

Erionite, Offretite and Stellerite: Solubility Assay

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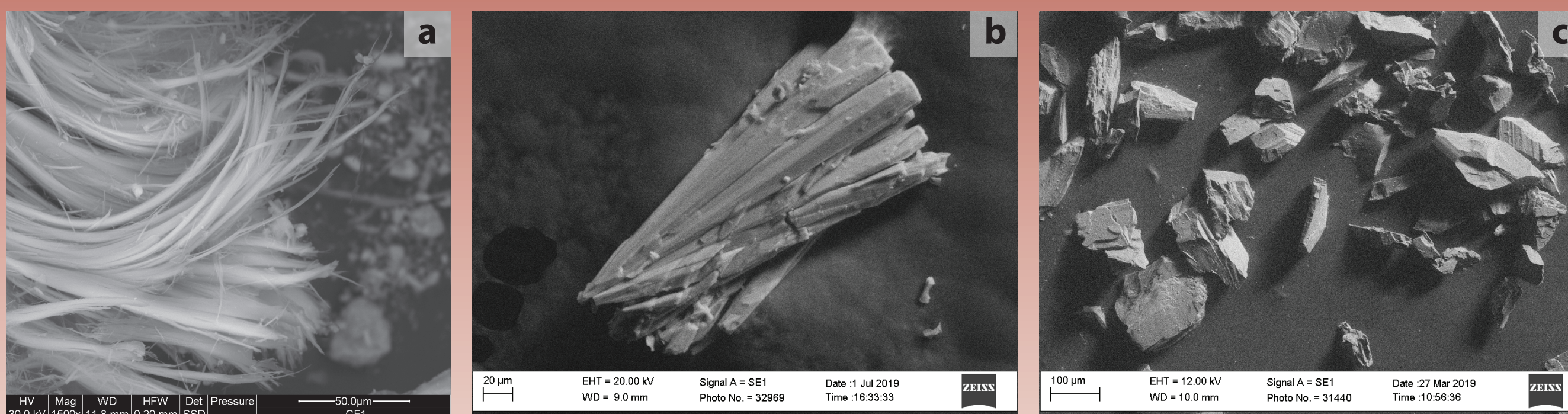
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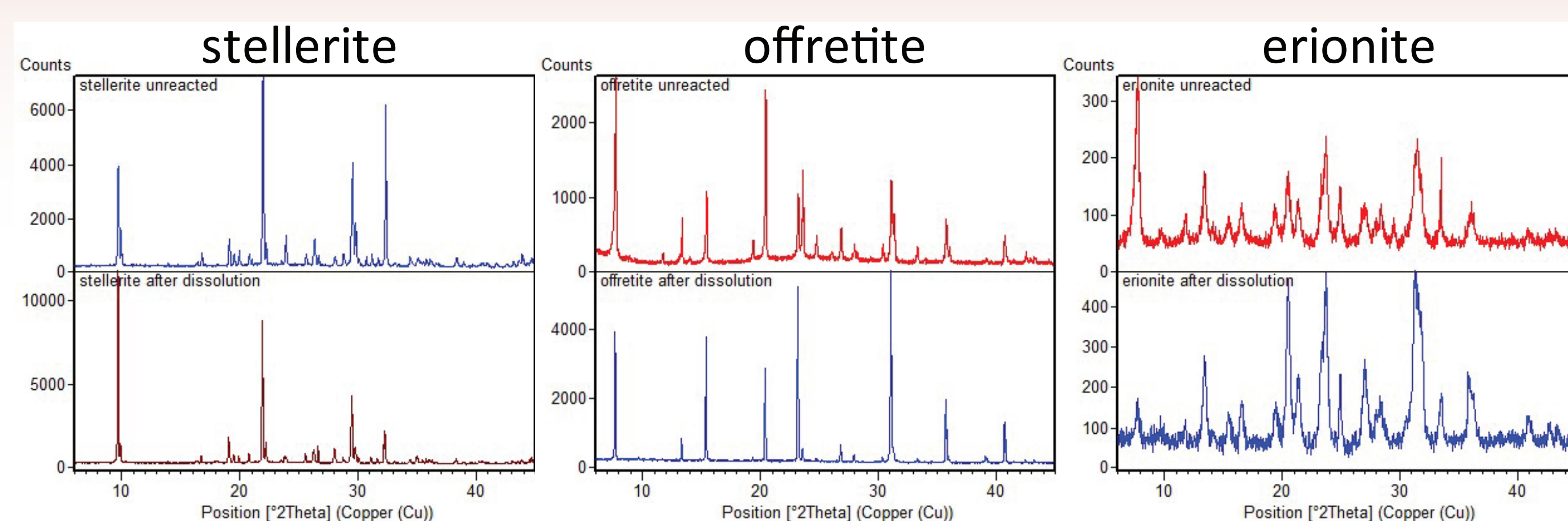
Introduction

Erionite is a well known carcinogenic fibrous zeolite being one of the most carcinogenic mineral fibre (IARC, 1987). In the last years other fibrous zeolites, such as offretite and ferrierite, assumed a growing interest in the scientific community, because of their probably carcinogenic effects to human after inhalation (Mattioli et al., 2018; Gualtieri et al., 2018).

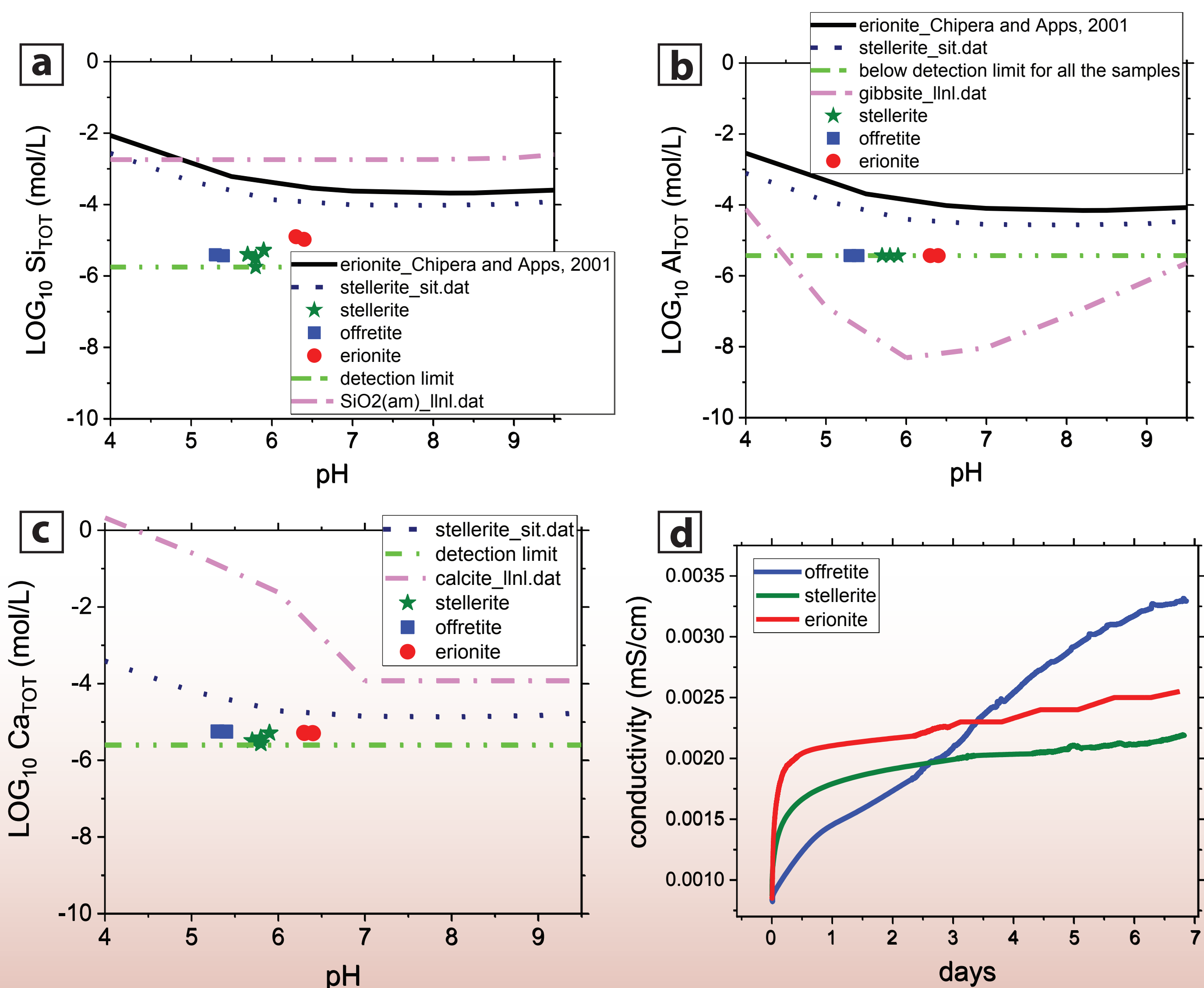
The toxicity of these minerals is mainly defined by two important parameters: biodurability and biopersistence. Solubility plays a key role on these parameters; however, to the best of our knowledge, the experimental determination of the solubility of erionite and offretite is still missing. The lack of these data for natural zeolites, even in the most simple system (i.e. water), represents a severe limitation for the understanding of the complex interaction with the biological environments.



SEM images of the studied natural zeolites before solubility process: a) erionite from Nevada, USA, b) offretite from Lessini Mountains, Italy, c) stellerite from Gibelsbach, Switzerland.



XRPD patterns of stellerite, offretite and erionite before and after dissolution at experimental conditions. No significant differences were observed.



Solubility of erionite, offretite, and stellerite predicted with PHREEQC and measured by ICP-OES after 1 week dissolution: a) total Si concentration b) total Al concentration c) total Ca concentration. Literature values were used for the solubility of stellerite (sit.dat) and erionite (Chipera and Apps 2001). d) Evolution of the aqueous conductivity recorded continuously during the dissolution experiments.

Concluding remarks

The aims of this study is to be a starting point for further detailed studies on the dissolution kinetics of zeolites. Our experimental setup for low temperature kinetic studies could allows to figure out (I) the behaviour in pure water and then (II) the effect of inorganic and organic additives (e.g. in Simulated Lung Fluids). The assessment of the individual role of each component is fundamental to better understand the observed processes, and could be a starting point for the comprehension of the risks associated to human health.

References

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Materials and Methods

Natural samples of erionite, offretite and stellerite (more abundant zeolite used as reference material) were used to perform dissolution experiments, at 25° C, to assess their aqueous solubility under the effect of atmospheric CO₂ concentration.

To obtain a relatively homogeneous crystal particle in the range 64 µm - 250 µm, the natural crystals were ground and sieved. The selected fraction was added to ultrapure H₂O (previously equilibrated with air for 30 minutes under stirring, i.e. in equilibrium with atmospheric CO₂ at pH 5). The dissolution process was followed over time with a conductivity probe equipped on a Metrohm OMNIS system. After several hours (days) under vigorous stirring (a floating stirrer was used to avoid a milling effect on the crystals), the samples were filtrated and the amount of Ca, Na, K, Mg, Al and Si was determined by ICP-OES (Agilent Varian, 700 ES). The powders were characterized before and after the interaction period. X-ray powder diffraction was used for the mineralogical characterization. The morphological characterization of the grains and the determination of the elemental formula were obtained by means of SEM-EDS and EMPA, respectively.

Results

Our preliminary results emphasize the limited solubility of these natural materials in this simple reaction medium (water in equilibrium with atmospheric CO₂). The thermodynamic solubility of stellerite (sit.dat) and erionite (Chipera and Apps 2001) is plotted together with the analytical measurements obtained by ICP-OES after 1 week of dissolution. Total silicon, aluminum and calcium are reported. The amount of silicon and calcium measured is above the detection limit of the ICP but significantly below the equilibrium value predicted from the solubility constant. This evidence demonstrates that dissolution took place, but in a low extent, because the kinetic of dissolution is very slow in this reaction medium. For aluminum, the quantification was not possible because the final concentrations were always below the detection limit of ICP. A reason for this lack of aluminum can be found in the low solubility of oxy-hydroxyl-aluminum phases, this low solubility could lead to the formation of new phases such as gibbsite (or another supersaturated Al-bearing phase). However, it was not possible to detect the formation of Al-bearing secondary phases by any of the used characterization techniques (XRD, SEM-EDS). Finally, we report the evolution of the aqueous conductivity over time recorded during the dissolution experiments. Erionite and stellerite follow similar behaviors and the higher silica content in erionite compared to stellerite is consistent with the higher conductivity of the solution. It is interesting to note that the solubility of offretite derived from conductivity was higher than the solubility of the other two phases. Despite this information seems in disagreement with the ICP measurements, it should be mentioned that a final concentration of 1.5 µmol/L of Mg was found in the experiments with offretite (Mg content is lower in erionite and stellerite).



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