Erionite, Offretite and Stellerite: Solubility Assay

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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 study of the solubility of these zeolites is 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.

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 DMN 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 after and before 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 equilibri-um 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, aluminium 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 aluminium, the quantification was not possible because the final concentrations were always below the detection limit of ICP. A reason for this lack of aluminium can be found in the low solubility of hydrous-alumin-ium 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, the low solubility observed in the ICP-OES measurements 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).

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 allow to figure out (I) the behaviour in pure water and then (II) the effect of inorganic and organic additives (e.g. in Simulated Lungs 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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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.

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.

XRD 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.

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