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Origin of mineral and thermal waters

title: **Stable isotope study on the origin of sulphate in the thermal waters of Budapest and its surroundings**

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INTRODUCTION

The karstic thermal water flow system of the Dunazug Mts. (Hungary) supplies plenty of luke-warm (18–30°C) and warm (30–77°C) water for balneological, recreational and wellness purposes with variegating chemical composition in Budapest, capital of Hungary. All of these waters coming from different depth (10–1000 m) are characterized by significant, but varying amount of dissolved sulphate (100–400 mg/l). For the origin of this sulphate there are two hypotheses; 1) Sulphate originates from the oxidation of pyrite in the Tard Clay Formation contacting the karstic aquifer; 2) Sulphate originates from the dissolution of gypsum and anhydrite contained in Permian and/or Triassic marine evaporites and carbonate rocks (lime-stone and dolomite). Stable sulphur and oxygen isotopic measurements have been made on the dissolved sulphate in order to determine its origin.

RESULTS AND DISCUSSION

Twelve thermal water well and four luke-warm spring were sampled for stable S and O isotopic measurements. The dissolved sulphate was precipitated as BaSO₄ by means of 10% solution of BaCl₂ on spot. The stable S and O isotopic measurements were made in the Mass Spectrometry Laboratory of the Institute of Physics, University of Marie-Curie Skłodowska, Lublin (Poland) (for details see Hałas, Szaran, 2001, 2004; Hałas, 2007).

The sulphur isotopic composition of dissolved sulphate in the thermal warm water (30–77°C) of Budapest is characterized by rather positive $\delta^{34}\text{S}$ values varying between 10.2 and 17.7 [‰]_{CDT} (mean is 13.6‰); however those of luke-warm water ranges from -5.7‰ to -2.5‰ (mean is -4.2‰). This characteristic difference between the $\delta^{34}\text{S}$ values of warm and luke-warm waters indicates different genesis.

Vető et al. (1999) published $\delta^{34}\text{S}$ values for the total sulphur (pyrite) in the Tard Clay Formation between -20‰ and +15‰ with a mean of 2.6‰. While the $\delta^{34}\text{S}$ values of Upper Permian evaporites are from 9.51‰ to 20.93‰ (mean value is 12.78‰; Hámor, 1997), and Lower Triassic evaporites are from 15.98‰ to 33.01‰ with large dispersion (mean $\delta^{34}\text{S}$ value is 24.28‰, Hámor, 1991). Based on these data the dissolved sulphate in the warm thermal water of Budapest originates from the Upper Permian evaporites, while that in the luke-warm water originates mostly from oxidation of pyrite in the Tard Clay Formation.

The $\delta^{18}\text{O}$ value of the dissolved sulphate in the warm thermal water varies in a very narrow range; from 4.2 to 6.4 [‰]_{VSMOW}, which is significantly lower than the marine sulphate of Triassic and Permian age (10–15‰). The water temperature ranges between 40 and 80°C, because cold water mixes to the upwelling hot water. An explanation for the lower $\delta^{18}\text{O}_{\text{SO}_4}$ values can be isotope exchange between the oxygen atoms of sulphate and water molecules. The maximum temperature of water calculated by means of the formula given by Kusakabe and Robinson (1977) based on the oxygen isotope fractionation between water and sulphate is 70–90°C, which matches well with the measured bottom well temperatures. This indicates that the oxygen isotopic equilibrium in the water-sulphate system can be reached at around 80°C within the time frame of 20 thousand years (the age of thermal water is estimated to be between 13 and 20 ka, Deák, 1979)

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