

Systematic estimation and correction of Ba induced interference in ICP-MS for direct and quick analysis of REEs in geothermal waters

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High barium concentration and Ba/REE ratios are commonly observed in geothermal waters such as Arima-type brines, making it difficult to precisely determine REE characteristics, e.g., Eu, Ce anomalies and REE patterns of this kind of high matrix (major solutes) and ultra-low REE waters. We systematically evaluated Ba induced molecular ions in ICP-MS operated at solution mode and established a new correction method for direct determination of REE in high salinity geothermal waters.

Ba has seven isotopes from ¹³⁰Ba to ¹³⁸Ba with natural abundance of 0.1% to 71.7%, each of them will produce molecular ions in forms of oxide, hydroxide, hydride and argide in argon plasma. These molecular ions cover a mass range from 139 (¹³⁸BaH) to 178 (¹³⁸BaAr), theoretically overlapping with most of REE isotopes in complicated combinations. For example, both BaO and BaOH overlap the masses of light to middle REE isotopes, especially Eu. Conventional correction method simply considers that bulk interfering on Eu is contributed by BaO, and may result in large uncertainty or erroneous of REE anomalies and patterns. In this work we separately evaluated production rates of Ba oxide, hydroxide, hydride and argide for each of Ba isotopes in solution mode ICP-MS. Our data show that BaOH and BaO are major interfering species over Nd, Sm, Eu and Gd peaks. BaH and ¹³⁸Ba peak tailing seriously overlap with La and Ce signals. Argides are ignorable. Heavy REEs and Pr are free from a significant overlapping with any of the Ba induced interference. All the interference can be quantitatively estimated and reliably corrected for REE analysis.

We demonstrated the correction strategy by analysis of reference riverine water (SLRS-4) doped with Ba to Ba/Eu=125,000 similar to Arima-type brines. Determined REE data of Ba-doped SLRS-4 agrees very well with certified values. The method was also applied to determine REE compositions of various spring waters including Arima-type brine of the Arima area in southwest Japan (Nakamura et al, 2015). In this case, Ba induced interferences contributed to La, Ce, Nd, Sm, Eu and Gd raw signals for 92%, 24%, 48%, 78%, 96% and 75%, respectively. The intra REE interferences, e.g., PrO, NdO and SmO overlapping over middle and heavy REE signals, were less than 2.7% (mostly <1%), thus ignorable for discussion.

Keywords: Ba-induced interference, REE, geothermal waters, ICP-MS