

## Geochemical assessment of geogenic Arsenic contamination in the Floridan Aquifer

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During the past 30 years various occurrences of elevated arsenic (As) in groundwater were reported. With a few exceptions the source of As was geogenic, i.e. naturally occurring in the aquifer matrix. The release of As from the aquifer matrix, however, is generally caused by anthropogenic perturbations of the physicochemical conditions.

Arsenic in the Floridan Aquifer, a very large limestone aquifer, is mostly associated with pyrite. Thus a change in redox conditions could cause the dissolution of pyrite and the release of As. This scenario is the current working hypotheses to explain elevated As observed during aquifer storage and recovery (ASR) operation in Florida, because the injected water is oxygenated. As a result, pyrite dissolves and As values in recovered water can be up to 130  $\mu\text{g/L}$ . To test this hypothesis a set of leaching experiments were performed with three types of water: native Floridan groundwater, Tampa tap water and water from a wetland. Aquifer material was packed into PVC columns of 0.3 m length and water was percolated from the bottom up at 2 mL/min. Results from the column experiments were also compared to results obtained from 1D reactive transport modeling.

No As was released during the experiments using native Floridan groundwater. Tampa tap water, which closely resembles injection water used in ASR operation caused the release of As from the columns. Values were higher than the current drinking water standard. The experiments using wetland water showed highest release of As (up to 68  $\mu\text{g/L}$ ). This was unexpected because the wetland water was much less oxygenated than Tampa tap water and thus should be less aggressive. Results from the reactive transport model correlated well to those from the column experiments.

The experiments demonstrated that perturbations of native aquifer conditions cause the release of As from the aquifer matrix, although reaction may not be as simple as the dissolution of pyrite by oxygen, but governed by a complex set of factors including water redox potential, concentration of DO,  $\text{SO}_4^{2-}/\text{S}^{2-}$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , DOC and microbial activity.

## Trace-element geochemical characterization of chalcopyrite using LA-ICP-MS – Possible application as an ore deposit discriminator

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Chalcopyrite is common in many sulphide-rich, magmatic-hypogene mineralizing environments, and therefore, has potential to use its trace-element signature to characterize and discriminate amongst ore systems. Here we report the results of an exploratory study to investigate the suitability of chalcopyrite in this context using an extended list of 24 trace elements. 447 grains from 16 deposits were analyzed for 24 isotopes using LA-ICP-MS. Ore suites include magmatic Ni-Cu-PGE deposits (e.g. Noril'sk, Sudbury), high-T hydrothermal systems represented by porphyry Cu-Au (e.g. Grasberg), IOCG and granite-hosted Sn-Cu (e.g. East Kemptville, San Rafael) deposits, lower-T hydrothermal systems represented by volcanogenic massive sulphide (e.g. Kidd Creek), orogenic gold (e.g. Hollinger-McIntyre) as well as a syenite-associated Cu-Au (e.g. Upper Beaver). Results indicate a chemical uniformity for both intra-deposit and inter-deposit sampling of the same ore deposit type. However, there is a marked difference in the trace-element signature among different deposit types, thus offering the potential to use chalcopyrite to discriminate among different sulphide deposit types. Predictable enrichments of chalcophile and siderophile elements occur in certain deposit types, plus enrichment of some economically significant elements (e.g. up to 3000 ppm In and 15 ppm Au).