

Trace elements origin and fate control in groundwater flow systems of the Sierra Madre Occidental and Mesa Central, Mexico.

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Fluoride (F), arsenic (As) and uranium (U) are naturally occurring trace elements that can cause adverse health effects when ingested by humans. Groundwater around the Mexican cities of Chihuahua, Zacatecas and Salinas has elevated concentrations of these elements. Through detailed hydrogeochemistry, bulk rock geochemistry, scanning electron microscopy (SEM), Raman spectroscopy, electron microprobe (EMP) and laser ablation (LA-) ICP-MS analyses in this study, we identified the primary sources of F, As and U in central and northern Mexico. Zacatecas and Chihuahua have volcanic rocks with Paleogene ages associated with the Sierra Madre Occidental (SMO), while the Salinas volcanic rocks (Neogene) are associated with the Mesa Central (MC). After characterization of igneous rocks showing a range of composition (mafic to felsic) in the three study areas, rhyolites, ignimbrites and granites are the main lithologies containing F, As and U-bearing phases, mostly the glassy matrix, F-apatite and biotite. Secondary sources (and primary sinks) are represented by Holocene basin fill sediments, erosion products of rhyolitic, ignimbrite and granite rocks. The bearing phases of these elements are linked to the volcanic lithics by their content in glassy matrix, F-apatite, biotite, and fluorite. In specific areas, tertiary sources (secondary sinks) formed in rhyolites and ignimbrites linked to iron oxides with As concentrations were detected near mining areas. The F, As and U-bearing phases contained in the different sources are vulnerable to mobilization mechanisms that act to release these elements into the environment. Weathering, dissolution, devitrification and oxidation have been identified as the main mechanisms favoring mobilization. Once the bearing phases encounter aqueous conditions, Eh-pH, temperature, groundwater residence time (water-rock interaction) and evaporation, control the enrichment of F, As and U in the groundwater. As a result of these processes, more than $\approx 77\%$ of the samples ($n=225$) for F, $\approx 67\%$ for As and $\approx 18\%$ for U, exceed the permissible limits for water use and consumption established by Mexican and international standards in the different study areas, exposing the potential public health impact of these elements in the groundwater flow systems contained in the volcanic sequences and basin fill sediments of the SMO and MC.

