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# Application of Rare-Earth Elements in Spring Waters to Indicate Surficial Water-Rock Interaction Process in the Wayang Windu Geothermal Field, Indonesia

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## ABSTRACT

Although water-rock interaction (WRI) process is important to characterize the nature of fluid composition, this process is very complex to be clarified by customary water geochemistry analyses. To approach this problem, examining behavior of rare earth elements (REEs) application as WRI indicator is worth to examine. Total eight samples of surface waters located within the conductive zones were collected from Wayang Windu geothermal field, West Java, Indonesia. The samples were separated to hot and spring waters by the temperature (16–63 °C), pH (1.3–8.4), and chemical composition. The hot spring waters were classified into two types: steam-heating product ($SO_4^{2-}$) and sulfate-bicarbonate, and all the cold spring waters were bicarbonate types. REEs concentrations range from $6.3\times10^{-7}$ to approximately 2 times chondrite. A REEs speciation model indicates that $LnSO_4^+$occupies up to 70% of the total dissolved REEs concentrations resulting enrichment in sulfate in hot springs and bicarbonate $LnCO_3^+$ (up to 80%) including lanthanides free ions $Ln^{3+}$ (up to 70%) in cold spring waters. Additionally, atypical HREE-enriched pattern compared to LREE-enriched patterns is caused by the preference of LREEs absorbance to the surfaces of particles, whereas HREEs are preferentially retained in solution. Consequently, $LnSO_4^+$ and $LnCO_3^+$ are proven as REEs mineralization and oxidation of sulfides and carbonates complexes during weathering process in surficial features.

## 1. INTRODUCTION

The rare earth elements (REEs) are extensively utilized as tracers for the study of geological and geochemical processes. In volcanic hydrothermal fields, REEs patterns observed in hot spring waters reflect geochemical processes involving water-rock interactions at a relative shallow depth that are directly connected with the environment in the area of interest. Their distribution patterns in geochemical samples give purposeful information on the mechanisms involved in geochemical processes connected to the occurrence of the samples. The relative abundance of the REEs in cold and hot springs is used in this study to define the competitive processes controlling REEs fractionation in a suite of samples collected within the Wayang Windu geothermal field (WWGF), Bandung, Indonesia (Figure 1). In this study, we attempt to establish the levels of REEs and their fractionation in cold and hot spring waters issuing from conductive zones located in WWGF.

## 2. STUDY AREA

Wayang Windu geothermal field (WWGF) is one of several developed geothermal fields in Indonesia. It is located in 48S UTM 784,000 to 796,000 mE and 9,212,000 to 9,202,000 mN 40 km southern part of the West Java's capital city, Bandung. Its reservoir extends from northern to southern part of concession area, and gradually changes it's characteristic from liquid-to vapor-dominated to the north (Bogie et al., 2008). Surficial manifestations such as fumaroles, altered grounds, mud pools, hot springs and cold springs are scattered from north to south part of the field. In this study, samples were taken from eight locations (Fig. 2). Cold springs CP, CHJ, and AW, and hot spring MBA are hosted by Mt. Puncak Besar in the northern part of the field. Mount Wayang in the central part hosts WYG and CITA hot springs as well as CIBI cold spring. On the other hand, Mt. Windu acts as a host to CIBO in the south border. According to Bogie and Mackenzie (1998), analysis of trace elements of fresh lavas from Mt. Puncak Besar, Mt. Wayang, and Mt. Windu show the age of the heat source is at 0.1-0.5 Ma. Theoretical groundwater basin boundary line (Soetrisno, 1983) divides sample locations hosted by Mt. Puncak Besar and Mt. Wayang from Mt. Windu (CITA and CIBO).

## 3. METHODS

### 3.1 Sample Collection

Fluid samples were collected at four surface water sites and four hot springs (T <100°C) on August 2017 as part of a comprehensive study to characterize hydrothermal flows and discharges in the WWGF (Fig. 2, Table 1). Physicochemical parameters of spring waters, such as temperature and pH were measured using a portable HACH multimeter.

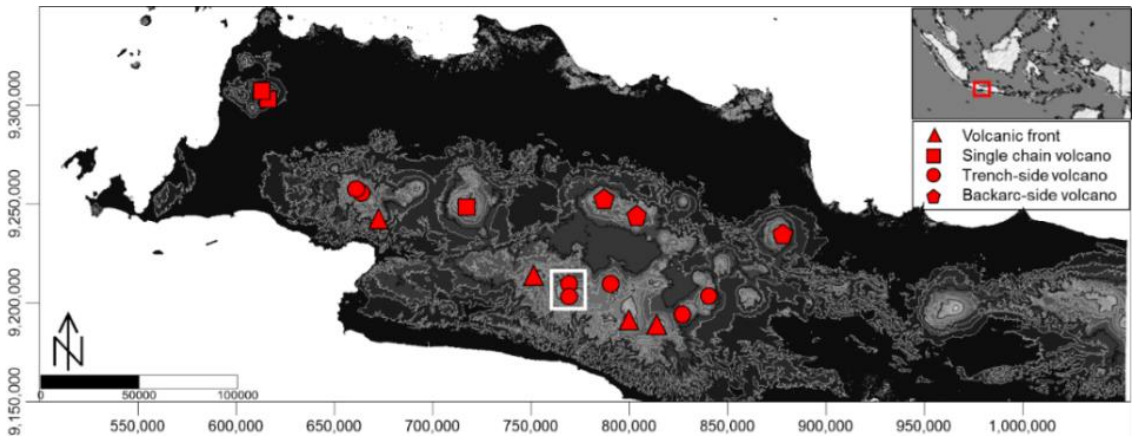


**Figure 1: Map showing Wayang Windu geothermal area is located in Bandung, West Java, Indonesia. One among several developed geothermal fields in Indonesia.**

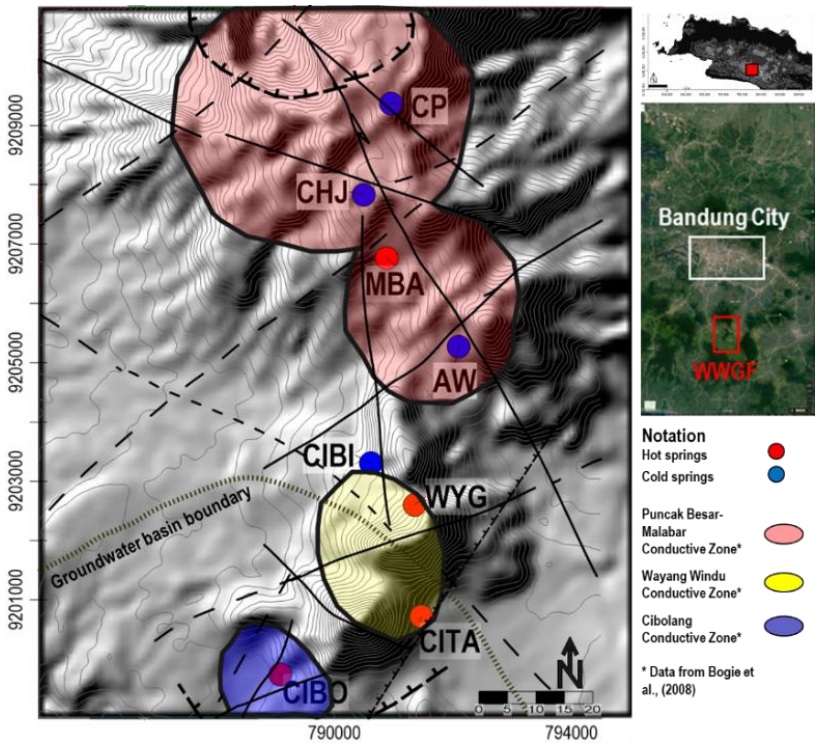


**Figure 2: Map showing samples collected from four cold springs and four hot springs in the study area, which are situated in different conductivity zones according to Bogie et al., (2008). Groundwater basin boundary line divides sample locations hosted by Mt. Puncak Besar - Mt. Wayang and Mt. Windu.**

Water samples were collected in 250 mL polythene bottles using trace metal clean procedures. The bottles were thoroughly washed with dilute hydrochloric acid and then with distilled water in the laboratory. In field, each bottle was filled and emptied twice with water before final sampling. Before sampling the filtering device was flushed with water sample. In addition, filtered water was used to rinse the sample bottle three times before the filtered sample was collected. Sample splits were acidified in the field to pH <2 of 0.01 M $HNO_3$, supra-pure quality, Merck, Germany for cation and REEs analysis. Unfiltered, unacidified samples were also collected for anion measurements. Water samples were then placed in clean plastic bags and clean Pelican cases before transported back to the lab. All samples were shipped (less than 1 week after collection) to Kyoto University, Japan.

### 3.2 Analytical Methods

Concentrations of major anion and cation in Table 1 were measured using an ion chromatograph (Prominence ion chromatograph system, Shimadzu Corp., Japan). The standard titration method by Nicholson (1993) was adopted to determine $HCO_3^-$ concentration. Each sample for REEs was pre-concentrated ten times before analyzed with ICP-MS Agilent Technologies at Research Institute of Humanity and Nature, Japan. Accuracy of the results (less than ± 10%) was obtained by the results of working standards. The equilibrium aqueous speciation of REEs and saturation indexes with respect to the main mineralogical phases were calculated using Visual MINTEQ software (Version 3.1) by Gustafsson (2012).

## 4. RESULTS AND DISCUSSIONS

### 4.1 Physicochemical Parameters

The physicochemical parameters and major anion cation in all samples, are summarized in Table 1 and represented in the Piper and ternary diagrams by Giggenbach (1991). The cold springs are characterized by pH ranging between 6.0 and 8.4 and temperature from 16.2° to 25.6° C. In addition to this, hot springs are identified by temperature ranging of 39.5° to 63° C. All hot spring samples except CITA, MBA and WYG show pH values higher than 6, reflecting their alkaline tendency. Cold springs are bicarbonate waters with Ca and Mg as major cations. The acidity of the Wayang Windu thermal springs is a consequence of magmatic acid gases such as $H_2S$ and $SO_2$ oxidation (Nicholson, 1993) at near surficial temperatures.

**Table 1. Physico-chemical parameters in WWGF. Units of major anion and cation concentrations are ppm.**

| NO | TYPE | ID | T | pH | $Li^+$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $HCO_3^-$ | $Cl^-$ | $F^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | mg/kg | | | | | | | | |
| 1 | Cold spring | AW | 16.2 | 7.4 | 0.00 | 2.87 | 1.54 | 4.97 | 1.91 | 11.3 | 0.94 | 0.20 | 2.82 |
| 2 | Cold spring | CHJ | 20.0 | 8.4 | 0.00 | 3.47 | 0.83 | 9.62 | 4.29 | 41.2 | 2.24 | 0.60 | 1.57 |
| 3 | Cold spring | CIBI | 25.6 | 6.8 | 0.00 | 2.17 | 0.75 | 4.49 | 2.17 | 16.5 | 0.68 | 0.18 | 4.07 |
| 4 | Cold spring | CP | 16.3 | 6.9 | 0.00 | 2.60 | 0.89 | 7.77 | 2.16 | 35.3 | 0.20 | 0.02 | 4.22 |
| 5 | Hot spring | CIBO | 63.0 | 7.1 | 0.58 | 56.6 | 20.5 | 65.7 | 39.5 | 184 | 14.6 | 0.14 | 201 |
| 6 | Hot spring | CITA | 40.3 | 6.2 | 0.00 | 67.8 | 15.5 | 115.2 | 40.1 | 67.1 | 0.71 | 0.04 | 517 |
| 7 | Hot spring | MBA | 44.7 | 2.8 | 0.00 | 4.81 | 1.55 | 5.17 | 3.13 | 0.00 | 0.48 | 0.18 | 160 |
| 8 | Hot spring | WYG | 56.3 | 1.3 | 0.00 | 8.05 | 22.7 | 5.84 | 3.39 | - | 13.8 | 0.00 | 3227 |

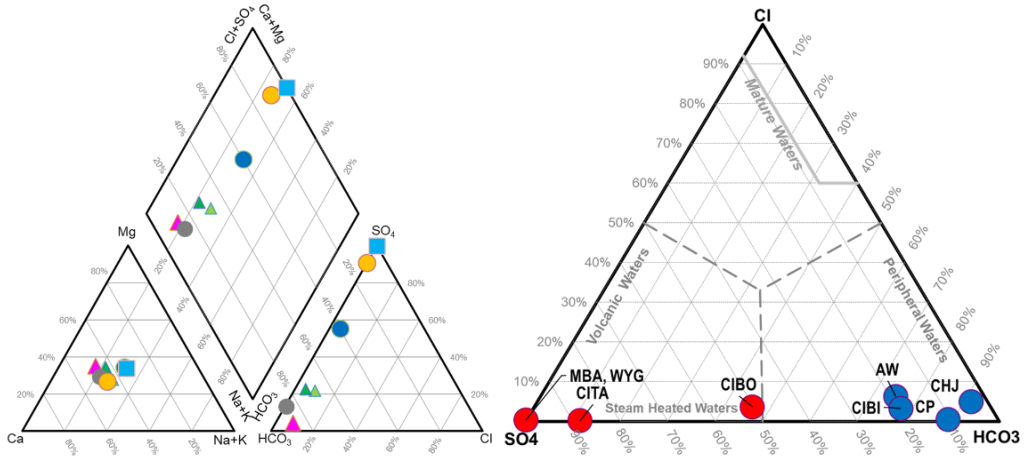


**Figure 3: Piper and ternary diagrams of cold spring and hot spring samples (Giggenbach, 1991).**

### 4.2 REEs Gull-wing Patterns

Obtained data indicate that low-pH geothermal fluids of the WWGF springs exhibit relatively high REEs contents in association with high sulfate hot springs. The thermal springs with low pH values (CITA, MBA and WYG) bear REEs contents up to 46,000 ppb, suggesting that pH and non-equilibrium complete dissolution with leaching cations from wall rocks are the main factors controlling REEs concentrations in thermal acidic hot springs. REEs contents in the cold spring samples exhibit lower range at $10^{-4}$ times of hot spring samples. Some REEs contents are below the detection limit.

Chondrite-normalized REEs pattern (Boynton, 1985) of the rock samples observed in WWGF shows gull-wing shapes in Fig. 4. Gull-wing pattern is identified not only in acid-sulfate geothermal systems but also in alkaline and chloride-dominated waters. It can be hypothesized that fluid interaction with the nature of reservoir rock play major role in the formation of gull-wing shapes to eliminate Oddo-Harkins effects (Peiffer et al., 2011). The most acidic hot spring WYG has similar pattern of the host rocks in the WWGF with high $(LREE/HREE)_{HR}$ fractionation except for the absence of its Eu anomaly. The Eu-anomaly (Eu/Eu*) defined as $Eu_N/(Sm_N*Gd_N)^{0.5}$, where N is the chondrite-normalized value. LREE enrichment is associated with alunite and the retained REEs in the rocks (Terakado and Fujitani, 1998). The REEs pattern of CIBO and WYG hot springs which are enriched in LREEs infers the association of fluid-alunite interaction. Equally important, MBA also has somewhat negative $(LREE/HREE)_{HR}$ fractionation with enrichment in HREE. MBA's pattern does not reflect any of the host rocks in WWGF. REEs in MBA are product of previously-mentioned, $H_2S$ and $SO_2$ oxidation, with shallow groundwater which shares similar rock aquifer with CHJ cold spring.

Acid hot springs have significant Eu-negative anomalies in which does not have same patterns of those host rocks. In samples from volcanic areas, Eu depletion in whole-rock-normalized REEs pattern of the samples can be explained by the co-precipitation of iron oxy-hydroxide and Ca-rich minerals under high temperature at depth. Depletion of Eu also increase with increasing precipitation of Fe-bearing phases (Fig. 6). This is attributable to precipitation and dissolution of secondary mineral at a relatively shallow depth. The almost all-visible pattern amongst cold springs belongs to CHJ which has positive anomalies of Gd. Chondrite-normalized of CHJ resembles the composition of MBA hot spring that shares the same conductivity zone in the north. One can infer that CHJ and MBA have shared similar groundwater rocks once before they emerged to the surface.

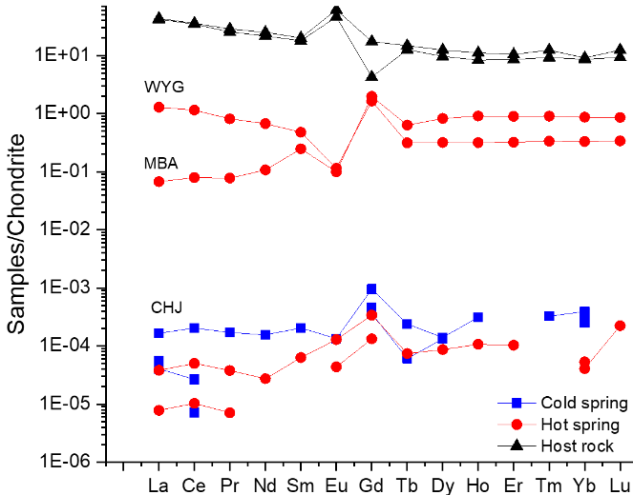


**Figure 4: REEs patterns from cold and hot springs normalized to chondrite (Boynton, 1985). CHJ has the highest concentration amongst all of cold springs, and WYG and MBA hot springs lead the group to be the most enriched REEs for hot spring samples. Samples of host rocks from two different locations: Puncak Besar (PB) and Windu (WI) from Bogie and MacKenzie (1998) are also displayed to compare the fractionation process.**

### 4.3 Speciation

Complexing agents that are involved in the REEs mobilization during groundwater-rock interaction can be analyzed by fractionation across the REEs series in chondrite-normalized pattern. Major aqueous species contribution is presented as percentage of the total dissolved REEs in Figure 5A-H. Sulfate compounds are distributed dominantly across lanthanide series in the sulfate hot spring samples. They also share dominant species with $LnF^{2+}$ as well as $LnCO_3^+$. Since cold springs categorized as bicarbonate waters (Fig. 3), $LnCO_3^+$ are distributed almost evenly through the lanthanide series in the samples. Concurrently, carbonate and hydroxide complexes are of potential importance in near-neutral environment and high pH environments (Cantrell and Byrne, 1987) as we can see in Fig. 5. Cold springs with pH around 7 are dominated by $LnCO_3^+$ except for CHJ which has pH > 7 with $LnCO_3^{2-}$ being 54-93% on the solution. This finding is congruent with previous studies (Wood, 1990; Lee and Byrne, 1992; Biddau et al., 2002) where increasing concentrations of REEs carbonate complexes is linear with increasing pH. $LnCO_3^+$ in cold spring samples may show the Ln-carbonate complexes as transport medium of carbonatites metals during weathering.

Relevant with the ternary diagram, $LnSO_4^+$ is the dominant species in MBA and WYG acid sulfate hot springs (67-75% and 61-71%, respectively). Hence, Ln-sulfate may accompany REEs mineralization and oxidation of sulfides during weathering process. Additionally, in acid-sulfate waters, concentration of carbonate and hydroxide ions are generally low to be competitive for REEs speciation (Wood, 1990). Only CIBO hot spring at pH 7.1 has oxy-hydroxide speciation. $LnF^{2+}$ related to fluid contact with alkaline igneous rocks, which also predominates WYG hot spring (25-32%). $LnF^{2+}$ normally is a significant complexer of REEs in acid-sulfate water (Serrano et al., 2000) and is also strongly associated with $Al^{3+}$. Hence, the presence of high aluminum concentration in hot springs is accountable for inhibiting the complexation of REEs by $F^-$ (Fig. 6). At pH <3, the $H^+$ ion effectively competes with REEs for $LnF^{2+}$ (Wood, 1990), so $LnF^{2+}$ are insignificant at low pH, i.e., CITA, MBA and WYG hot springs. The lack of $LnCl^{2+}$ in all hot springs (except for WYG, having a very little amount of this species) is probably due to dilution of the feeding hot springs from geothermal reservoir at shallow depth.

## 5. CONCLUSIONS

WWGF gull-wing shapes with enrichment in LREE implies fluid interaction with rocks in the reservoir. Chondrite-normalized REEs patterns of hot spring samples in only Wayang conductivity zone have almost similar to those of the WW reservoir rock except for its negative Eu anomalies. Samples with only LREE enrichment trends infer that those fluids have contacted with secondary mineral alunite in the altered zones on their pathways to the surface. Apparently hot springs are located in the same group within groundwater basin boundary line have similar REEs patterns, even though they are located in different conductivity zones. Acid hot spring MBA is one of the examples of how sulfides oxidation product (Ln-sulfate) contacted with shallow groundwater rocks that also host CHJ cold spring in the same conductivity zone.

Absorption of Eu in liquid phase will increase as the consequence of non-equilibrium complete dissolution with leaching cations from wall rocks and plagioclase minerals decomposition from the aquifer material by lower pH and higher temperature environments. Additionally, Ln-carbonate complexes are possible to transport REEs mineralization and carbonatites metals. In parallel, $LnF^{2+}$ act as tracers of fluid contact with reservoir as long as aluminum concentration is negligible. After all, not only WRI is confirmed by REEs analyses, but also tracing of fluid flow, absorption and weathering processes in surficial fluids.

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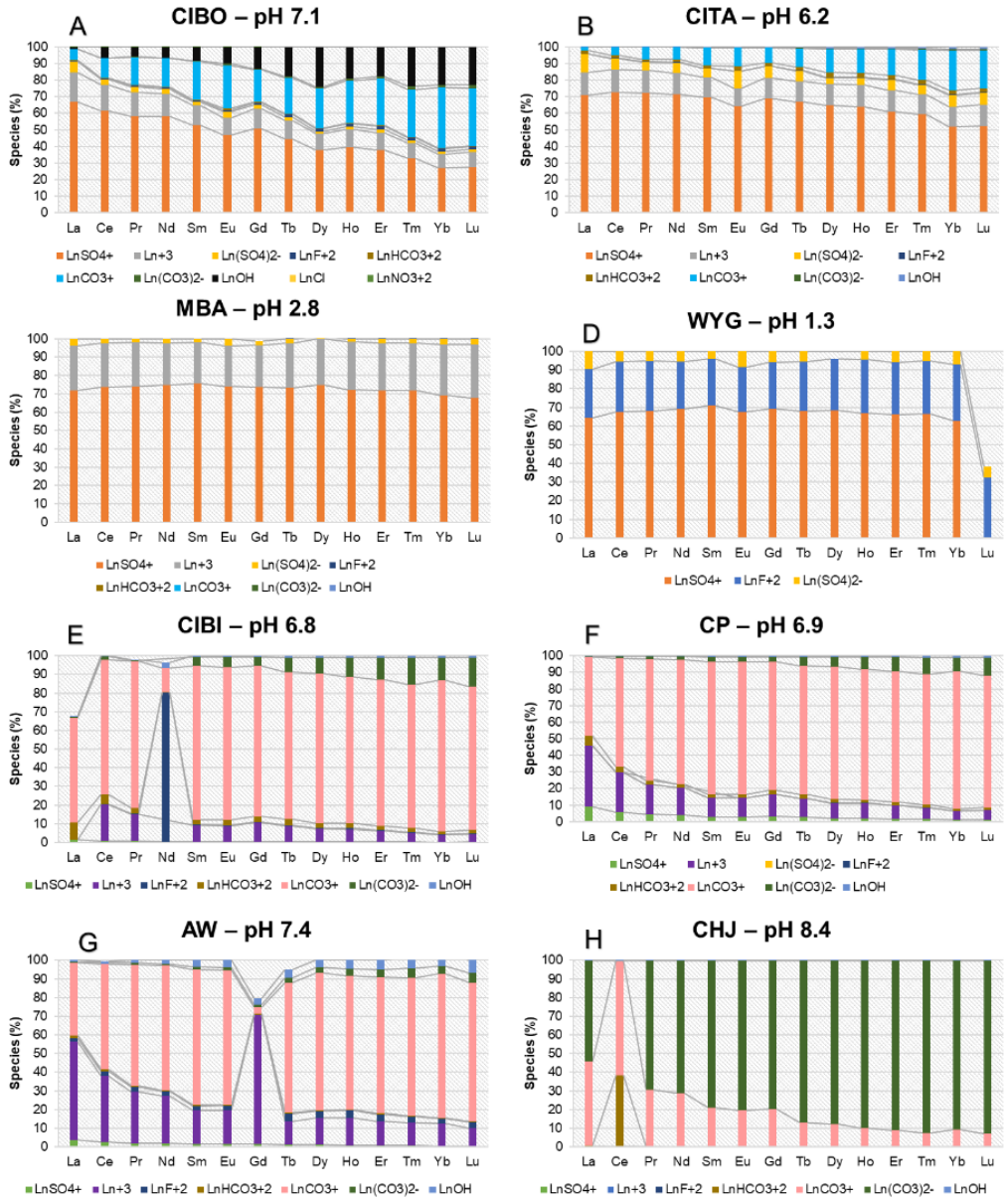


**Figure 5: REEs speciation patterns from hot springs (A-D) and cold spring samples (E-H). Major species such as $Ln(SO_4)^{2-}$, $LnCO_3^+$ and $LnF^{+2}$ predominate the hot spring samples, whilst cold springs with pH around 7 are typical of $LnCO_3^+$.**

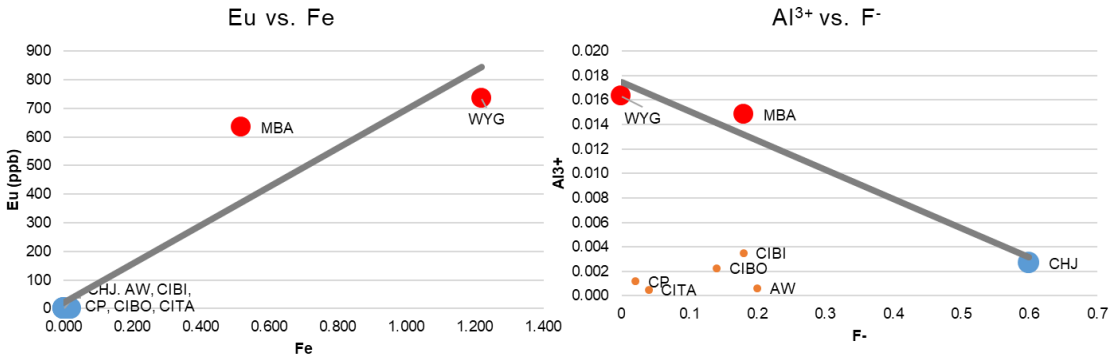


**Figure 6: Relationship between Eu and Fe indicating Fe precipitation did not occur in the acid sulfate water samples (left). Precipitation, dissolution and co-precipitation of secondary mineral Fe-bearing phases at a relatively shallow depth will lower Eu absorption. Competitive relationship between $Al^{3+}$ and $F^-$ as inhibitor of the REEs (right).**

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