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Systematics of Rare Alkalis and Halogens in the High-Temperature Mahanagdong Geothermal Field, Leyte, Philippines

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ABSTRACT

The analyses of rare alkalis and halogens in water samples obtained from production wellheads were studied to further understand the characteristics of the high-temperature geothermal field of Mahanagdong, Leyte, Philippines. The fluids are saline and mineralized that typically characterize fields associated with subduction zones and hosted by andesitic rocks.

The rare alkali metals Li, Rb and Cs (which are reactive in the deep parts of the reservoir beyond drilling depths) have highly positive correlations with Cl, suggesting that they are considerably mobile and are least affected by relatively shallow processes. Ternary diagram following the methods of Giggenbach (1991) shows data points departing from the composition of the rocks in the crust but closely retain the rocks' original Li/Cs ratio. The fluids discharged from wells drilled in the northeastern part of the field show upflow characteristics (i.e., most depleted Rb and least loss of Cs). Cross plots of Na/Li and Rb/Cs were also done taking advantage that the levels of very mobile alkalis Li and Rb are elevated in fluids from higher temperatures but decrease at lower temperatures as they tend to be fixed by secondary minerals. Consistently, fluids from two of the northeastern wells are inclined towards the "upflow corner". The updated data of northern well postulated to be nearest the upflow area prior to the drilling of the northeastern wells have shifted towards higher Na/Li and lower Rb/Cs indicating probable loss of Li and Rb in the fluid of the producing area.

Fluoride levels in Mahanagdong range 1-5 mg/kg and are generally undersaturated with fluorite. A significant positive correlation between the activities of F- and OH- in the modeled aquifer fluids is observed. Br concentrations are on the average one order of magnitude higher than those of F at ~18 mg/kg. Br has strong positive correlation with the mobile Cl. The Cl/Br ratios (383-557) plot within the seawater and evaporite region but are lower than seawater value (650). The Cl/Br ratios suggest that the magmatic-related components in Mahanagdong geothermal fluids are likely derived from seawater or crustal fluids recycled in subduction zones.

1. INTRODUCTION

The high-temperature geothermal field of Mahanagdong is located on the island of Leyte, central Philippines, ~700 km south of the capital Manila (Figure 1). Mahanagdong is part of the ~1,200 MWe geothermal steamfields operated by Energy Development Corp. (EDC) which accounts for 61% of the country's geothermal capacity. The ~10 km^2 field is the southern part of the Greater Tongonan Geothermal Field and lies along a NW-SE trending chain of Quaternary volcanoes associated with the subduction of the Philippine Sea Plate. Episodes of volcanism and sedimentation mostly contributed to its rock units. The geothermal fluids from a liquid-dominated reservoir are saline and mineralized that typically characterize fields associated with subduction zones and hosted by andesitic rocks.

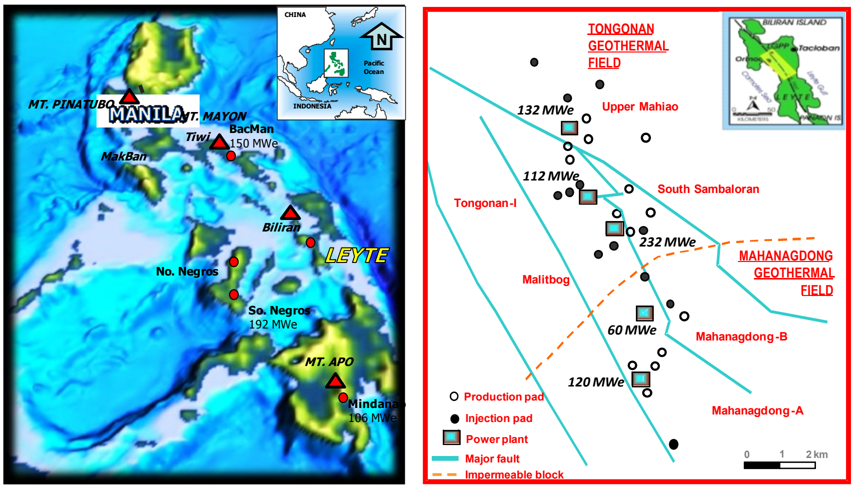

Figure 1: Geothermal production fields of Energy Development Corp. in the Philippines (left) and the Tongonan and Mahanagdong geothermal fields in the island of Leyte, Philippines (right).

Mahanagdong is a subject of numerous studies such as Salonga et al. (2004) where the major reservoir processes affecting the field are discussed and illustrated in Figure 2. A geochemical assessment of Mahanagdong after ~15 years of production was conducted by Angcoy (2010) using fluids sampled from 26 production wells in 2009, and include wells drilled in the northeastern part of the field from 2008 onwards. Mahanagdong is a liquid-dominated geothermal system but some producing wells have "excess" discharge enthalpy (i.e., higher than that of vapor-saturated liquid at the aquifer temperature). The initial aquifer fluids feeding the Mahanagdong wells were modeled primarily with the aid of the speciation program WATCH of Arnórsson et al. (1982) and Bjarnasson (1994). Wells discharging "excess enthalpy" were modeled following the phase segregation model discussed by Angcoy and Arnórsson (2011). This work focuses on the analysis and interpretation of halogens (Cl, F and Br) and rare alkalis from the Mahanagdong production wells sampled by Angcoy (2010). This study deals only with total dissolved concentrations and does not explore on the speciation of these minor to trace elements in the solution.

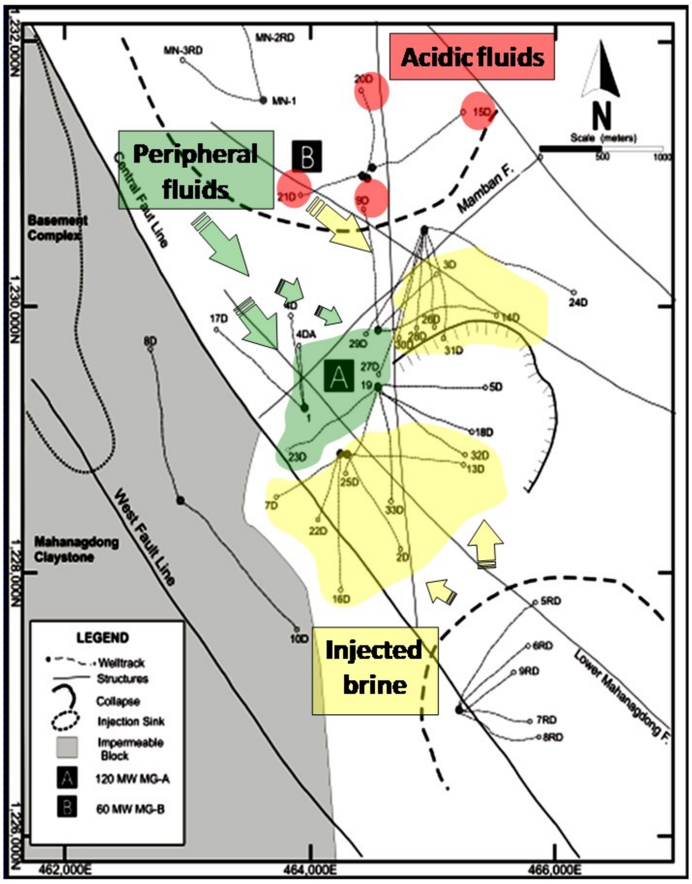

Figure 2: General reservoir processes affecting the Mahanagdong geothermal field adapted from Salonga et al. (2004).

2. DATA COLLECTION AND WATER ANALYSES

The fluids were sampled from Mahanagdong geothermal wells using a double-cyclone Webre-separator to separate the vapor and liquid phases near the wellheads. This allows liquid and steam phases to be collected at the same sampling pressure and within 3 psi from the two-phase line pressure to minimize the effect of liquid flashing into steam. All liquid samples were cooled via stainless steel coil, collected in plastic bottles (HDPE or PP) and passed through 0.45 µm pore size membrane filter (except in 3 well samples) to prevent contamination of the samples by suspended particles that may dissolve when the samples are acidified by 50% reagent grade nitric acid (HNO3). In this work, water analyses of Na, Li, Cl, Br (ICP-AES) and F (ion chromatography) were analyzed in the Institute of Earth Sciences, University of Iceland laboratory. ICP-MS in University of California-Merced laboratory was used to analyze Rb and Cs. Representative analytical data from production wells drilled in the Mahanagdong field shown in Figure 2 are presented in Table 1.

Table 1: Analytical data of representative Mahanagdong wells.

Well	Sampling Pressure barg	pH (25ºC)	Cl mg/kg	Br mg/kg	F mg/kg	Na mg/kg	Li mg/kg	Rb mg/kg	Cs mg/kg
North-Easternmost 1 (NE1)	8.1	5.13	7455	37.99	3.01	3724	15.2	6.434	1.1042
North-Easternmost 1 (NE2)	8.2	3.98	7159	34.89	2.66	3486	12.1	4.856	0.9306
Northern (N)	9.9	6.40	5672	25.79	1.32	3232	10.3	3.454	1.0609
Western flank (W)	12.8	7.80	2286	10.62	1.74	1446	3.93	1.321	0.5222
Central (C)	10.9	6.79	609	3.58	2.85	896	1.34	0.585	0.2601
Southern flank (S)	10.4	6.08	4396	19.78	1.57	2551	8.38	2.982	1.0600

3. RESULTS AND DISCUSSIONS

The concentrations of the elements in water samples from Mahanagdong (represented in Table 1) are typical of hydrothermal solutions. These levels are more enriched compared to primary geothermal waters in the basaltic rocks of Krafla, Iceland (e.g., Arnórsson et al. (2007)), comparable with fluids associated with andesitic setting in Miravalles, Costa Rica and much lower compared to the hypersaline and mineral-rich geothermal brines shown by Gallup (1998) in Salton Sea, California and Cheleken Peninsula in Caspian Sea or the oilfield brines of the Mississippi, Salt Dome Basin.

3.1 Rare alkalis

The rare alkali metals Li, Rb and Cs are reactive in processes occurring in the deeper and hotter parts of the reservoir and are therefore not totally conservative. The works of Goguel (1983) indicated that these rare alkali metals were dissolved from rocks far beyond drilled depths and were added to rather than leached from the altered rocks. Figure 3 shows that Li, Rb and Cs have highly positive correlations with the conservative element Cl, suggesting that once added to the solution, they are considerably mobile and are least affected by shallow processes.

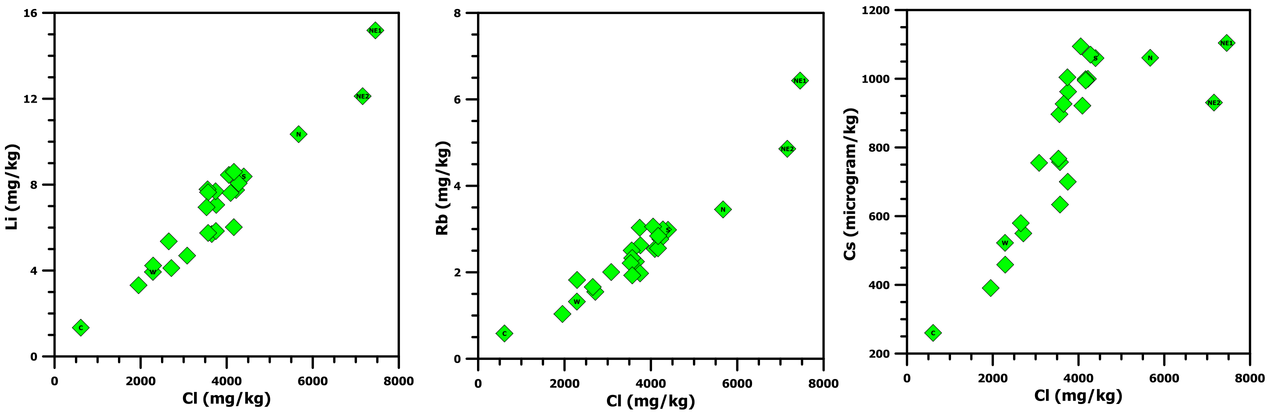

Figure 3: Cross plots of Li, Rb and C with Cl in Mahanagdong waters (refer to Table 1 for label of data points).

The relative concentrations of Li, Rb and Cs and the processes that may change their concentrations in the waters are shown in Figure 4 following the ternary diagram of Giggenbach (1991). The data points are far from the composition of the crustal rocks but approaches the rocks' original Li/Cs ratio. The samples cluster in the middle suggesting that they are affected by the secondary processes by almost similar extent. The northeastern wells (NE1 and NE2) show the most extensive depletion of Rb (occurring at elevated temperatures >300°C) and the least loss of Cs (favored at temperatures <300°C). Thus the data points of wells NE1 and NE2 in Figure 4 shifting towards lower Li/Cs ratio suggest relative proximity to an area characterizing a hotter region.

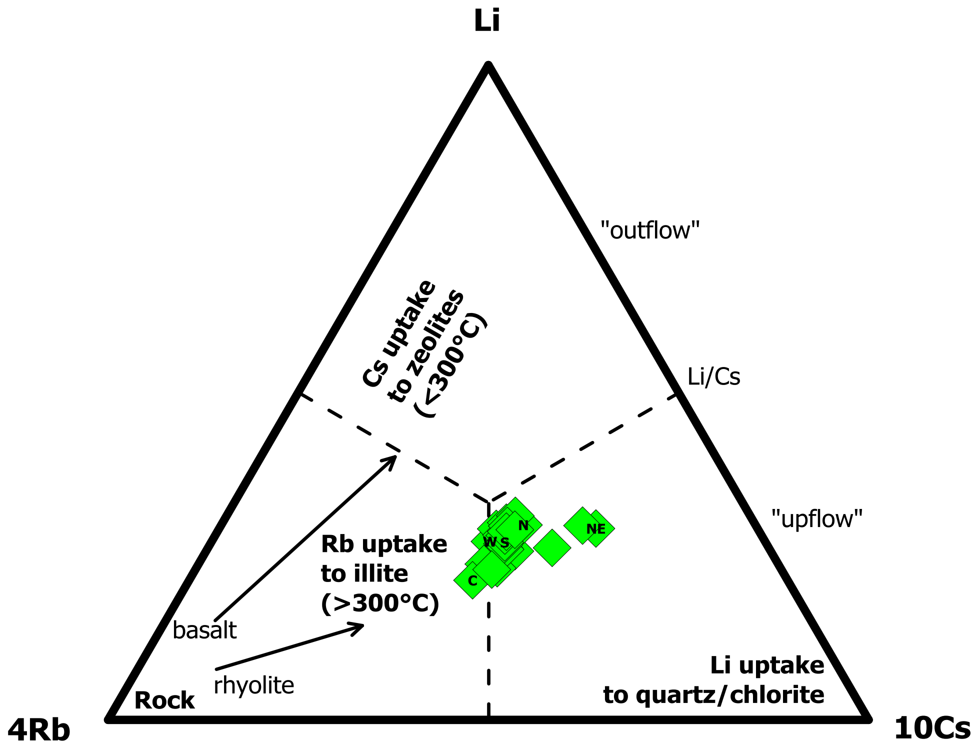

Figure 4: Li, Rb and Cs profile in Mahanagdong waters following the ternary diagram of Giggenbach (1991). Refer to Table 1 for the labels of data points.

The very mobile alkalis Li and Rb are abundant in fluids of high temperatures. In contrast, Li and Rb tend to be fixed by secondary minerals at lower temperatures. Figure 5 is a cross plot of molar ratios involving other mobile elements: Na/Li and Rb/Cs. Consistently, the northeastern wells (NE1 and NE2) are also inclined towards the "upflow" corner. Prior to the drilling of northeastern wells, Salonga et al. (2004) mentioned that the area intersected by the northern well (N) encountered "upflow" characteristics such as the highest measured temperature and reservoir Cl level. In Figure 5, the updated rare alkali behaviors of the northern well (N) show a general shift away from the "upflow" corner, likely affected by the cooling effect of the injected brine returning into the area as illustrated in Figure 2.

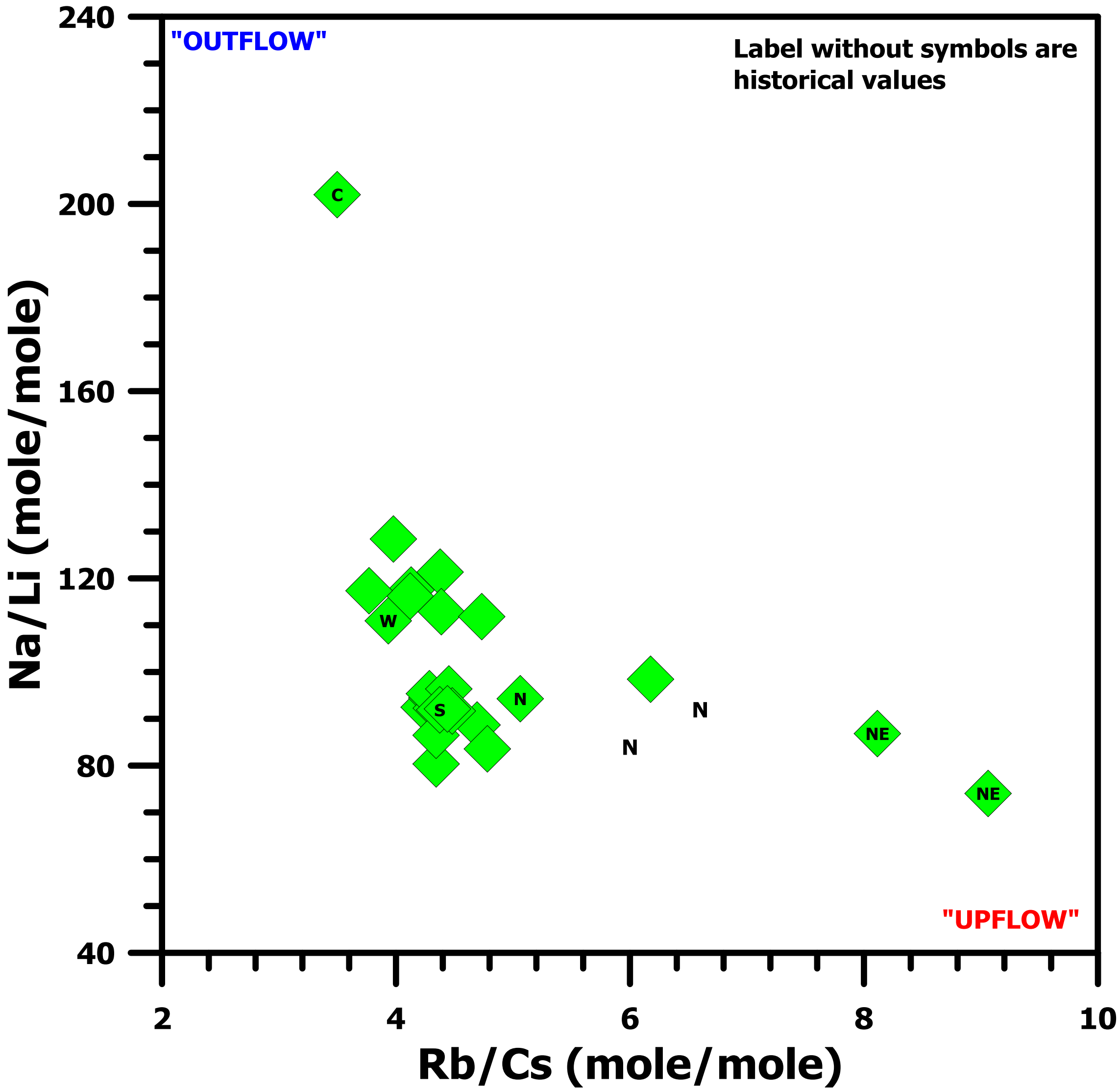

Figure 5: Na/Li vs Rb/Cs cross plot of Mahanagdong water samples. Refer to Table 1 for the labels of data points.

3.2 Halogens

The halogens (F, Cl, Br, I and At) are very reactive in elemental form since they only need one electron to complete the octet in their outermost shell. Thus they are rarely found in natural native form and are instead combined as halide ions in salts, solutions and gases. For this study, analytical data are only available for F, Cl and Br which are also the three most abundant halogens in the Earth's major geochemical reservoirs. As volatile components in most magmas, their concentrations are: Cl (800-7,500 ppm), F (10-1,000 ppm but sometimes >5%) and Br (0.06-300 ppm). Compounds of F and Cl are significant in crustal rocks (about 550 ppm and 240 ppm, respectively) while Br is usually <1 ppm (e.g., Aiuppa et al. (2009)).

Fluorine is very reactive being the most electronegative of the elements. During magma differentiation, ascent and degassing, F tends to be retained in silicate melts compared to Cl and Br. As the magma evolves, F may be removed to a variable degree from the residual melt by fluorite, fluoroapatite, micas and amphiboles, reducing the F in the melt that would have been available for a gaseous magma phase. These behaviors of F may explain why its concentrations in Mahanagdong geothermal waters only range 1-5 mg/kg (ave. 1.85 mg/kg) as detailed in Angcoy (2010). Arnórsson, S., and Gunnlaugsson, E. (1983) pointed out that geothermal fluids are undersaturated with fluorite in basaltic setting but tend to be in equilibrium with this phase in more felsic volcanic rocks. In the andesitic setting of Mahanagdong, the modeled liquid aquifers using the WATCH software conducted by Angcoy (2010) are generally undersaturated with fluorite, by 2.4 log units on average (Figure 6) and thus fluorite is rarely reported.

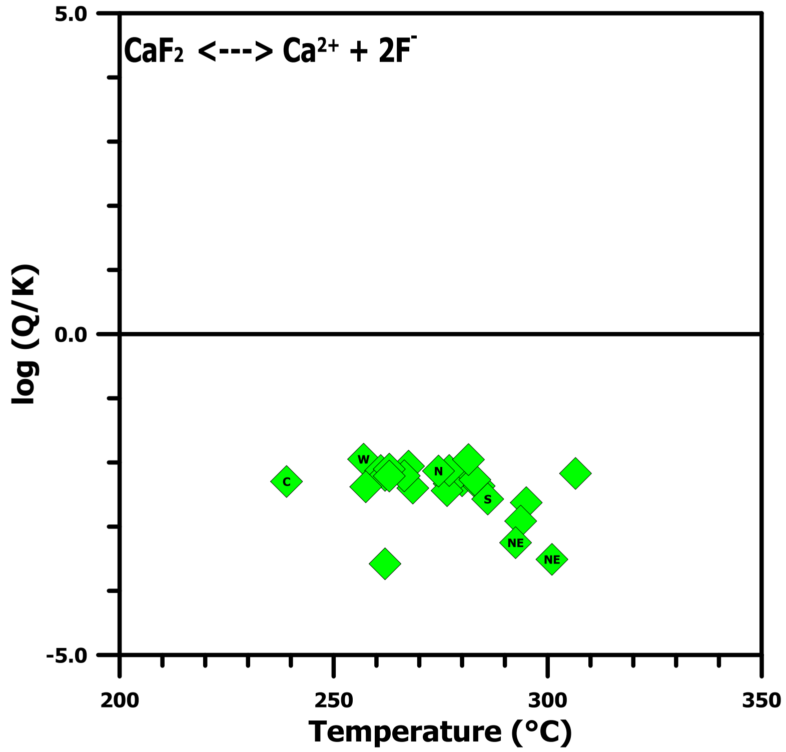

Figure 6: Saturation indices of fluorite in modeled total fluid assuming liquid enthalpy in Mahanagdong (refer to Table 1 for label of data points).

F also has one of the smallest radii of any anion and very similar to the ionic radius of oxygen. Studies show that F substitutes for hydroxyl and for oxygen in silicate crystals and melts (e.g., Arnórsson and Gunnlaugsson (1983)). Fluoride may be consumed by hydroxide-bearing silicates at deeper reservoir levels where it replaces OH^- resulting in insufficient F activity to saturate the solution with fluorite. Figure 7 presents a significant positive correlation between the activities of F^- and OH^- in the modeled aquifer fluids of Mahanagdong. With this linear correlation, the analysis of F in the waters may be potentially used to infer the reservoir pH of geothermal fluids. F analysis has high degree of accuracy compared to pH measurement of water samples which are affected by various factors that may propagate the errors in modeling the pH at reservoir conditions.

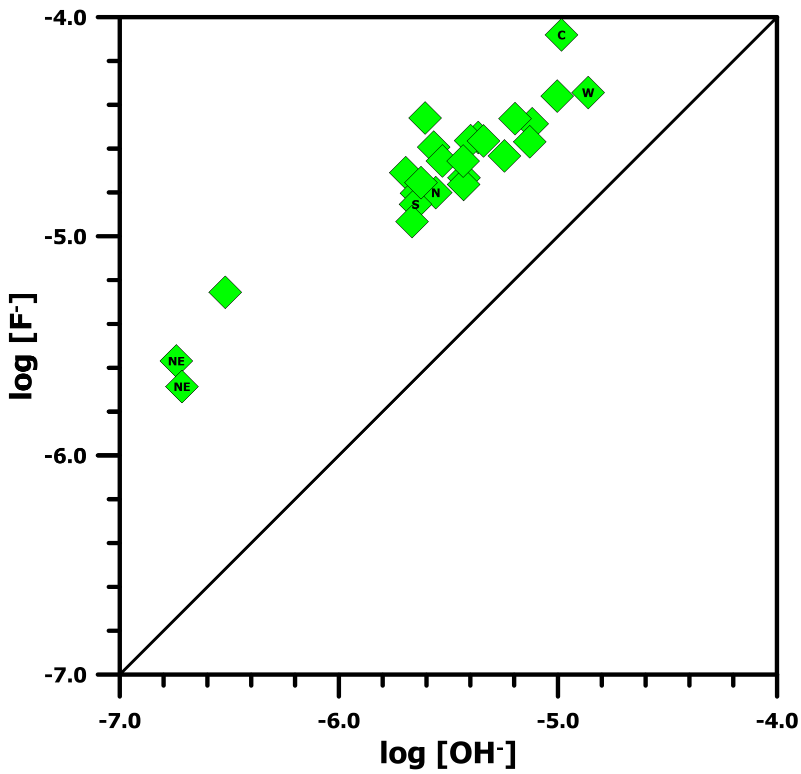

Figure 7: Comparison of the activities of F- and OH- in the modeled liquid aquifers of Mahanagdong (refer to Table 1 for label of data points).

Despite its relative scarcity among the halogens, Br concentrations in Mahanagdong waters at ~18 mg/kg are on the average one order of magnitude higher than those of F. Figure 8 shows a strong positive correlation of Br with Cl indicating similar geochemical behavior of the two elements. The Cl/Br molar ratios in Mahanagdong (383-557) approach but are typically lower than seawater value (650). Taran et al. (2008) observed that molar Cl/Br ratios of the acidic hydrothermal waters at El Chíchon volcano, Mexico also plot within the seawater and evaporite region despite evidences of magmatic contributions. Since previous works such as by Alvis-Isidro et al. (1993) also established the magmatic component on Mahanagdong waters based on stable ^{18}O and ^{2}H isotopic data, the Cl/Br ratios suggest that the magmatic-related sources are derived from seawater or crustal fluids recycled in subduction zones. The decreasing Cl/Br ratio of Mahanagdong waters relative to seawater may also support the experimental findings of Liebscher et al. (2006) where they demonstrated that during phase separation of fluids with initial seawater composition (380-450°C, 23-42 MPa, H_2O-NaCl-NaBr system), Br is more enriched than Cl in the liquid phase.

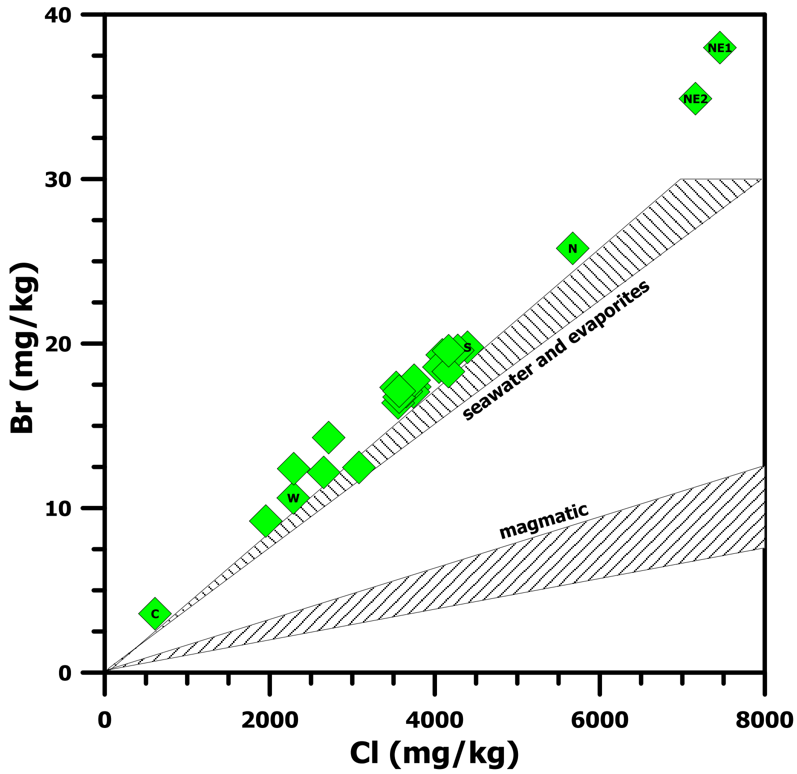

Figure 8: Cl vs Br concentrations in the sampled Mahanagdong geothermal waters (refer to Table 1 for label of data points).

4. SUMMARY AND CONCLUSIONS

The analyses of rare alkalis and halogens in water samples obtained from production wellheads provided recent insights on the high-temperature Mahanagdong geothermal field. The systematics of the mobile alkali metals Na, Li, Rb and Cs suggest fluids discharged from wells drilled in the northeastern part of the field have "upflow" characteristics. Updated data of northern wells previously postulated to be nearest the "upflow" area prior to the drilling of the northeastern wells have shifted away from the "upflow" signatures likely reflecting the cooling effect of injected brine returns after ~15 years of production.

In Mahanagdong, the halogens F and Br exhibit contrasting behaviors with respect to mobile element Cl. F is reactive with levels ranging 1-5 mg/kg in the waters. Mahanagdong waters are generally undersaturated with the major F sink, fluorite. Geochemical modeling using WATCH indicates a significant positive correlation between the activities of F^- and OH^- in the reservoir fluids potentially making use of F analysis as a tool to predict reservoir fluid pH. Br is highly mobile and exhibits strong correlation with Cl. Br concentrations in Mahanagdong waters are on average ~18 mg/kg. The Cl/Br ratios plot within the seawater and evaporite region suggesting that the magmatic-related components in Mahanagdong geothermal fluids are likely derived from seawater or crustal fluids recycled in subduction zones.

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