

## **An enigmatic salinity source in the Mediterranean coastal aquifer and Gaza Strip: Utilization of isotopic (B, Sr, O) constraints for searching the sources of groundwater contamination**

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### **The Scope of the Problem**

The southern Mediterranean coastal aquifer is suffering from a severe water quality crisis that endangers future exploitation for a population of over one million living in the coastal area of Israel and the Gaza Strip. The most conspicuous phenomena are the ongoing salinization (>2000 mgCl/l), boron (<4 mg/l), and nitrate pollution (<460 mg/l).

### **Results and Discussion**

In the framework of the European research project BOREMED, co-financed by the European Community, geochemical and isotopic (B, Sr, O) investigation of groundwater was conducted in the southern coastal aquifer of Israel and Gaza Strip. It reveals three major water types: (1) Eastern saline groundwater with Na/Cl >1, high B/Cl ( $9 \times 10^{-3}$ ), and  $\delta^{11}\text{B}$  values (48‰) and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.70802 to 0.70819; (2) Sea-water intrusion with Na/Cl <0.86, low B/Cl ( $<8 \times 10^{-4}$ ) and high  $\delta^{11}\text{B}$  values (>40‰); and (3) Nitrate-rich groundwater within the Gaza Strip with high Ca content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.70815 to 0.70875.

We use the geochemical variations to reconstruct the principle flow paths. The eastern saline groundwater component is the major source of salinity in a large area of the aquifer. Over-exploitation in the Gaza Strip resulted in declining water levels, which resulted in intensification of east-west flow. Nitrification process enhances dissolution of the carbonate matrix of the calcareous aquifer, as evident by linear relationships between  $\text{NO}_3$ , Ca, and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios.

### **The Boron Source Enigma**

The  $\text{Na-SO}_4\text{-HCO}_3$  composition of the eastern saline groundwater can be interpreted by several possible geochemical mechanisms (e.g., gypsum and carbonate dissolution coupled with base-exchange reactions, silicate hydrolysis such as alteration of albite into kaolinite, flushing of seawater intrusion by freshwater). The enrichment of both elemental boron and  $\delta^{11}\text{B}$  values rules out, however, all of these possibilities. The origin of the eastern saline groundwater, which is the major source of salinization in the Gaza Strip, has yet to be resolved.

## **Laser-based oxygen isotope analysis of biogenic silica**

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Oxygen isotope compositions of biogenic silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) provide a powerful paleoenvironmental proxy, particularly for regions where biogenic carbonate is rare or absent such as fresh water lakes, high-latitude oceanic regions, and the deep sea below the carbonate compensation depth. However, measurements of the O isotope composition of biogenic silica are complicated as it may contain as much as 13 weight % water, much of which is exchangeable. To obtain accurate estimates of the original O isotope composition it has been necessary to use fairly complex extraction procedures that avoid the exchangeable oxygen, or where controlled isotopic exchange approaches estimated original compositions for this component. Methods used either require relatively large amounts of sample (tens of mg) and/or are questionable for cases where it is difficult to estimate the original isotopic composition of exchangeable oxygen such as for fresh-water systems. To overcome these analytical problems, a method has been developed that employs a 30 W  $\text{CO}_2$ -laser to spontaneously heat and melt the biogenic silica in a vacuum, followed by fluorination of the residual melt bead. Initial rapid heating avoids exchange between released water vapors and the Si-bonded oxygen, as the vapors are condensed in a trap cooled with liquid nitrogen. The melted sample beads are then transferred to a new Pt sample holder for oxygen extraction using the  $\text{CO}_2$ -laser and ultrapure  $\text{F}_2$  as reagent. Use of a distinct sample holder for melting eliminates cross-contamination that may occur through vaporization during melting and condensation of the vapors on the sample holders of a common sample chamber.

Tests on several 1 to 3 mg-sized quartz standards and samples of biogenic silica from sponge spicules indicate that vaporization during melting is limited and has no effect on the O isotope composition of the  $\text{SiO}_2$ . Repeated measurements are precise to within 0.2 permil. For sponge spicules from fresh waters (Lake Baikal, Biwa Lake) and the Caribbean Sea, for which the temperature and isotopic composition of water are known or can be estimated with reasonable certainty, temperatures calculated are in good agreement with actual temperatures. However, for other species of sponge spicules from the White Sea and the Weddell Sea, the agreement is poor, suggesting species-specific fractionation, isotopic exchange of the silica with pore fluids, or poor estimates of actual conditions. Experiments using cultured species of sponge spicules are in progress to place further constraints on these possibilities.