ISOTOPE COMPOSITION OF LITHIUM, BORON AND METHANE IN HYPERALKALINE SPRINGS OF NORTHERN APENNINES (ITALY)

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1. Boron and Lithium

Spring waters issuing from serpentinized ultramafic rocks of Taro-Ceno Valleys (Emilia-Romagna, Italy) were analyzed for major and trace elements and for isotopic composition by δ^{11}B, δ^{7}Li and δ^{18}O and δ^{2}H of water molecula. Similarly to other worldwide springs from serpentinites, the chemical composition of the waters evolves with water-rock interaction starting from Ca-bicarbonate, passing through Mg-bicarbonate up to Na-(Ca)-OH composition. The investigated hyperalkaline springs (PR10 pH = 11; UM15 pH = 10) have a quite high boron content (2 to 13 mg/L, respectively), unexpected for fresh water, but with B/Cl ratios comparable with those of the leached serpentine and olivine of the area (Boschetti & Toscani, 2008). Most of the Ca- and Mg-bicarbonate springs have a δ^{11}B range between +16.3 to 23.7‰, in line with the range of +16 to +24‰ of the low P-T serpentinites. Differently, two springs from Mt. Prinzera show very high δ^{11}B (PR10 = +39‰; PR01 = +43‰). These values may be explained by a mix with seawater (39-40‰) or other seawater-derived fluid like those from mud volcanoes or brine waters. However, considering that B/Cl, Br/Cl and I/Cl ratios in these springs are in line with those of serpentinites, the δ^{11}B value may be related to the pH increase during water-rock interaction coupled with oxide, clay and brucite precipitation. In a similar way, the high δ^{7}Li up to +34.7‰ (total range is +19.4 to +34.7‰) in hyperalkaline springs can be related to isotopic fractionations occurring during secondary phase precipitation (e.g. Lemarchand et al., 2010).

2. Methane

In order to substantiate the typical presence of abiotic hydrogen and methane in the hyperalkaline fluids, the chemical and isotopic gas analysis was also performed in PR10 and UM15 springs. Surprisingly and differently from Lost City (The Atlantis Massif), near Alpine (Liguria, Italy) or Semail Nappe (Oman), in the hyperalkaline fluids of the Taro-Ceno Valleys hydrogen was not detected; however, a more accurate extraction is in progress. Moreover, dissolved methane (PR10 = 1.3 mg/L, UM 15 = 0.1 mg/L) have a biogenic-thermogenic signature of -57.5‰ < $\delta^{13}C(CH_4)$ < -40.8‰. Considering that these values are quite comparable with those of methane from local hydrocarbons explorative wells and natural seeps, we hypothesize that methane in the hyperalkaline springs investigated in this study may derive from organic matter in the sedimentary (flysch and arenaceous) formations occurring below the ophiolitic unit, whereas an abiotic serpentinization origin of methane is not evidenced, at the moment.

3. Conclusions

From the above discussion we can conclude that: i) boron isotopes are fractionated due to pH effect and Li due to formation of new mineral phases, respectively; ii) a mixing between the most evolved (and deepest) hyperalkaline waters with a seawater-derived fluid may be excluded; iii) on the contrary, the isotope composition of methane testify a solubilization of gaseous hydrocarbons in the aquifer at the boundary between ophiolitic units and the below flysch and/or arenaceous formations. This effect could have overwritten the abiotic serpentinization signature of the gas dissolved in the hyperalkaline waters.

4. References

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