic water was performed to investigate the impacts of rock dissolution and absorption of deep magmatic gases on the chemistry of the aqueous solutions circulating in the high-temperature geothermal reservoirs of Menengai and other similar systems of the East African continental rift zone. It was found that sulfate and sulfide as well as dissolved carbonate species are entirely contributed to the aqueous solution by absorption of deep magmatic gases, whereas Cl and F are supplied to the aqueous phase by both rock dissolution and absorption of magmatic gases.

Since there is a satisfactory match between the data obtained through computer experiments and the analytical solute concentrations of Menengai geothermal liquids, reaction path modeling results can be used to investigate the aqueous speciation of these liquids and to derive practical implications on the expected performance of Na-K and K-Mg geothermometers and the low silica scaling potential of Na-HCO$_3$ liquids.

This study represents a preliminary attempt to understand the geochemistry of the Na-HCO$_3$ geothermal liquids typically present in the continental rift zone of East Africa. A significant research effort must be done to investigate the peculiarities of these geothermal systems, especially in terms of hydrothermal mineralogy and fluid geochemistry and to improve the presently used geochemical techniques, with possible implications on geophysical methods, especially magnetotellurics.

1. INTRODUCTION

Sodium-HCO$_3$ geothermal liquids are present in the continental rift zone of East Africa, including some wells of the Olkaria geothermal system (Karingithi et al., 2010), the Menengai geothermal system (Kipng'ok, 2011), the Lake Bogoria hot springs (Cioni et al., 1992), as well as several geothermal sites along the main Ethiopian Rift Valley (Gizaw, 1996). The Na-HCO$_3$ character of these geothermal liquids contrasts with the Na-Cl composition of most geothermal "mature" liquids. Actually, in the Olkaria geothermal system, Na-Cl liquids prevail over Na-HCO$_3$ liquids, but reservoir chloride content is relatively low, with a median of 373 ± 185 (1σ) mg/kg, and the most abundant dissolved constituent is total CO$_2$, with a median of 646 ± 4706 (1σ) mg/kg (Karingithi et al., 2010).

Although available data for volcanic gases are comparatively limited in number, they indicate that subduction-zones volcanic gases are enriched in Cl relative to hot-spot and divergent-plate volcanic gases (e.g., Symonds et al., 1994; Sawyer et al., 2008). Therefore, the comparatively small supply of Cl-bearing magmatic gas species (chiefly HCl) in the root of the continental-rift geothermal systems might be responsible of the comparatively low Cl contents of the geothermal liquids of interest, accepting that these are produced through neutralization of the initially acidic meteoric-magmatic aqueous solutions circulating at depth as suggested by several authors (e.g., Giggenbach, 1997).

This communication intends to present preliminary results obtained through geochemical (reaction-path) modeling of water-rock interaction processes (Helgeson, 1968; Helgeson et al., 1969, 1970) presumably occurring in the geothermal systems located in the continental rift zone of East Africa and to draw related implications.

2. SETTING UP THE REACTION PATH MODELS

Two distinct reaction path modeling simulations were carried out to investigate separately the impacts of rock dissolution and absorption of deep magmatic gases on the chemistry of the aqueous solutions circulating in the high-temperature geothermal reservoirs of the continental rift zone of East Africa. Both runs were performed by means of the software package EQ3/6, version 8.0 (Wolery and Jarek, 2003), using the thermodynamic database data0.ymp.R5, whose characteristics are described by Wolery and Jove-Colon (2007).

Both computer program experiments were performed in reaction progress mode assuming bulk rock dissolution. In other words, no constraint was placed on the dissolution rates of primary solid phases. This is a reasonable approach for single-phase glassy rocks, which are not uncommon at Menengai (e.g., Omondi, 2011) and other volcanoes of the East African rift zone.

A pantellerite was selected as representative rock, averaging six chemical analyses of the Menengai post-caldera lavas, including Cl and F among the analyzed constituents (Leat et al., 1984). Although no data is available for the S content of these rocks, it is

reasonable to assume that it is nil to negligible (Macdonald et al., 2011). Consequently, it can be anticipated that S species are entirely contributed to the aqueous solution by the deep magmatic source whereas Cl and F are contributed by both absorption of deep magmatic gases and rock dissolution.

The two computer experiments were carried out at 250°C, under closed system with a defined set of secondary solid phases which are allowed to precipitate (albite, alunite, anhydrite, calcite, clinochlore-14A, clinozoisite, daphnite-14A, epidote, fluorite, K-feldspar, muscovite, paragonite, prehnite, pyrite, quartz, and sulfur) and open system with CO_2, at a P_{CO2} of 2.63 bar. This P_{CO2} corresponds to the so-called full equilibrium value, as it is constrained by coexistence of a Ca-Al-silicate and calcite (Giggenbach, 1984).

In one simulation, the average Menengai pantellerite was dissolved in pure water, initially containing negligible concentrations of all the chemical components of interest: H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Al^{3+}, SiO_2, F^-, Cl^-, SO_4^{2-}, and HCO_3^-. In the other simulation, the same rock was dissolved in diluted magmatic water, initially characterized by negligible contents of cations and aqueous SiO_2, as well as 1.007 mol/kg total HCO_3, 0.01085 mol/kg Cl, 0.002113 mol/kg total S and 0.0006633 mol/kg F. To obtain these anion concentrations the average composition of the magmatic gases emitted by Nyiragongo in 2005-2007 (Sawyer et al., 2008) were suitably readjusted to reproduce the chemistry of Menengai reservoir liquids (Kipng'ok, 2011). In fact, the comparison of these two fluids highlighted that the supply of magmatic components to the geothermal system cannot be modeled through simple vapor condensation, total gas absorption and dilution, but implies other processes determining fractionation of the chemical components of interest. The pH of the diluted magmatic water was constrained by charge balance and resulted to be 1.99, whereas its log f_{O2} was fixed at -31.7 based on the magmatic SO_2/H_2S redox buffer of Giggenbach (1987).

3. RESULTS

The hydrothermal parageneses produced in the two computer experiments are one another similar as both include the same stable minerals, namely: quartz, albite, K-feldspar, calcite, and two chlorite components, i.e., daphnite-14A and clinochlore-14A (Figure 1). Moreover, muscovite and epidote appear in both simulations but have ephemeral existence being substituted by K-feldspar and calcite, respectively.

Other metastable Ca-bearing solid phases, anhydrite and fluorite, are produced during the rock dissolution in diluted magmatic water only. Both disappear upon epidote production. The metastability of Ca-bearing minerals (epidote, anhydrite and fluorite) probably reflects, at least partly, the scarcity of Ca in the average pantellerite, which has a CaO content slightly lower than 1 wt %.

Alunite and pyrite are also produced as ephemeral minerals during the rock dissolution in diluted magmatic water. Alunite is substituted by pyrite and muscovite, whereas pyrite destruction causes an increase in both the amount of daphnite-14A and the concentration of dissolved S species.

All in all, there is a satisfactory agreement between the results of geochemical modelling and the main hydrothermal minerals recognized in Menengai geothermal wells MW-01 and MW-02 comprising quartz, calcite, albite, epidote, and pyrite (Omondi, 2011).
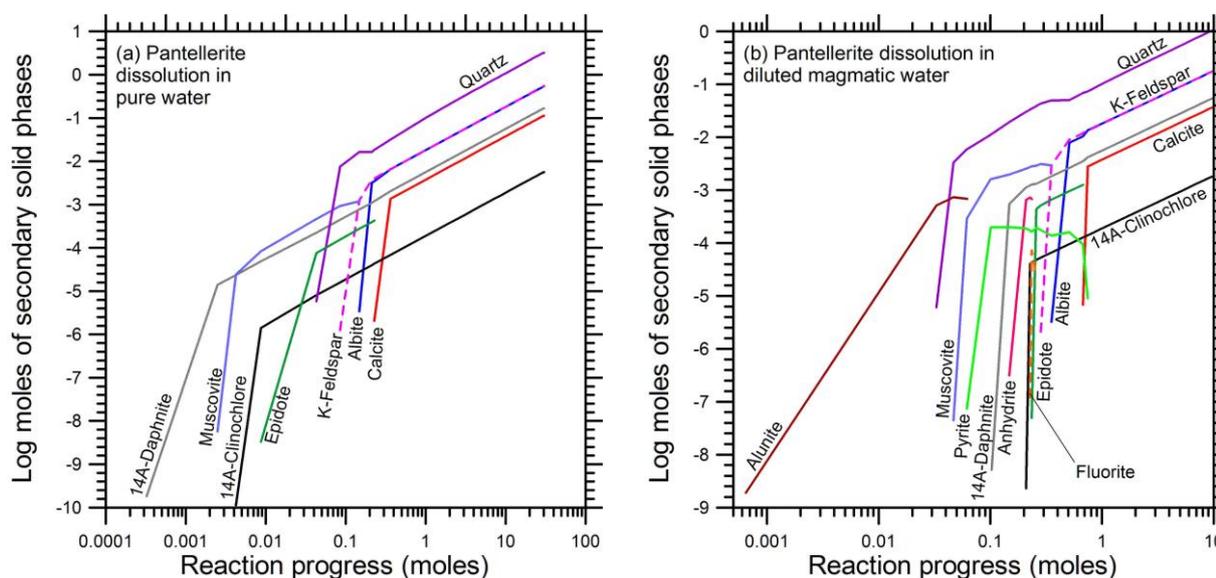

Figure 1: Log-moles of secondary solid phases precipitated during the progressive dissolution of the average Menengai pantellerite in (a) pure water and (b) diluted magmatic water at 250°C and under a full-equilibrium P_{CO2} of 2.63 bar.

In spite of the very different pH of the initial aqueous solution in the two simulations, the difference in pH decreases progressively with the increase in the reaction progress variable until final pH values close to 8.5 are attained in both runs (Figure 2a). Similarly, the difference in redox conditions, here described by the decimal logarithm of oxygen fugacity, declines with increasing rock dissolution until final values of -36.6 to -37.6 are achieved in both simulations. Interestingly, these figures are quite similar to the log f_{O2} constrained by the hydrothermal FeO-FeO$_{1.5}$ redox buffer (Giggenbach 1987) at 250°C, -37.8. In the pure water simulation, due to the virtual absence of S species, the redox potential is evidently constrained by the Fe^{2+}/Fe^{3+} redox couple. In contrast, in the

magmatic water simulation, the redox state is fixed by dissolved HS^- and SO_4^{2-} whose concentrations are higher than those of Fe^{2+} and Fe^{3+} aqueous species by some orders of magnitude.

It is now instructive to compare the computed concentrations of relevant solutes with the analytical data of the Menengai well MW-01 (Kipng'ok, 2011) by means of suitable chloride plots (e.g., Figures 3 and 4). These diagrams show that analytical values are consistent with the theoretical data predicted by rock dissolution in diluted magmatic water, under a full-equilibrium P_{CO2} of 2.63 bar, whereas rock dissolution in pure water, under the same P_{CO2} value, is not able to reproduce the observed concentrations of dissolved chemical components in Menengai geothermal liquids.
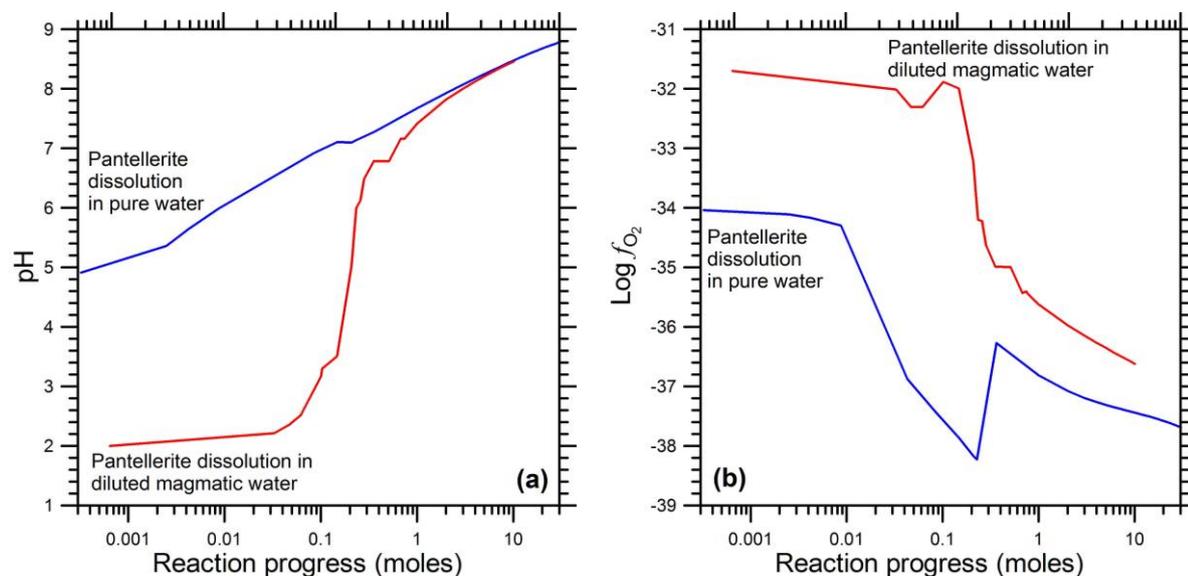

Figure 2: Changes in (a) pH and (b) decimal logarithm of oxygen fugacity during the progressive dissolution of the average Menengai pantellerite in pure water and diluted magmatic water at 250°C and under a full-equilibrium P_{CO2} of 2.63 bar.
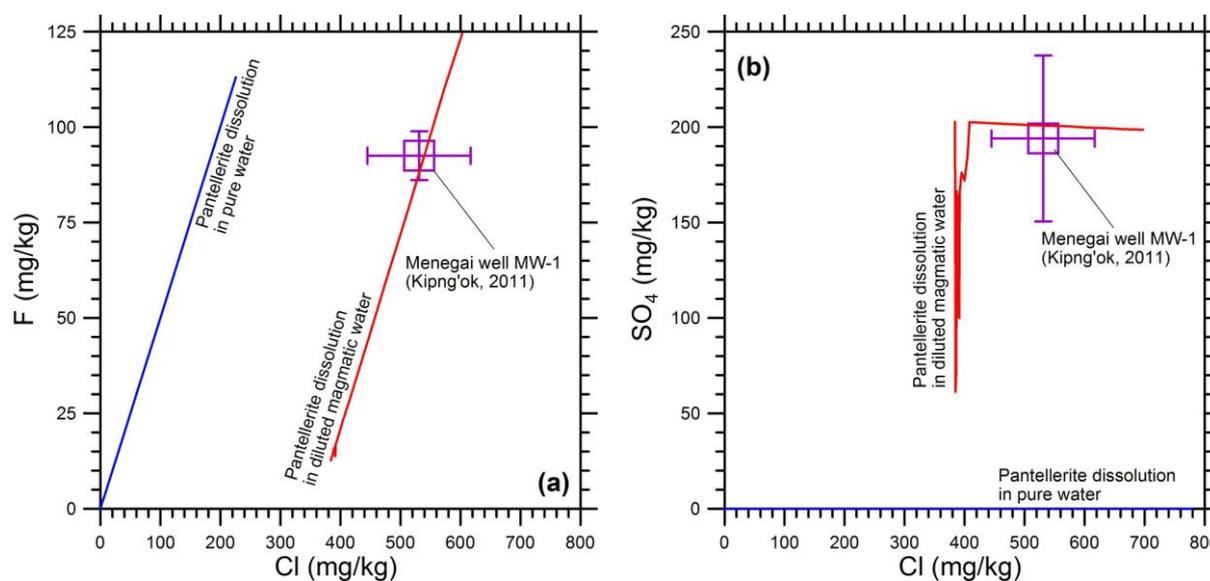

Figure 3: Chloride plots of (a) fluoride and (b) sulfate showing the concentrations of these chemical components during the progressive dissolution of the average Menengai pantellerite in pure water and diluted magmatic water at 250°C and under a full-equilibrium P_{CO2} of 2.63 bar as well as the analytical data of the Menengai well MW-1 (Kipng'ok, 2011).

Dissolved silica speciation is of interest for practical consequences. In the aqueous solution produced at the end of the magmatic water simulation, $SiO_{2(aq)}$ is the prevailing silica species, with a concentration of 7.69 mmol/kg, corresponding to 54.9% of total dissolved silica. Nevertheless, the aqueous solution is also characterized by important concentrations of both $HSiO_3^-$ ion (3.99 mmol/kg, corresponding to 28.5% of total dissolved silica) and the $NaHSiO_{3(aq)}$ aqueous complex (2.32 mmol/kg, corresponding to 16.6% of total dissolved silica). Incidentally, the aqueous complexes $CaHSiO_3^+$ and $MgHSiO_3^+$ are also included in the EQ3/6 thermodynamic database, but their computed concentrations are very low, $3.01 \cdot 10^{-9}$ and $1.96 \cdot 10^{-10}$ mol/kg, respectively. The considerable contents of dissociated and complexed silica are due to the comparatively high pH of the aqueous solution, 8.46, which is lower than the pK of silicic acid, 9.04 at 250°C, by half logarithmic unit only.

The speciation of cations involved in the geothermometric functions Na-K and K-Mg is also of interest for practical implications. In the aqueous solution produced at the end of the magmatic water simulation, the prevailing species of Na and K are the free ions Na^+ and K^+, representing the 93.1% and the 98.8% of total dissolved Na and K, respectively. In contrast the speciation of Mg is dominated by the complexes $MgHCO_3^+$, $MgOH^+$, $MgCO_{3(aq)}$, and MgF^+ cumulatively accounting for 97.1% of total dissolved Mg, whereas the contribution of the free ion Mg^{2+} is 2.4% only.
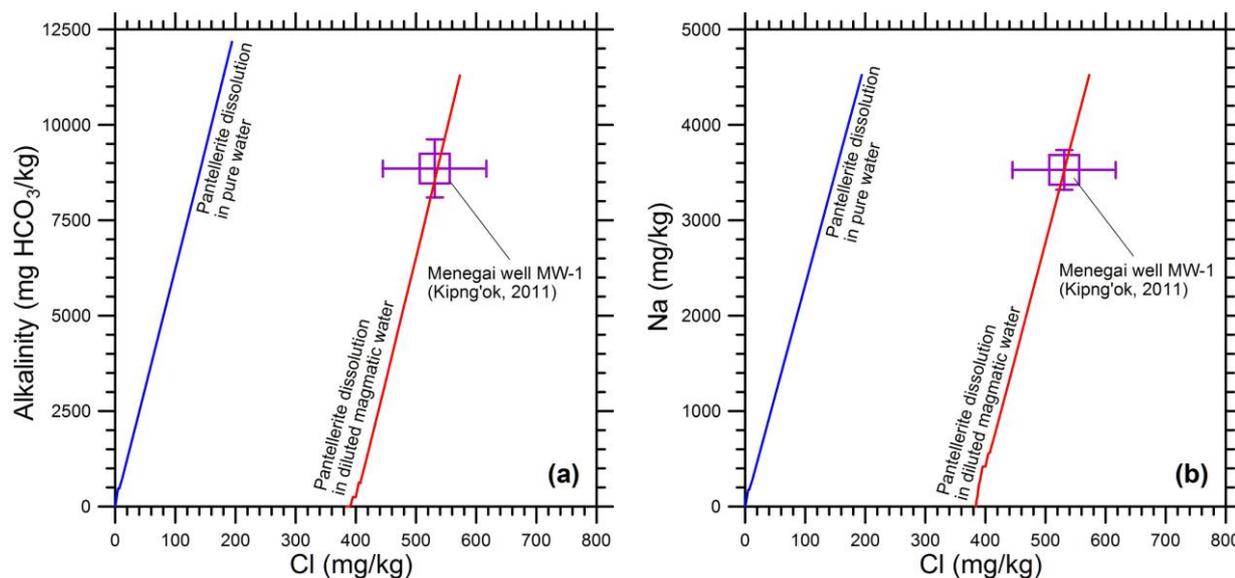

Figure 4: Chloride plots of (a) alkalinity and (b) sodium showing the concentrations of these variables during the progressive dissolution of the average Menengai pantellerite in pure water and diluted magmatic water at 250°C and under a full-equilibrium P_{CO2} of 2.63 bar as well as the analytical data of the Menengai well MW-1 (Kipng'ok, 2011).

4. DISCUSSION

Since the results of reaction path modeling of pantellerite dissolution in diluted magmatic water satisfactorily reproduce the measured solute concentrations of Menengai geothermal liquids, computed data can be used to inspect the chemistry of these liquids and to draw practical implications.

The large prevalence of the free ions Na^+ and K^+ among the aqueous Na and K species implies that the Na/K Total Concentrations Ratio (TCR) is very similar to the corresponding free ion activities ratio (FIAR), in agreement with early observations by Guidi et al. (1990) and Chiodini et al. (1991). The Na/K TCR involves the analytical data which are inserted in the Na-K geothermometer. The Na/K FIAR is the parameter uniquely fixed, at a given temperature, by the albite – K-feldspar – aqueous solution equilibrium condition controlling the Na-K geothermometer (Arnórsson et al., 1983; Giggenbach, 1988). Consequently, the Na-K geothermometer is expected to provide reliable results for the Na-HCO_3 aqueous solutions typically present in the continental rift zone of East Africa.

In contrast, owing to the predominance of Mg aqueous complexes over the free ion Mg^{2+}, the K^2/Mg TCR ratio is expected to be significantly different from the K^2/Mg FIAR, in line with previous considerations by Guidi et al. (1990) and Chiodini et al. (1991). Again, the K^2/Mg TCR involves the analytical results which are introduced in the K-Mg geothermometer, whereas the K^2/Mg FIAR is the parameter uniquely constrained, at known temperature, by the muscovite – K-feldspar – clinochlore – quartz – aqueous solution equilibrium condition governing the K-Mg geothermometer (Giggenbach, 1988). Therefore, the K-Mg geothermometer might give unreliable computed temperatures for the Na-HCO_3 aqueous solutions of the continental rift zone of East Africa.

As underscored in the previous section owing to the relatively high pH of Na-HCO_3 geothermal liquids, a significant proportion of dissolved silica is present in ionic and complexed forms. These aqueous silica species are not involved in silica polymerization and precipitation of amorphous silica. Upon boiling and loss of CO_2 and H_2S, the pH of the separated liquids is expected to increase, promoting a partial conversion of undissociated silica to $HSiO_3^-$ ion and $NaHSiO_{3(aq)}$ aqueous complex. Consequently, silica polymerization and precipitation of amorphous silica appears to be unlikely in boiled Na-HCO_3 liquids, in spite of the increase in the concentration of total dissolved silica upon boiling and although the polymerization and depolymerization reactions of silicic acid are catalyzed by hydroxide ion (Weres et al., 1980 and references therein).

5. CONCLUSIONS

Reaction path modeling of the dissolution of an average pantellerite from Menengai volcano in pure water and in diluted magmatic water indicates that sulfate and sulfide as well as dissolved carbonate species are entirely contributed to the aqueous solution by absorption of deep magmatic gases, whereas Cl and F are supplied to the aqueous phase by both rock dissolution and absorption of magmatic gases.

Computed data satisfactorily reproduce the measured solute concentrations of Menengai geothermal liquids and, therefore, can be utilized to explore the aqueous speciation of these liquids and to draw practical consequences, such as the good performance of the Na-K geothermometer and the misleading results possibly given by the K-Mg geothermometer for Na-HCO_3 aqueous solutions, and the unlikely occurrence of silica polymerization and precipitation of amorphous silica in boiled Na-HCO_3 liquids.

This study represents a preliminary attempt to understand the geochemistry of the Na-HCO$_3$ geothermal liquids typically present in the continental rift zone of East Africa, whose chemistry contrasts with the Na-Cl composition of most geothermal "mature" liquids coming from convergent-plate boundaries. Since most geochemical techniques were derived by studying high-temperature geothermal systems situated along convergent-plate boundaries and mid-ocean ridges (e.g., Iceland), we believe that a significant research effort must be done for understanding the peculiarities of the geothermal systems of the continental rift zone of East Africa, especially in terms of hydrothermal mineralogy and fluid geochemistry to improve the presently used geochemical techniques. The outcomes of these researches might be relevant also for geophysics, especially magnetotellurics, whose results are strongly dependent on the development and type of clay minerals constituting the cap-rock.

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