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Rare Earth Elements and Yttrium Distribution in Surface and Geothermal Waters of Bacon-Manito Geothermal Field, Philippines

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ABSTRACT

Advancements in inductively coupled plasma-mass spectrometry (ICP-MS) technology and sample preparation techniques in the past decades made rare earth elements (REE) and trace elements analyses possible in fluids, opening the possibility of studying them as geochemical tools in geothermal exploration and production field monitoring. In order to evaluate this potential, rare earth elements and yttrium (REY) in rivers, hot springs, and well fluids from the Bacon-Manito Geothermal Field (Bacman), Philippines, were sampled using state-of-the-art solid phase pre-concentration and separation techniques. Filter residues were also acid-pressure-digested at high temperature to evaluate the potential impact of suspended particles on REY distribution and transport in surface and geothermal fluids.

REY concentrations in the brine from geothermal wells are 2-3 orders of magnitude lower compared to hot springs and rivers, due to REY partitioning into vapor during phase separation. Bulk rock- as well as chondrite-normalized REY plots from wells also show large positive europium (Eu) anomalies, suggesting fractionation of Eu from the crystal lattice of secondary minerals at reservoir conditions due to the predominance of divalent Eu at temperatures exceeding about 250°C. The absence of Eu anomalies in the hot springs may indicate water-rock interaction at temperature below about 200°C or admixture of large amounts of low-temperature surface waters. Relative light rare earth element (LREE) depletion and heavy rare earth element (HREE) enrichment in one (1) well sample apparently reflects the signature of reinjection returns. Filter residue-normalized REY patterns in eluates suggest that the transport of REY in Bacman surface and geothermal waters is dominantly controlled by adherence to nanoparticles and colloids smaller than 0.2 μm.

The presence of a positive Eu anomaly can be used as a geochemical indicator of a high temperature fluid source (≥250°C). Hence, REY geochemistry shows strong potential for “fingerprinting” different fluid sources but should always be used with utmost caution, and should be complemented with other geochemical proxies.

1. INTRODUCTION

Current geochemical techniques in geothermal exploration and production monitoring greatly rely on major element and isotope geochemistry. Although already proven to be effective, these geochemical tools are nevertheless limited by stringent equilibrium and steady state conditions, and by various assumptions. To close the gap posed by these limitations, this study evaluates the potential of rare earth elements and yttrium as a new geochemical tool by characterizing their concentrations in surface and well fluids, to determine the correlation of hot spring REY chemistry with that of the reservoir source fluid within the Bacon-Manito (Bacman) Geothermal Field, Philippines.

1.1 Location and Geologic Setting

The Bacman Geothermal Field is located ~350 km southwest of Metro Manila, in the Bicol Region in the Philippines (Figure 1). Its unique geologic setting is a consequence of the complex interplay between the Philippines Sea Plate (PSP) and the Sundaland-Eurasian Plate, and the oblique convergence of the PSP and the Philippine Mobile Belt (PMB) during subduction (Aurelio, 2000a; Aurelio, 2000b; Yumul et al., 2008; Lagmay et al., 2009). The shear partitioning from the obliquity of convergence gave birth to the ~1200 km sinistral Philippine Fault System (PFS) (Aurelio, 2000b), where the ~260 km Bicol volcanic arc formed in the central eastern margin of the PMB (Andal et al., 2005). The Bicol volcanic arc hosts several active volcanoes including Mt. Mayon, and potentially-active and inactive volcanoes which includes the Pocdol mountains, where Bacman is located. The major synthetic splay of the PFS transecting the Bacman area is locally named as the Bacman Fault Zone (BFZ), with a geomorphic imprint of a highly dissected terrain, where several volcanic domes of Late Miocene to Pleistocene age were emplaced (Andal et al., 2005; Braganza, 2014). This geologic setting created favorable conditions for a high enthalpy geothermal system to form and mature.

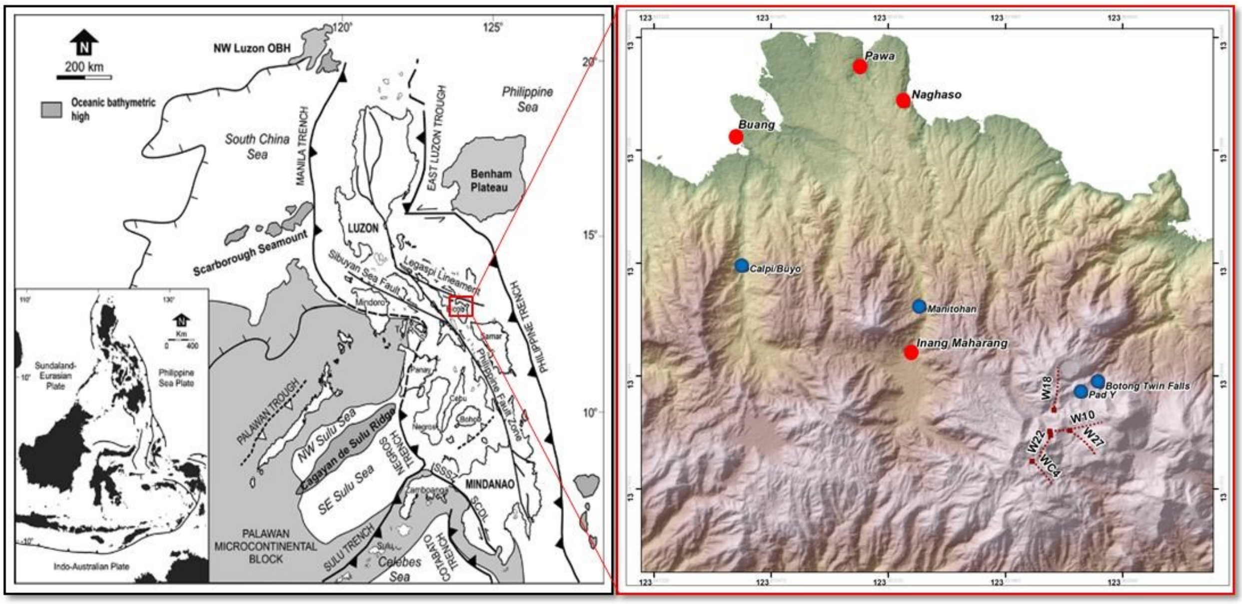

Figure 1. Location and regional geologic setting (Yumul et al., 2008) of Bacman Geothermal Field, Philippines, including location of samples taken for this study.

Bacman, which was first explored in the 1970s, produces 140 MWe of clean, green, renewable energy which provides for the need of the region and its neighboring islands. From the surface exploration to deep well data, the present integrated geothermal resource model of Bacman indicates upflow of neutral pH, high temperature (up to 338°C), two-phase fluids in the Osiao-Pangas sector, with high non-condensable gas content (Figure 2). The primary heat source driving the convection of the geothermal fluids is the emplaced volcanic domes of the Pocdol Volcanic Formation. The fluids are also being channeled through the BFZ, and the associated damage zones, and fractures therein, providing secondary permeability where primary permeability is absent (Braganza, 2014). The fluids then outflow towards the Manito Lowlands, where secondary boiling processes, exsolution of gases, and mixing with surface waters occur. The resulting fluids then surface near the coast, in the Pawa, Naghaso, and Buang springs.

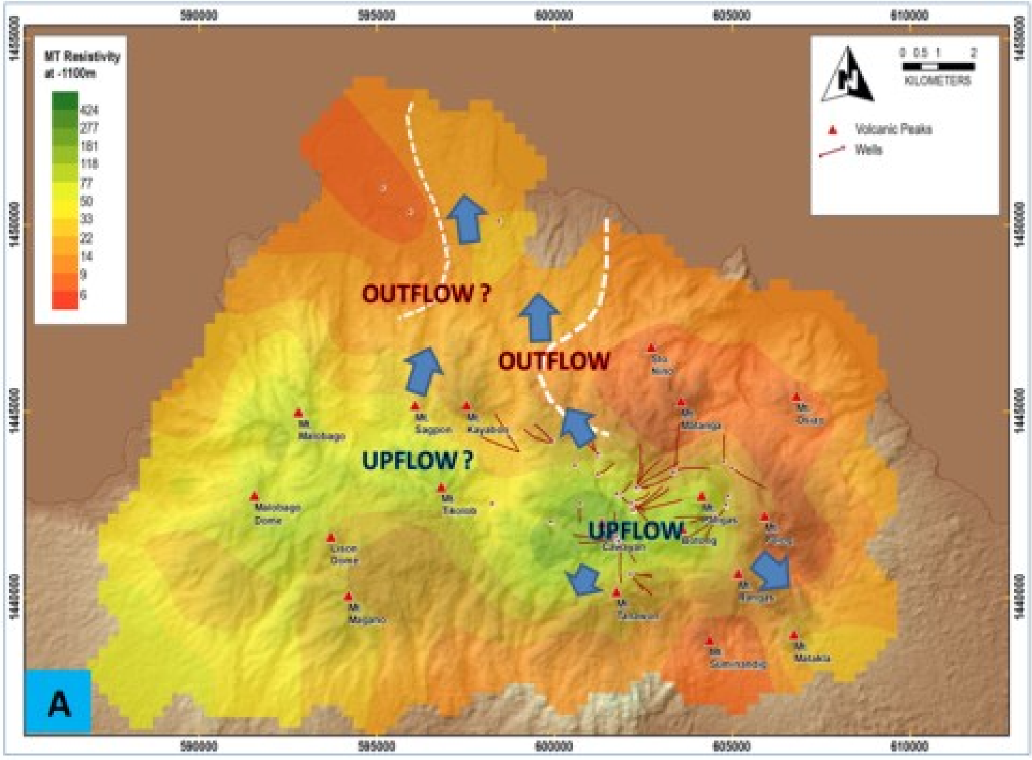

Figure 2. Present geothermal model of Bacman Geothermal Field, based on major element chemistry from surface and well data from Tugawin et al. (2015).

1.2 Rare earth elements and yttrium (REY) in geothermal waters

The aqueous behavior of REY, in contrast to magmatic systems, was described by Bau et al. (1996) as non-**CH**arge-and-**RA**dius-**C**ontrolled (non-CHARAC), showing non-chondritic ratios mainly due to chemical complexation and the lanthanide tetrad effect.

Particularly in hydrothermal systems, REY seldom occur as lone ions (Ln^{3+}), but commonly as complexes with major ligands such as OH, F, Cl, HCO_3, SO_4, etc. (Lewis et al., 1998; Moeller, 2000; Hannigan, 2005; Moeller et al., 2006). The dominance of the prevailing complexes is controlled by pH, salinity, temperature, and ligand availability.

The role of these REY complexes in fluid transport is intertwined with their stability at different temperature and pH conditions, and ligand electronegativity linking to bond strength (Haas et al., 1995; Wood, 1990; Williams-Jones et al., 2012). Recent experimental studies show that at high temperatures (>150℃), light rare earth element (LREE) complexes become more stable compared to heavy rare earth elements (HREE) complexes for the most common ligands, such as Cl and F (Gammons et al., 1996; Migdisov et al., 2007; Migdisov et al., 2008a; Migdisov et al., 2009; Williams-Jones et al., 2012; Loges et al., 2013). Other ligands, such as SO_4, show relatively stable complexes, although data seems limited to several members of the REE series (Migdisov et al., 2006; Migdisov et al., 2008b). Generally, the free lanthanide ions dominate at lower temperatures and at low pH, while complexes with metal-ligand ratios of 1:2 and 1:3 become increasingly dominant at high temperatures (Migdisov et al., 2006; Migdisov et al., 2008a; Williams-Jones et al., 2012).

Phase separation by boiling and decompression, and deposition and precipitation of minerals from the aqueous phase, is responsible for REY partitioning in geothermal and hydrothermal systems. REY are observed to conservatively partition in the vapor phase in magmatic systems, deep sea hydrothermal waters, and in some geothermal systems (i.e., Larderello-Travale, Italy and Kizildere, Turkey) (Moeller et al., 2003; Wood and Shannon, 2003; Moeller et al., 2008). REY transport in gas is not exclusively driven by dry volatility, but is also controlled by solvation and complexation processes (Douville et al., 1999; Gilbert and Williams-Jones, 2008; Williams-Jones et al., 2012). Decompression and temperature changes that drive precipitation of mineral scales, such as amorphous silica, calcite, anhydrite and gypsum, also fractionate REY by co-precipitation (Moeller et al., 2008; Moeller et al., 2003).

The observed anomalous behaviors of cerium (Ce), europium (Eu), and Yttrium and Holmium (Y-Ho) pair, in Larderello-Travale and Kizildere geothermal fields are important geoindicators of fluid processes (Moeller et al., 2003; Moeller et al., 2008). Ce, occurring as Ce^{3+} and Ce^{4+}, responds to changes in redox conditions in the fluid, rock alteration, as wells as precipitation of Fe-Al-Mn oxyhydroxides, and marine Fe-Mn nodules (Bau, 1994; Bau et al., 1996; Bau, 1999; Moeller, 2000). On the other hand, Eu (i.e., Eu^{2+} and Eu^{3+}) redox equilibrium is strongly controlled by temperature up to 600℃, and to a lesser extent by pressure, pH, oxygen fugacity, and chemical complexation (Sverjensky, 1984; Bau, 1991). Eu exists almost entirely divalent at ≥250℃ (Bau, 1991), which is equivalent to most high enthalpy geothermal reservoir conditions. Finally, the slightly higher particle-reactivity of Ho relative to the pseudolanthanide Y, allows temperature-independent decoupling of these elements during fluid processes and migration (Bau, 1991; Bau, 1994). This results in the development of a positive Y anomaly over time (Moeller, 2000). Moreover, Y/Ho correlated with Zr/Hf could be important geochemical indicators of the source of the mineral to which the hydrothermal fluids have reacted to (Bau et al., 1996).

2. METHODOLOGY

Four (4) major hot springs (Naghaso, Buang, Pawa, and Inang Maharang) (Figure 3), four (4) rivers (Manitohan River and its tributaries), and five (5) geothermal wells in Bacman were sampled in this study. The geothermal well waters representing the upflow (W10, W27), and the outflow (W18, W22, WC4) were sampled using a twin cyclone Webre separator, where the vapor phase was discarded. In all sampling locations, water samples for major elements (Li, Na, K, Mg, Ca, Fe, As, Al, Mn, Rb, Cs, Cl, SO_4, HCO_3) were taken using standard Giggenbach sampling techniques (Giggenbach, 1991); 1L of air-free, untreated samples, and 1L of filtered (0.45μm cellulose acetate), acidified (10 mL of 35% v/v HNO_3). Analyses for major elements were done using ICP-OES for metals, UV-VIS Spectrophotometry for SiO_2, and various titrimetric/potentiometric methods for other components in EDC-Chemistry, Isotope, and Environmental Laboratory Services.

Figure 3. Thermal springs in the Manito lowlands where samples were taken for this study.

The REY sampling process involves working under clean conditions, which requires careful pre-processing in the site laboratory, and working with high purity reagents. One (1) liter of fluid sample was filtered using 0.2 µm cellulose acetate, adjusted to pH=1.8-2.0, and spiked with ~0.25 mL of 100 ppb Tm standard. About 50 mL of the pre-processed sample was reserved for Tm spike recovery and other trace metals (Li, Rb, Cs, Sr, Sc), while the rest of the samples were passed through ion exchange resins (Waters C_{18} Sep Pak) loaded with 2-ethylhexylphosphate ester. The sample amounts were determined by weight difference. The ion exchange resins were then eluted with 40 mL of 6M HCl, and evaporated to incipient dryness at 180℃ until all the strong acids are evaporated. The eluates, ~3-5 mL, were then transferred to sample vials, where 100 µL of 100 ppb Ru-Rh-Re-Bi internal standard were pre-added, and were further diluted ten times yielding ~10 mL of sample concentrate. The 50 mL samples that were reserved were processed in a similar manner, but using only 1 mL of the original sample and diluted also up to ten times. The REY and trace metal analyses were carried out using a Perkin Elmer NEXion 350X quadrupole ICP-MS in the Geochemistry Laboratory of Jacobs University Bremen. Analysis was aided by an APEX-Q desolvator for extremely low element concentrations.

The filter residues of each REY sample were initially oven-dried at 70℃, where the amount of particulate matter was determined by weight difference. The samples were then acid-pressure digested using the Picotrace digestion system along with an internal rock standard. The acid concoction added to digest the samples was 3 mL of 30% HCl, 1 mL of 69% HNO3, and 1 mL of 40-45 mL HF. An acid blank was also prepared for each digestion setup. The samples were slowly degassed and then tightly sealed for the 12h digestion at 180℃. The digested samples were then processed and analyzed the similar to the REY eluates.

3. RESULTS

3.1 Major Elements

The geothermal waters of Bacman are generally Cl-rich, containing significant levels of HCO_3 and SO_4, a typical feature of high enthalpy geothermal fluids from a volcano-hosted geothermal reservoir in island arc settings. The Cl levels in wells were within 7500-9200 mg/kg, while hot spring Cl levels are more dilute (700 and 3000 mg/kg) (Figure 4). On the other hand, SO_4 concentrations fall below 52 mg/kg; the lowest values are observed in river waters and in WC4. Hot springs generally have higher SO_4 (>38 mg/kg). Field HCO_3 (up to 250 mg/kg) and lab HCO_3 concentrations (20-118 mg/kg) have a large discrepancy, up to almost three times, which will be further investigated.

The dominant major metals in Bacman fluids are Na, K, and Ca, with increasing concentrations from rivers to hot springs to geothermal wells (Figure 4). Na concentrations are highest in wells (4000-5100 mg/kg), moderate in hot springs (350-1700 mg/kg) and low in river waters (5-7 mg/kg). K also follows the same trend, where the highest concentrations are observed in well waters (740-1100 mg/kg), then hot springs (50-245 mg/kg), and rivers (≤ 1.5 mg/kg). Highest Ca concentrations were also found in well waters (180-270 mg/kg), then in hot springs (30-100 mg/kg), and then rivers (5-10 mg/kg). On the contrary, Mg is decreasing from surface waters to well fluids (0.1 mg/kg to 4 mg/kg), with the exception of Buang spring (35 mg/kg).

Based on major element data, Inang Maharang spring apparently has a closer affinity to the chemistry of surface/river waters, than to those of the hot springs or well waters.

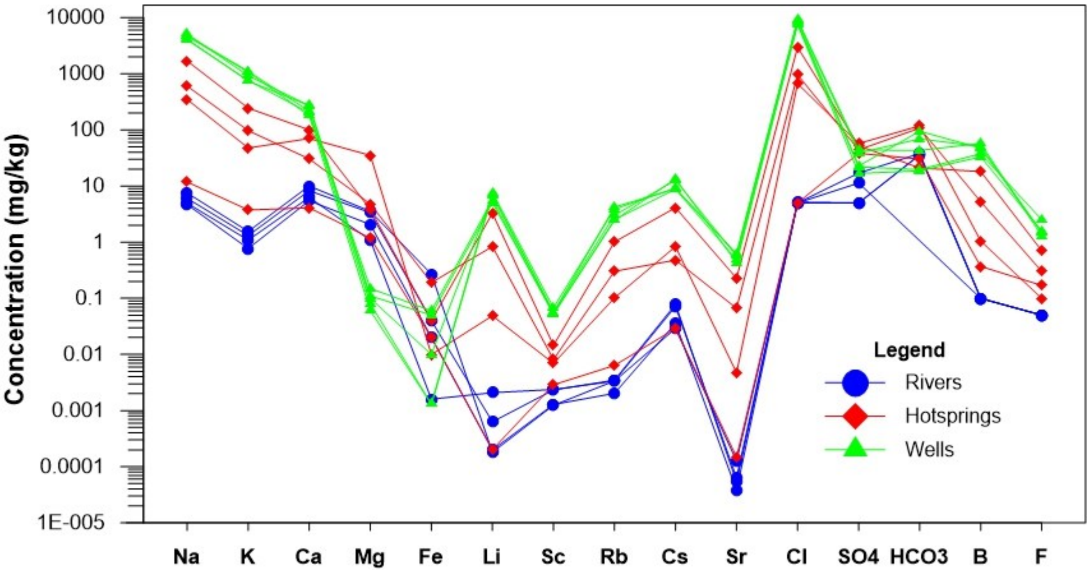

Figure 4. Schoeller diagram of major elements of Bacman surface and geothermal fluids.

3.2 Trace metals

The trace metals analyzed from the "original" fluid that are well above the LOQ of the ICP-MS analyses are Li, Sc, Rb, Sr, and Cs (Figure 5). Among these five metals, Sr has the highest range of concentrations, in well brines (9 to 13 mg/kg), in hot springs (0.5-4 mg/kg) except Inang Maharang (0.03 mg/kg), and in rivers (0.02-0.07 mg/kg). Li has the second highest concentration range, in well brines (5-7 mg/kg), in hot springs (0.04-3.3 mg/kg) except Inang Maharang (0.0002 mg/kg), and in river waters (< 2 ppb).

The geothermal well brines in Bacman have Rb concentrations in the range of 2.5-4.2 mg/kg, while the hot springs contain lower Rb (0.1-1 mg/kg) (Figure 4). Rb in river waters is lowest, in the range of (2-6 ppb). Similarly, Sc is highest in brines (0.05-0.06 mg/kg), moderate in hot springs (7-14 ppb) except Inang Maharang (~3 ppb), and lowest in river waters (1-2 ppb). The same trend is observed for Cs in wells (0.5 to 0.6 mg/kg), hot springs (5-22 ppb) except Inang Maharang (0.15 ppb), and rivers (0.1 to 0.6 ppb).

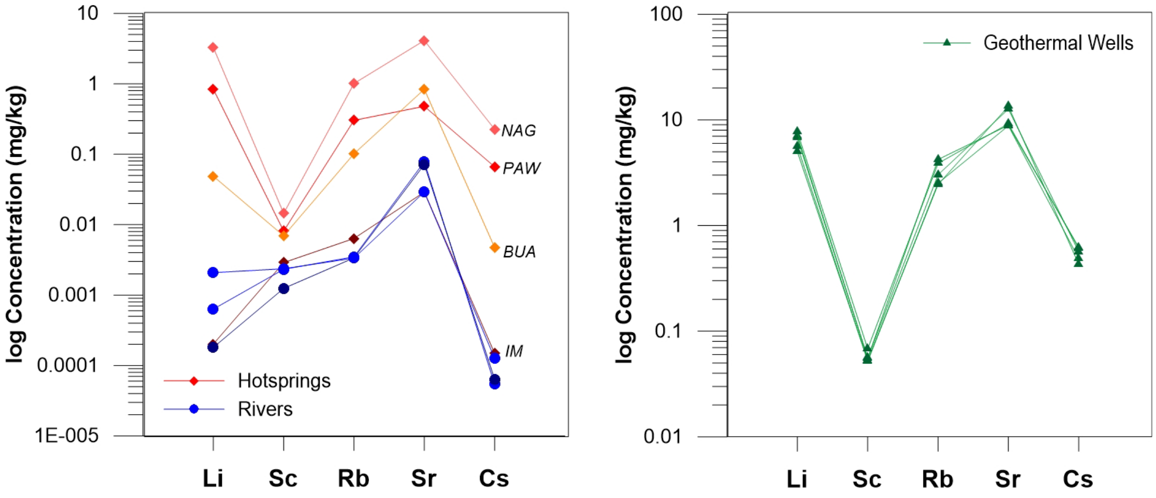

Figure 5. Schoeller diagram of trace metals in Bacman surface and geothermal waters.

3.3 REY Geochemistry

The total REY concentration of Bacman fluids vary from 10^{-5} to 10^{-8} mg/kg, or 0.1 to 100 ppt. The hot springs and river samples have higher REY, by one order of magnitude, compared to well fluids. In contrast to these eluates, their corresponding filter residues have higher total REY concentration, which is probably due to clay minerals, sediment load, and co-precipitated REY in scales, such as silica and calcite. REY in filter residues span the range of 10^{-1} to 10^{-3} mg/kg, in which the hot springs display wider variability, within four (4) orders of magnitude.

The C1-chondrite-normalized (REY_{CN}) plots of all eluates show depletion relative to chondrite, and relatively flat to slightly enriched LREE to HREE, consistently (Figure 6). River samples show slight LREE-enrichment (i.e., negative slope), while the hot spring samples show flat profiles, except for Naghaso and Buang springs. The wells samples exhibit more pronounced LREE-enrichment and HREE-depletion, except for W18 fluids.

Based on the REY_{CN} plots of the eluates (Figure 6), the following trends are observed:

1) Large, positive, La anomalies (~10^{-4} mg/kg) are consistently seen in all samples regardless of source, which leads to suspicion of contamination. The exact nature of contamination could not be definitely traced, thus La is excluded from plots and the discussion.

2) All river samples, except the Manitohan River samples, show distinct negative Ce anomalies.

3) All the well samples have large positive Eu_{CN} anomalies. Flat patterns are observed in hot springs, except Pawa, which shows a negative Eu_{CN} anomaly. A smaller Eu_{CN} anomaly is also observed in Botong Twin Falls.

4) W18 and W18-15 shows a unique and distinct REY pattern, which is relative LREE-depletion and HREE-enrichment depicting a concave-downward, dome-like pattern.

5) Distinct positive Y_{CN} anomalies in all samples, except in Inang Maharang, which shows the opposite.

When normalized to filter residues (REY_{FR}), the REY patterns of Bacman eluates still appear to be relatively depleted, but by one order of magnitude less than in chondrite-normalization (Figure 6). The same anomalies are also observed, as in REY_{CN} plots, but the "negative slope" attributed to LREE enrichment is not observed.

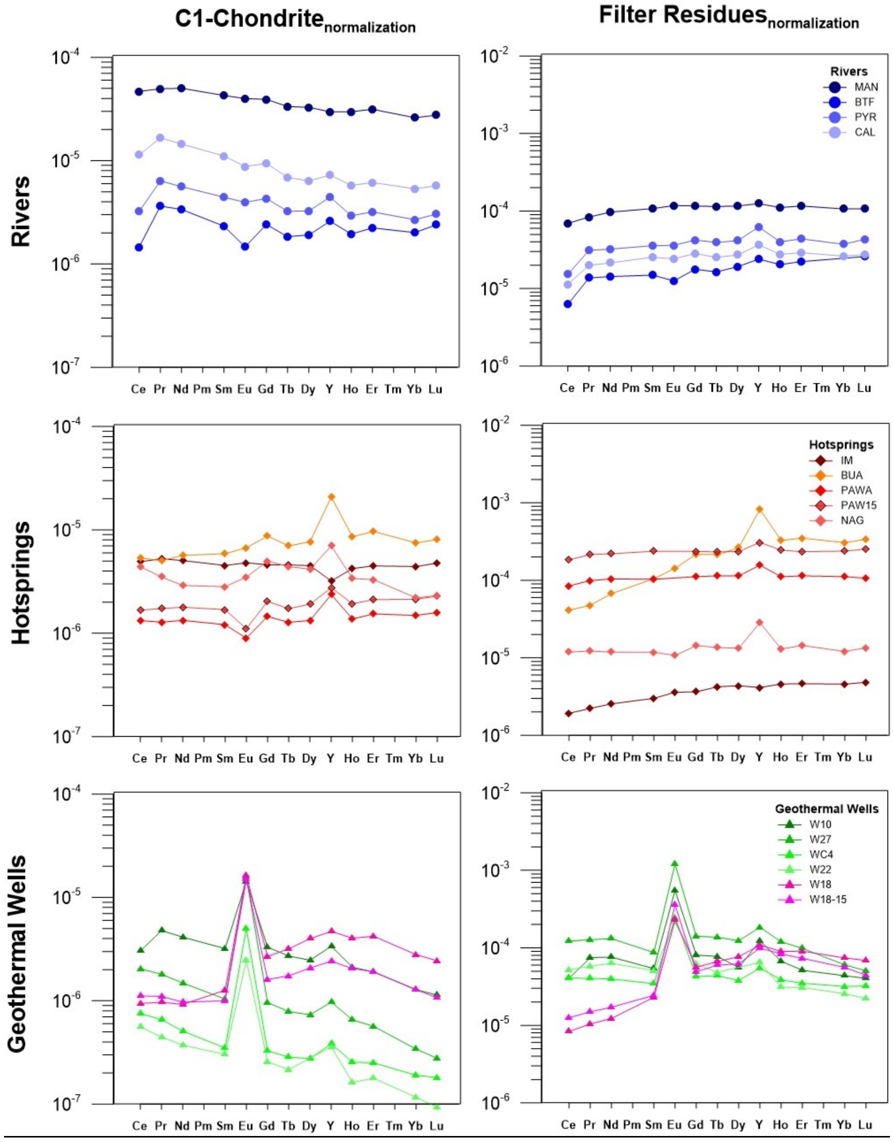

Figure 6. Chondrite-normalized and filter residue-normalized REY plots of Bacman surface and geothermal waters. Note that La is removed from the series due to suspected contamination.

4. DISCUSSION

4.1 Major Element and Trace Metal Chemistry

Based on the Cl-SO_4-HCO_3 water classification of Giggenbach (1991), Pawa, Naghaso, and Buang springs are classified as mature-Cl waters, suggesting that they best represent the deep reservoir fluids at the surface (Figure 7). The well fluids are also classified as mature Cl waters and plot tightly to the Cl apex. On the other hand, the Inang Maharang boiling springs are classified as mixed SO_4-HCO_3-Cl waters, while the rivers are mostly peripheral HCO_3-rich, with the exception of Calpi/Buyo river.

The discrepancy between the in-situ HCO_3 measurements and the laboratory results could be explained by CO_2 exsolution during sample transit. Although the sampling procedure involves taking air-free and air-tight samples, the long transit time (>7 days) between sampling and lab analysis appears to be sufficient to change the "original" HCO_3 concentrations. However, it should be noted that the field test kit is not as accurate as the established laboratory methods, such that the values are taken as close approximations of in-situ conditions.

The extremely high dilution of Cl reflected in the hot springs can be attributed to either mixing with surface waters during fluid migration towards the outflow, or seawater infiltration. For Pawa and Naghaso, seawater infiltration is less likely, or at least kept to a minimum as shown by their very low Mg content (< 4 mg/kg) compared to seawater. Stable isotope and Cl mixing models by Martinez-Olivar et al. (2005) also show the divergence of these hot springs from the seawater mixing line. On the contrary, the higher Mg content (35 mg/kg) of Buang spring, compared to surface waters, points to a possibility of either seawater mixing or shallow water-rock interaction with surrounding rocks, but the exact nature cannot be determined solely by major element data.

Based on the Na-K-Mg geoindicator from Giggenbach (1991), most hot spring fluids are classified as immature waters, with the exception of Naghaso, which is partially-equilibrated with the reservoir rocks (Figure 7). The other hot springs are largely diluted by surface waters. Nevertheless, the mixing trend with surface waters and the hot springs suggests source temperatures of ~260℃, while the well samples plot on the full equilibration line indicating deep temperatures of 280°-300℃.

The major element data of Inang Maharang showing its close affinity to river waters indicates that its origin may not be direct binary mixing of geothermal and meteoric waters (Figure 4). Inang Maharang is classified as steam-heated water, which is a result of the interaction of gases and steam with ground/surface water (Figure 7).

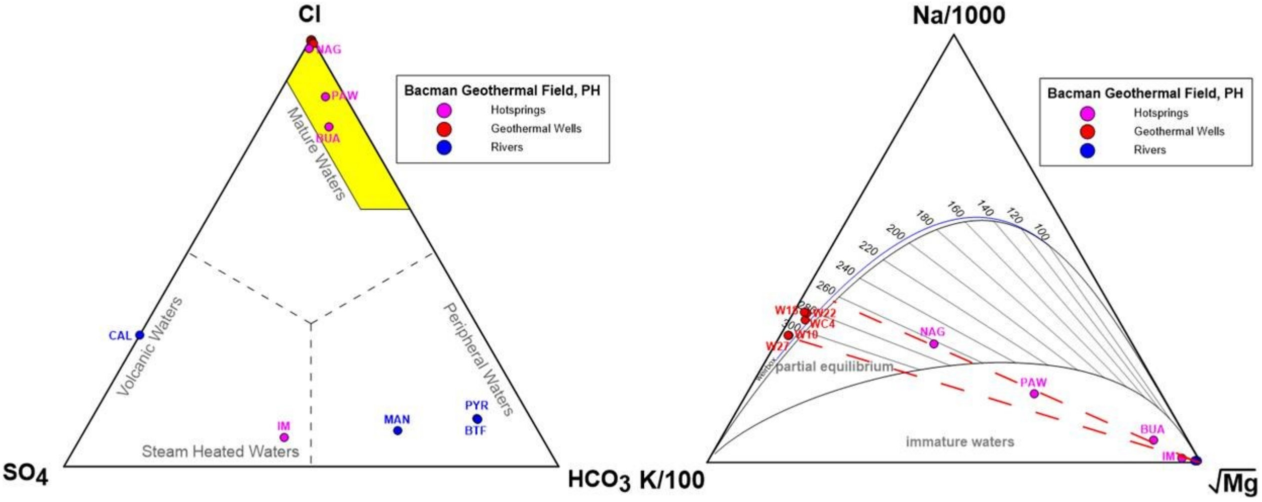

Figure 7. Classification of Bacman surface and geothermal waters based on major anions (Cl-SO_4-HCO_3) and major cations (Na-K-Mg) from Giggenbach (1991). Legend: NAG-Naghaso, PAW-Pawa, BUA-Buang, IM-Inang Maharang, CAL-Calpi/Buyo, MAN-Manitohan, PYR-Pad Y River, BTF-Botong Twin Falls.

Dilution and mixing between geothermal and surface waters can also be evaluated using conservative metals. For example, in binary mixing fluids, Sr is conservatively diluted similar to Cl, except during precipitation of scales. The Cl vs. Sr crossplot shows that the hot springs are indeed a result of mixing between meteoric waters (low Cl, Sr) and parent geothermal water (higher Cl and Sr) (Figure 8). This mixing model also shows that only a small fraction of the parent geothermal water is mixed with a tremendously large amount of surface water, as the hot spring Sr-Cl composition plots closer to river water composition.

Presently, there is no consensus regarding the nature and behavior of Sc, whether it behaves like an REE or completely different. Bacman fluid data show that Sc might be conservatively diluted and transported similar to the mixing of Sr and Cl (Figure 8).

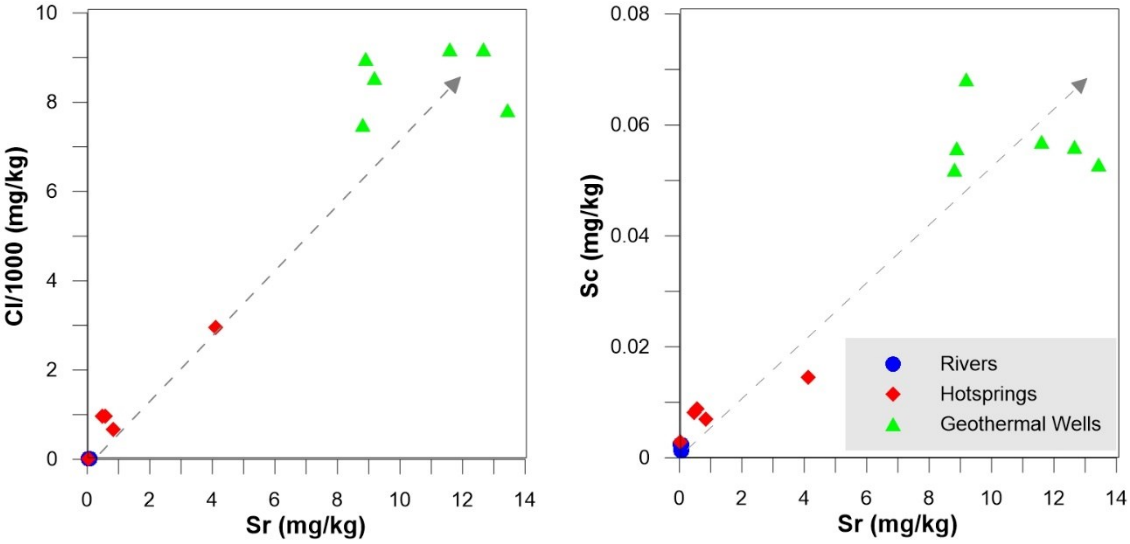

Figure 8. Crossplots of trace metals Sr and Cl, and Sr and Sc, showing large fraction of surface waters compared to deep geothermal waters during mixing and dilution.

4.2 REY Geochemistry

4.2.1 Controls on REY Transport in Geothermal Fluids

The REY concentration difference of about one order of magnitude between the hot springs and rivers, and geothermal wells, could be attributed to "REY loss", an effect of phase separation during well sampling (Moeller, 2000; Moeller et al., 2008). REY conservatively partitions into the vapor phase, as observed in the Larderello-Travalle and Kizildere geothermal fields, and in Oldoinyo-Lengai Volcano (Moeller et al., 2003; Moeller et al., 2006; Gilbert and Williams-Jones, 2008). Unfortunately, the steam and gas fraction of each well were not sampled, and fractionation in vapor cannot be properly quantified and elucidated for Bacman samples.

The REY_{FR} plots highlight the similarities and differences between the REY controlled by the larger fractions (> 0.2μm) in the filters, and the REY controlled by smaller fractions (<0.2 μm) that passed through the filter. The absence of the "negative slope" suggests that REY transport in Bacman river and hot spring samples is dominantly controlled by adherence to nanoparticles and colloids (Figure 6). On the contrary, Buang and Inang Maharang springs show some deviation from a flat profile, showing that the LREE are apparently controlled by particles ≥0.2 μm in these springs. The geothermal wells also present the same trends, but the slight HREE depletion in W10 and W27 samples may suggest that "truly dissolved" HREE partly control REY mobility in geothermal fluids in the reservoir condition.

4.2.2 REY anomalies as geochemical proxies

Almost all the river samples taken in Bacman show distinct negative Ce_{CN} and Ce_{FR} anomalies related to oxidative weathering of the river catchment lithology and fractionation of Ce during transport (Figure 6). The negative anomalies could be attributed to the faster oxidation of Ce^{3+} to Ce^{4+} relative to other REY during surface weathering of rocks. The immobile nature of Ce^{4+} fractionates it from the rest of the REY by retention in the residual rock.

The eluates from the Bacman geothermal wells show distinct, consistent, and large Eu_{CN} and Eu_{FR} anomalies (Figure 6) suggesting a deep fluid source temperature of >250°C, due to the dominance of divalent Eu at these temperatures, preferably fractionating it to the fluid (Sverjensky, 1984; Bau, 1991). Secondary minerals that form at reservoir conditions and during fluid convection discriminate Eu^{2+} due to charge-size disparity between the ion and the crystal lattice site. The process relatively enriches Eu in the fluid producing positive anomalies within the REY profile. This general behavior of Eu was shown in theoretical calculations up to ~1000°C and in experimental conditions up to 250°C (Bau, 1991). The results of this study prove the divalence of Eu in a natural setting at higher temperatures, in the range of 280° to 300°C, which is the measured reservoir temperature of this sector of the Bacman geothermal reservoir.

4.2.3. Mixing and dilution processes

The REY profile of W18 eluates (samples W18, and W18-15) shows a unique characteristic compared to the rest of the well samples, which is the extreme depletion of LREE and the strong enrichment of HREE (i.e., dome-shaped, convex upward profile) (Figure 6). W18 is a production well drilled in the NE part of the Bacman resource toward the direction of the fluid outflow, where further north the hot reinjection fluids (~160-180°C) from the separator vessels are being injected both at shallow and deeper levels. Years of fluid extraction at the center of the resource induced a pressure gradient and fluid drawdown that stimulates the encroachment of peripheral fluids, including these hot RI fluids that are now being channeled through the well. The RI returns hamper productivity of the well by decreasing the temperature and even have the potential to quench the hot reservoir. The REY signature of W18 points to the possibility that the LREE might be more readily and easily partitioned to the vapor phase during fluid flashing, leaving a residual fluid which is LREE-depleted and relatively HREE-enriched. This LREE-depleted RI fluid is then reheated by the high geothermal gradient (thus, a positive Eu_{CN} anomaly) and returns to the production sector, where it is re-tapped by the production wells.

Surface manifestations of geothermal waters such as hot springs, fumaroles, and solfataras are often the result of mixing and dilution of the parent geothermal fluid, and either surface water, groundwater, or river water. The major element chemistry of these waters already reflect these processes, even by using simple binary mixing models using conservative elements (e.g., Cl, Sr, Cl-^{18}O, and Cl-H_{TD}). In this study, the trace element crossplots of Sr-Cl and Sr-Sc also show and confirm this binary mixing, where the mixing fraction from the parent geothermal fluid is very small. However, the REY profiles of hot springs do not show any similarity with the well fluids (Figure 6). The total REY concentration of the hot springs is one order of magnitude higher than those of the wells, which suggest that simple dilution and relative enrichment through phase separation would be improbable as REY has been observed to partition in the vapor phase (Moeller et al., 2003; Moeller et al., 2006; Moeller et al., 2008; Gilbert and Williams-Jones, 2008).

A more obvious incoherence of REY profiles between the hot springs and wells is the absence of the large positive Eu_{CN} anomalies in the former (Figure 6). The reason for this absence could be attributed to the following:

1. A large fraction of surface water in comparison to the well fluids, such that the deep fluid signatures are dwarfed by those of the surface fluids, as seen in the trace elements. Negative Eu_{CN} anomalies in Pawa, the mature Cl spring that supposedly best represents the reservoir fluid at the surface from major element data, are even observed that could be due to interaction with lithology during convection and outflow at shallower and surface depths.

2. Due to the oxygen-rich nature and lower temperature of surface waters that mix with the parent geothermal fluid, Eu^{2+} could be oxidized to Eu^{3+} during mixing, dilution, and fluid migration towards the outflow, thereby being accommodated in the secondary minerals that form synchronously or thereafter.

Overall, it is apparent that REY may not be diluted conservatively, and their highly reactive nature increases the probability of re-equilibration and re-fractionation during fluid convection and outflow. Thus, they are not very effective tools for mixing models and reconstruction of original fluid composition.

5. CONCLUSIONS

The major and trace element, and REY distribution of geothermal fluids and corresponding 0.2μm filter residues, river sediments, and reservoir rocks from drilling representing the encountered main lithologic formations of the Bacman Geothermal Field, Philippines were investigated using a robust separation and solid phase extraction pre-concentration technique. Based on the results of this study, REY transport in geothermal fluids is apparently dominantly controlled by adherence to nanoparticles and colloids (<0.2μm). The occurrence of other less dominant control mechanisms such as the lanthanide tetrad effect, and lone ions and chemical complexation are also not negligible, as demonstrated by the HREE concentrations of some samples.

Bacman fluid samples from rivers, hot springs and geothermal wells have REY concentrations in the range of 10^{-5} to 10^{-8} mg/kg. The hot springs and river waters have higher REY concentrations, up to one order of magnitude greater than the well fluids, which is attributed to "REY loss" from fractionation in the vapor phase. Their corresponding filter residues have higher REY concentrations of 10^{-1} to 10^{-3} mg/kg; the hot spring filters show the widest variability of up to four orders of magnitude.

Geothermal well fluids with temperatures in the range of 260°-280°C have shown large positive Eu_{CN} anomalies, which correlate to the dominance of divalent Eu at high temperature fluid sources of ≥250°C. The presence of this anomaly could be used as a temperature proxy, supplementing the present established cation geothermometers in geothermal exploration. However, its absence in hot springs does not indicate low temperature sources, since REY are mixed and diluted non-conservatively, and are prone to be affected by other processes (i.e., redox, co-precipitation, etc.) during outflow due to their extremely reactive nature.

A different REY signature characterizes the W18 reinjection returns coming from the northern reinjection sink, as shown by a highly-depleted LREE and enriched HREE. The fractionation mechanism may have occurred as early as phase separation in the separator vessels, or during pipe delivery prior to reinjection as the fluids cool slightly to a temperature at which secondary minerals may form and discriminate them. However, the actual RI fluid before the injection should be sampled to see whether it is indeed LREE-depleted and HREE-enriched. Simultaneously, REY sampling of the brine and vapor phase with a Webre separator should be done to confirm the mechanism of LREE-depletion and HREE-enriched by phase separation. The presence of previously injected artificial organic/organometallic tracers could also affect the behavior of REY through chemical complexation.

The lack of a complete and accurate thermodynamic database, including reliable stability constants of each REY complex specie, remains as the primary hindrance in speciation modeling across various temperatures and pressures. Sparse data on REY fractionation in the vapor phase, both at high temperature and during decompression, should also be addressed to complete the final picture.

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