

Multi tracer study (^{36}Cl , $^{234}\text{U}/^{238}\text{U}$, ^{14}C) of the Tunisian Continental Intercalaire: inferring recharge areas and groundwater ages.

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Assessment of groundwater recharge and ages is critical to study the sustainability of groundwater resources. However, determining “active” recharge areas within large aquifer systems, such as the North-Western Sahara Aquifer System (NWSAS) remains challenging. Here, we combine three geochemical tracers (^{14}C , ^{36}Cl and U isotopes) to infer past or recent recharge and evaluate groundwater ages in the Tunisian Continental Intercalaire (CI) Aquifer, the confined aquifer unit of the NWSAS.

Thirty-two boreholes were sampled, covering the whole Tunisian part of the CI aquifer. We paid a special attention on the Dahar Mountains where CI formations outcrop (11 samples). Only two samples located in the Northern Dahar are significantly above background in ^{14}C activity (1 pmc and 1.1 pmc). Uranium content varies from 2.8 to 5×10^{-4} ppb and $^{234}\text{U}/^{238}\text{U}$ activity ratio from 1 to 14. The stepwise decrease in U concentration goes with a high increase of the $^{234}\text{U}/^{238}\text{U}$ ratio followed by a decrease, clearly indicating the occurrence of a redox front. $^{36}\text{Cl}/\text{Cl}$ ratio varies from 5 to 10^{-15} . Four samples in the upper range ($35\text{-}40 \times 10^{-15}$) are again located in the northern oxidizing region of the Dahar as revealed by U concentration. Therefore, these data all converge to indicate that mixing with recent recharge waters occur to some extent in the northern Dahar region, while the southern part of this region shows no evidence of recent recharge.

This constitutes valuable information for hydrodynamic model and comparison with direct simulation of groundwater age (e.g. age-mass approach). We will assess at the meeting the consistency of these data with flow lines of water circulation inferred from piezometric data and hydrological modelling. Crude time constraints and mixing ratios will be also estimated from the comparison between these samples and those collected from the shallower Continental Terminal (CT) aquifer closer to present-day recharge waters.

A structure refinement for monoclinic hydrohematite

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Introduction

In ferruginous soils, nano- to micro-scale hematite ($\alpha\text{-Fe}_2\text{O}_3$) plays a central role in redox processes and contaminant cycling. Hematite is known to incorporate structural OH^- and water, and the requisite charge balance is achieved by iron vacancies. Prior researchers have suggested that the defective hematite structures form unique phases called “protohematite” (PH) and “hydrohematite” (HH) [1-3]. These phases are distinguished from stoichiometric hematite (SH) by their degree of hydration and iron deficiency. Furthermore, past infrared and Raman spectroscopic studies have assigned a lower-symmetry space group to PH/HH ($R3c$) relative to that of SH ($R-3c$) [4]. However, the existence and structure of these phases has been contentious, largely due to the lack of *in situ* X-ray diffraction data [5].

Here we present a new structure refinement for HH in a monoclinic space group ($I2/a$) using time-resolved X-ray diffraction (TR-XRD) data collected at the Advanced Photon Source (APS). Starting with ferric chloride solutions, we collected TR-XRD data during the *in situ* hydrothermal precipitation of akaganéite and its transformation to HH. Sealed quartz capillaries (1.0 mm diameter) were heated at 200 °C while XRD data were collected every 25 – 30 seconds. Rietveld refinements suggested a new monoclinic HH structure.

Results and Conclusions

In our experiments, distinct peak splitting was observed in the hematite diffraction patterns, indicating a violation of the 3-fold rotational symmetry. The observed peak splitting in our data was outside the range calculated for sample displacement, and furthermore video footage obtained during the reaction showed particles uniformly convecting throughout the volume of the capillary. We therefore refined the structure in the various subgroups of $R-3c$. As the fit using $I2/a$ was statistically no worse than that in lower symmetry groups, we selected this space group for our refinement. A monoclinic unit cell with parameters of $a = 13.7493(15) \text{ \AA}$, $b = 5.0121(4) \text{ \AA}$, $c = 5.4418(6) \text{ \AA}$, $\beta = 147.6250(17)^\circ$ provided a good fit and significant reduction in χ^2 and R_{wp} relative to S.G. $R-3c$. Our results demonstrate that the *in situ* formation of the defective hematite phase, HH, was successfully captured. Moreover, HH is structurally distinct from SH and may form as a lower-symmetry monoclinic phase in soils.

[1] Dang *et al.* (1998) *Hyperfine Interact.* **117**, 271-319. [2] Wolska (1981) *Z Kristallogr.* **154**, 69-75. [3] Gualtieri and Venturelli (1999) *Am. Mineral.* **84**, 895-904. [4] Burgina *et al.* (2000) *J. Struct. Chem.* **41**, 396-402. [5] Cornell and Schwertmann *The Iron Oxides*, 2nd ed. Wiley-VCH, Weinheim (2003).