## Hydrogeochemical Evolution of the Geothermal Waters in the Busan area, Korea

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## **ABSTRACT**

The Haeundae and Dongrae geothermal areas are located in the Busan city. Haeundae is famous for the summer resort area, having the largest beach in Korea and the Dongrae area is located about to 10 km northwest to Haeundae. Both of the areas have been recorded as hot spring areas in the historical archives and characterized by high Cl content compared to other geothermal waters in Korea. The geochemical and isotopic studies on thermal waters in the Busan city, on the southeastern tip of Korea, were carried out in order to identify the source of Cl, mixing process and geochemical evolution.

The ion concentrations of the Dongrae geothermal water are increased with well head temperature, whereas those of the Haeundae water show distinctively a negative relationship with the well temperature. The TDS of the Haeundae and Dongrae geothermal waters tend to have positive correlations with pH. The relationships of major ions versus Cl show linear trends, indicating mixing process between a Cl-poor fresh groundwater and a Cl-rich water at depth. Although most of the solutes do not fall close to the seawater dilution line, the linear relationship between Br and Cl strongly indicates that the solutes of the thermal waters in the Busan area is contributed by seawater. For the Dongrae water, the positive relationship between ion concentration and well head temperature can be explained by the mixing of cold fresh water during ascending of the geothermal waters. In case of the Haeundae water, the ion concentrations are decreased with the increasing of the measured temperature. It indicates that the Haeundae geothermal water is mixed with the cold seawater during ascending of geothermal waters.

All  $\delta$  <sup>18</sup>D and  $\delta$ D data for the study area are plotted to the worldwide meteoric water line, indicating that all waters are of a local meteoric origin. Although the isotopic data are plotted in the narrow range without a large deviation to the seawater

mixing line, the  $\delta^{18}$ O-Cl diagram clearly show that the Haeundae geothermal water lies on a mixing line between a meteoric end member and the seawater from off-shore of Busan. The carbon isotope result shows very depleted values (-14.8 to -23.5 m), indicating that the organic carbon was contributed to both thermal waters. The  $^{14}$ C data (71.4 and 71.8 pmc, respectively) indicate large contribution of modern carbon. It indicates that the salinities of the Dongrae and the Haeundae geothermal waters might be derived from the present seawater intruded beneath the Busan area. The overall hydrogeochemical features indicate that the sulfate in thermal waters is contributed by seawater. The  $\delta^{34}$ S values of dissolved sulfate of the thermal water (+ 10.6 to +19.3 m) support the mixing with seawater ( $\delta^{34}$ S<sub>seawater</sub> = +20 m). However, the SO<sub>4</sub>/Cl ratio is low, compared with seawater should be explained. The sulfate reduction by bacterial activity is a possible explanation for decreasing of sulfate in waters, but cannot explain the low sulfur isotopic values of sulfate in water. As explanation of SO<sub>4</sub> removal, the SO<sub>4</sub> and Ca in water can be transferred to solid such as gypsum in depth with high temperature.

The multicomponent mineral equilibrium approaches are applied to estimate the reservoir temperature of the Dongrae geothermal water at depth. This approach to determine equilibrium conditions can be limited by a lack of reliable Al analyses and dilution of thermal water through mixing with fresh water. The hypothetical Al concentration can be determined for each temperature by applying the FixAl method and considering mixing ratio with fresh water. The mineral equilibrium geothermometer temperatures and therefore the probable reservoir temperatures are estimated to be about 110°C to 130°C. It is very complicate to apply the multicomponent equilibrium geothermometer fro the Haeundae water, due to high chemical disturbance of thermal water by the contribution of cold seawater. mixing of thermal waters with cold seawater result in decreasing of temperature as well as enrichment of chemical constituents. Although the hydrogeochemistry of the Haeundae water shows the mixing with seawater of SiO2 concentration, the Haeundae water still shows high silica content, showing that the reservoir temperature might be higher than temperature estimated by silica geothermometer.

Key words: Geochemistry, geothermal water, mixing, reservoir temperature, geochemical evolution