



Identification of groundwater sources by trace elements and isotopes

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A combination of rare earth element (REE) and Y distribution (henceforth combined to REY) and stable oxygen and hydrogen isotopes is used to identify the sources of groundwaters. Contrasting the group of major elements in groundwater, trace elements and in particular REY behave differently. Their low concentrations (pmol/l) result from adsorption onto mineral surfaces and coprecipitation with alteration minerals. REY are also constituents of major minerals but the solubility behaviour of REE differs widely from that of their carriers because of dominant surface complexation. For instance, REY saturation in groundwater is achieved when that of calcite is only one thousandth. This means that REY saturation is achieved immediately, whereas that of the major elements takes considerably more time. Besides being easily adsorbed, dissolved REY undergo ion exchange with the surface of minerals when migrating through pores. However, in geological time-spans, REY adsorbed on all surfaces are in static equilibrium with REY abundance in groundwater established in the catchment area. Even if the lithology changes, the REY patterns of groundwater, established in the catchment area, pass different lithologies unchanged because all surfaces are in adsorption equilibrium with the percolating water after long times. Therefore, trace elements bear mostly the signature of the interaction of REY with those minerals occurring in the catchment area which adsorbed REY by surface complexation. In contrast, major elements are controlled by the most leachable minerals in the aquifer rocks. Both together reflect the flow path of water.

Stable isotopes are commonly used to determine the probable sources and the mixing of different water bodies. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are less controlled by water-rock interaction

than by climatic and geomorphological factors at the time of replenishment. Only under enhanced temperatures $\delta^{18}\text{O}$ is shifted to enhanced values. In $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ cross plots, data clusters are structured by grouping the isotope data according to REY patterns of the groundwaters and thus yield more detailed information on the source and flow path of groundwater.

REY distribution and stable isotopes of H and O are applied to discuss sources and flow paths of groundwaters in Israel. These examples reveal the progress in both isotope and trace element geochemistry. Examples in which REY patterns revealed a different source of groundwater than by isotopes alone will be discussed in detail.