Geochemical Characterization of Trace Elements in Thermomineral Waters of Greece

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Trace elements have a fundamental role in natural and anthropogenic systems. In waters, they present a great variability of concentrations that mostly depends on the degree of gas-water-rock interactions and geochemical conditions such as pH, temperature, redox and/or exchange reactions, etc. Even though, they are present in very low contents in host-rocks, elevated concentrations in ground or surface waters may have a hazardous impact on human and animal health and thus, it is important to both quantify and try to understand their behaviour in natural systems.
Here we present the results of about 300 cold and thermal mineral waters collected along the entire Hellenic territory. Physicochemical parameters (temperature, pH, electrical conductivity and Eh) were measured in situ, whilst samples were analysed by Ionic Chromatography (IC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for their major and trace elements' content. The great variability in hydrogeological settings justifies the wide range of temperatures (6.5 - 98°C) and pH (1.96 - 11.98). Total Dissolved Solids (TDS) values also covered a wide range, from 0.06 to 43 g/L. Based on the combination of pH, T and TDS, samples were subdivided into 5 classes: i) thermal waters; ii) thermal waters affected by sea water contamination; iii) cold CO_2-rich waters; iv) hyperalkaline waters; and v) acidic waters.
The great variability in chemical composition of the sampled waters is reflected in the large range of trace element contents (four to five orders of magnitude). Thermal waters affected by seawater contamination show the strongest enrichments in Li (up to 17,600 µg/L), B (up to 38,200 µg/L), Sr (up to 80,000 µg/L) and Rb (up to 9230 µg/L), mostly deriving from water-rock interaction. Cold CO_2-rich waters display elevated concentrations of Mn (up to 3970 µg/L), Ni (up to 111 µg/L) and Fe (up to 218,000 µg/L), whilst at the water outflow an extensive precipitation of iron oxi-hydroxides is observed. Hyperalkaline waters are generally strongly depleted in trace elements due to the precipitation of secondary minerals, however they are enriched in Al (up to 421 µg/L). Aluminium becomes soluble at extreme pH conditions and therefore also acidic waters present enhanced concentrations (up to 100,000 µg/L). Acidic waters show also enrichments in Fe (up to 58,400 µg/L), Mn (up to 15,600 µg/L) and Ni (up to 101 µg/L).
In some cases, the maximum contaminant levels (MCLs) fixed by the Directive 98/83/EC for drinking water (and subsequent updates), are strongly exceeded in the under investigation waters. Such elevated concentrations of harmful elements may create hazards to human health either via direct consumption of cold mineral waters or through mixing of highly mineralized waters - even in small proportions - with shallow groundwater. For instance, As (MCL 10 µg/L) in the sampled waters reaches concentrations up to 1820 µg/L that derive from high temperature water-rock interaction within the hydrothermal circuit.

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