## Geochemical and isotopic monitoring of dissolved carbon dynamic in a karst aquifer, located above the Rousse site test for CO<sub>2</sub> geological storage

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## A new method for monitoring CO<sub>2</sub> sequestration.

A near surface perched karst aquifer is considered as an integrative system of putative  $CO_2$  leaks above the Rousse site test of  $CO_2$  storage (operated by Total near Pau - France). We develop a low cost and long term geochemical monitoring of spring waters in order to describe the natural forcings that drive the dynamics of the dissolved carbon. Such procedure is mandatory in order to determine dissolved carbon thresholds above which excursions can be anomalies.

The chemical composition of the groundwater is ultradominated by calcium and bicarbonate ions. Dataset of 4 main springs is obtained with:

(1) high frequency measurements (15') of conductivity (C<sub>25</sub>), pH & hydrodynamics (C<sub>25</sub> and pH are used to determine the dissolved carbonate system: pH, pCO<sub>2</sub>, DIC & alkalinity .

(2) bi-monthly geochemical and isotopic samples which give another appreciation of the dissolved carbon dynamics.

We show that the  $C_{25}$  is a very robust proxy of the alkalinity because a strong linear relation has been established between  $C_{25}$  and carbonate composition in all meteorological conditions. At present, after three years of monitoring, we note that the dominant natural forcing of dissolved carbon is the hydrodynamic which is linked to pluviometry.

Modelisation of the geochemical impact induced by an input of  $CO_2$  in the aquifer is in progress, using thermoddem database [1] with the software PHREEQC [2].

Other aquifers will be tested like a typical carbonate karst: "Parc des Grands Causses".

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## Formation mechanism of hematiterutile pseudomorphs from Mwinilunga (Zambia)

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In geologic environments we often find minerals which formed by replacement reactions from a parent mineral as a consequence of solid-liquid interactions [1]. The newly formed mineral or mineral assemblages retain some characteristics of the parent minerals like their euhedral shape, whereas the chemical composition and texture of the products may be different. The changes are readily used for the interpretation of geological history of the samples.

In our work we studied rutile-hematite intergrowths from the Mwinilunga locality in Zambia. Samples can be described as euhedral hematite crystals intergrown with oriented rutile crystals. The general relationship between rutile and hematite can be determined already by macroscopic observation of hematite crystals and larger rutile crystals on their surface as  $\langle 010 \rangle (101)_{RUT}$  II  $\langle 001 \rangle (110)_{HEM}$ . Besides single rutiles, also rutile twins on (101) and (301) planes are found on the surface of the samples [2].

In order to determine the mechanism of ilmenite replacement by hematite and rutile, we analyzed the sample with different methods of electron microscopy. Detailed structural analysis of the sample interior along the  $[001]_{\text{HEM}}$ confirmed the macroscopically observed orientation relationship and all six possible orientations of rutile crystals within the single-crystal hematite ma trix were found. The stable hematite-rutile interface was determined from the HRTEM images. In the perpendicular orientation, i.e. along the [100]<sub>HEM</sub> zone axis, we found nano-sized relicts of parent ilmenite and we observed the diffusion paths of Ti-ions towards the rutile lamellae. The results of our analyses suggest that re-crystallization of ilmenite to hematite and rutile is structurally controlled. The transformation is possible since all three minerals (ilmenite, rutile and hematite) have a common oxygen sublattice which is controlling the re-crystallization to rutile and hematite [3].

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