A freeze-drying technique applied to the analysis of hot-spring waters: Implications for the origin of hot-spring waters from SW Japan

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Trace elements are usually very low abundances in natural waters, especially hot-spring water (HSW), resulting into difficulty in precise determination. To discuss about origin of HSW in SW Japan, we have developed highly precise analytical technique for determination of very low abundances of multi-elements in HSW with preconcentration using freeze-drying. The result showed recoveries of twenty-eight trace elements in the tested standard solution were ~100±5%. ICP-MS analyses on the reference material of Ottawa River water (SLRS-5) showed a good agreement with the reference values [1]. Compared with direct measurements, the method showed about 5 and 25 times improvement of the precision and detection limit for most trace elements, respectively. The blank contributions are typically low, <1% for most elements. Only 4% of the sample solution is consumed for forty-three elements, remaining 96% was used for Sr isotopic analyses. The method was applied to Misasa HSW collected from central part of Tottori, SW Japan. Based on the newly obtained data, Misasa HSW is compared with those of basement rocks and the other fluids. Major element compositions are distinct from the brine and volcanic waters, but is similar to the other hot-springs from granitic terrance in Tottori [2]. Misasa HSW showed extremely low REE abundances, 10^6 to 10^7 times lower than those of basement rocks, and LREEs were strong depletion relative to HREEs. The REE pattern of Misasa HSW showed no correlation to that of basement rocks. In the unfiltered HSW, significant amounts of REE (~80%) are hosted by the suspended particles, which are identified as Fe oxyhydroxide aggregates coating by minor black Mn oxide. The $^{87}Sr/^{86}Sr$ ratio of Misasa HSW was 0.7061±1 (n=9, 2σ), which is slightly higher than basement andesite (0.7041-0.7056), but is much lower than that of granite (0.7125, [3]). The Sr isotopic composition is distinct from the brine and volcanic waters (0.7078-0.7106), but is associated with the other hot-spring from granitic region (0.7065) [4].

[1] Yeghicheyan et al. (2013) *Geostand. Geoanal. Res.* **37**, 449–467. [2] Matsubaya et al. (1973) *GJ*, **7**, 123-151. [3] Feineman et al. (2013) *Geochem. Geophys. Geosyst.*, **14**, 3009-3031. [4] Notsu et al. (1982) *Appl. Geochem.*, **6**, 543-551.