CRYSTAL-CHEMICAL CHARACTERIZATION AND THERMAL STABILITY OF FIBROUS ERIONITE. CATION MOBILITY AND IRON OCCURRENCE AS A KEY FOR UNDERSTANDING ITS TOXICITY

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INTRODUCTION

Erionite is a zeolite group mineral that has been thoroughly investigated because of its linking with malignant mesothelioma (MM). Despite erionite is a nominally iron free-phase, it can acquire iron after inhalation because of its ion exchange properties (Bish *et al.*, 2001). As a consequence, similarly to amphibole asbestos, erionite toxicity has been partially ascribed to the presence of iron that participates to Fenton chemistry generating reactive oxygens species that induce genotoxic damage. However, the molecular mechanism by which mineral fibers induce the reactive species is still unclear. Several chemical analyses of natural erionites reported a Fe_2O_3 content up to 3 wt.% and it has been hypothesized that iron adheres on zeolite surface before it is inhaled. Ballirano *et al.* (2009) conducted a combined spectroscopic and structural analysis of erionite from rock formations in Rome (Oregon) and they showed that the small amount of iron could be represented by oxide-like nanoparticles with dimensions between 1 and 9 nm. This was the starting hypothesis of the submitted research project that was aimed to determine what kind of nanoparticles occurred on erionite and how they were linked to the possible development of MM. Hence, it has been decided to carry out a parallel investigation on natural erionite fibers from different localities, to evaluate chemical and structural differences, as well as on synthetic iron-oxides nanoparticles, to understand what role they can play in MM development. However, although a preliminary chemical analysis indicated the occurrence of iron on natural erionite samples, confirming the starting hypothesis, the following detailed chemical characterization of the same samples demonstrated that the detected iron do not belong to fibers. As a consequence the nanoparticles characterization has been suspended and the research concentrated on erionite fibers investigation, to understand what kind of process is involved in their toxicity.

IRON-OXIDES NANOPARTICLES

Two polymorphs of FeOOH (goethite and lepidocrocite) and two polymorphs of Fe_2O_3 (hematite and maghemite) were chosen to test their possible presence on zeolite surfaces.

Iron-oxides nanoparticles were synthesized by condensation in aqueous medium at the Department of Chimie de la Matière Condenseé, Université Pierre & Marie Curie (Paris).

Nanoparticles were investigated using both Angular Dispersive X-Ray Diffraction (ADXD) and Energy Dispersive X-ray Diffraction (EDXD). ADXD is the conventional crystallographic method used for structural analysis of powders, that implies evaluation of diffraction data in reciprocal space, considering only Bragg scattering. From EDXD data it is possible to obtain a good Pair Distribution Function (PDF) and to perform a structural analysis by exploiting the information included into both the Bragg and diffuse scattering, operating in direct space. Both techniques were used, to compare results from reciprocal and direct space analysis.

Despite the PDF analysis of nanomaterials requires collecting data up to high values of the reciprocal space vector ($Q > 10$ Å^{-1}), not accessible with the usual XRD monochromatic CuKα radiation, it has been demonstrated that combining ADXD and EDXD techniques it is possible to characterize at structural level such nanoparticles. This approach represents a valuable alternative to synchrotron radiation beamline, a not always available instrumentation. The characterization of samples with different sizes confirmed that the definition of nanoparticle is compound specific and that 1-100 nm range is actually a reference range too wide. Although

XRD pattern was affected by strong absorption and it was difficult to model particle shape, the combined spectroscopic and structural characterization of hematite and lepidocrocite nanocrystals demonstrated that up to *ca*. 60 nm and *ca*. 50 nm, for hematite and lepidocrocite respectively, their structural and magnetic properties do not change significantly with respect to the reference bulk materials reported in literature. In addition, the expansion of cell parameters with respect to the corresponding bulk minerals, reported in reference data, does not occur as well as the high values of microstrain typical of nanocrystalline phases. However, although the samples are not strictly classified as nanoparticles, their structural investigation was not straightforward. The conventional Rietveld approach to the study of these materials provides limited information, despite Fundamental Parameters Approach (FPA) approach allows a more detailed microstructural analysis, as demonstrated in the case of lepidocrocite. It is important to underline that the choice of the shape model plays a crucial role for the extraction of microstructural data, especially in the case of very small and anisotropic crystallites. As far as the goethite sample is referred to, the most relevant result concerns the PDF interpretation. Its oscillations decay at a lower value (about 10 nm) with respect to that expected and determined by Rietveld refinement [54(1) nm]. It has to be considered that in the case of conventional powder diffraction, the effect of structural disorder and particle size on PDF data are highly correlated, and in many cases PDF fitting, that includes additional size and morphology parameters, can be implemented with difficulty in stable and efficient codes. Hence, the use of an independent method to extract particle size and shape is strictly recommended. However, in the specific case of goethite sample the gap between the estimated sizes is very large. This is why it has been hypothesized that the effect of an early truncation is due to instrumental effects. In particular, the software PDFgui (Farrow *et al.*, 2007) allows the refinement of the Qdamp parameter that refers to the resolution damping for the selected data. Its refined value was of $Q_{damp} = 0.044(1)$, that provides an envelope function that drops to zero at *ca*. 120 Å. As a consequence, the size value is underestimated because the effect of resolution prevails on the size effect. This can be confirmed by considering the case of the maghemite nanoparticles. The characterization of the four samples has demonstrated that they show strain and cell parameters values typical of nanocrystalline materials. In this case PDF peak intensity and oscillations resulted in good agreement with those expected from nominal size. Therefore, no underestimation was observed as in the case of goethite. This is probably due to the fact that maghemite particles are small enough and the fall-off of intensity, due to the resolution, occurs after that due to the size value.

ERIONITE FIBERS

New structural and chemical data of four erionite samples from different localities were obtained combining X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM). Such data will be used as a necessary base for a planned toxicity investigation. In particular, two samples are from Oregon (USA) one from Durkee and one from Rome. The remaining (labelled as MD-08-02 and MD-08-43) are from, Cappadocia (Turkey) from one of the villages struck by the well-known mesothelioma epidemic disease. An enrichment technique has been developed especially for the samples from Rome and for those from Cappadocia, because other phases occurred in association with erionite. The main analytical techniques consist of scanning electron microscopy (SEM) and field-emission scanning electron microscopy (FE-SEM) for chemical characterization and X-ray powder Diffraction (XRPD) for the structural investigation. The reliability of the chemical data used to calculate chemical formulae has been established on the basis of the guidelines proposed by Dogan *et al.* (2006), that is the balance error test, -10% < E < +10% (Passaglia, 1970), and the Mg-content test (Mg^{2+} cations can be present up to 0.80 atoms per formula unit).

A complete structural characterization by Rietveld method was carried out only on erionites from Oregon, because, in the case of Turkish fibers, it was impossible to enrich the samples enough to perform a reliable structural refinement. Erionite is hexagonal, space group *P*63/*mmc*. It belongs to the ABC-6 family (Gottardi & Galli, 1985).The periodic unit building in the ABC-6 family consists of a hexagonal array of non-connected planar rings of 6 tetrahedra, related by pure translations along the *a* and *b* axes. Neighbouring periodic units can

be connected in different ways, depending on the shift along the *a* and *b* axes of the single layers. In the erionite structure the stacking sequence is AABAAC. Its framework consist of tetrahedra linked together to form single-six rings (S6R) and double-six rings (D6R). The S6R originate erionite cages (occupied by Na, Ca, and Mg) by linking adjacent columns at the level of the cancrinite (ε) cages (fully occupied by K). D6R connect columns of ε cages along the z direction. A simplified chemical formula $K_2(Na,Ca_{0.5})(Al_{10}Si_{26}O_{72}) \bullet 30H_2O$ (Coombs *et al.*, 1997) has been proposed. However, due to a significant chemical variability, erionite has been elevated to the group status and three different species, erionite-K, erionite-Ca, and erionite-Na have been identified, depending on the most abundant extra-framework cation.

Structural characterization

Starting structural data were taken from Alberti *et al.* (1997), consisting, a part of the framework, of four EF cationic sites, K1, Ca1, Ca2 and Ca3, and six water molecules sites (OW7, OW8, OW9, OW10, and OW12). Both the occupancy of all EF cationic and water molecules sites and the displacement parameters of all sites were refined. However, because of the occurrence of correlations, displacement parameters of the various sites were constrained as follow: $B_{T1}=B_{T2}$; $B_{O1}=B_{O2}=B_{O3}=B_{O4}=B_{O5}=B_{O6}$; $B_{Ca1}=B_{Ca2}=B_{Ca3}$; $B_{OW8}=B_{OW9}=B_{OW10}=B_{OW11}=B_{OW12}=2B_{Ow7}$.

The structural characterization of the two samples from Oregon, allowed to determine the suitable location of the EF cations.

Hence, the Ca3 site, present in Durkee's erionite-Na and also in reference erionite-Ca (Alberti *et al.*, 1997), favourably host Na cation rather than K, which, as demonstrated in Ballirano *et al.* (2009), is located at K2 site. On the contrary, the Ca3 site was removed from the refinement of the Rome erionite-Na sample, because an attempt to refine its occupancy and fractional coordinates provided bond distances inconsistent with a meaningful coordination. This was in good agreement with chemical data that highlighted a lower amount of sodium with respect to Durkee's erionite. In both cases, cationic partition obtained from structural refinement is consistent with chemical results.

Chemical results

The SEM and FE-SEM results showed that the morphology of the samples strictly varies depending on the origin of the fibers, in particular that the erionite fibers from Durkee, are constituted by woolly rounded bundles, in contrast with respect to the sample from Rome that is prismatic in habit. Turkish fibers, although they have not a woolly appearance, are more acicular, and their length is up to *ca.* 70 μm.

Although all samples have been classified as erionite-Na, the chemical results have highlighted that the main difference among the Turkish fibers and the other erionites is related to the EF cations content. The Mg-content exceeds the limit found by Passaglia *et al.* (1998) and is also larger than the Mg a.p.f.u. found in this work for erionites from Oregon.

On the other hand, in the Turkish fibers the Na content is lower with respect to that of the Oregon fibers, whereas the potassium amount does not vary significantly among the different samples. Besides, despite reference data consistently reported the occurrence of both iron and calcium in the erionite composition, the present work has demonstrated that in all the investigated samples, these elements occur as impurities.

Moreover, the results obtained for both Turkish samples are significantly different with respect to those reported by Dogan *et al*. (2006) for erionite fibers from several Cappadocian villages (Karlik, Karain, Tuzkoy and Old Sarihidir). The most relevant difference is the absence of iron and calcium, that in reference data are in the range of 0.86-1.50 and 1.07-2.12 wt.%, respectively.

Another important difference concerns the EF cations content: Na and Mg amount reported in reference data are significantly lower (1.74-3.18 and 0.59-0.85 wt.%, respectively) than those observed in the present work, and K results the most abundant EF cation, with the exception of erionite from Tuzkoy village, classified as erionite-Na.

As far as the Mg content is referred to, no analysis passed the Mg-content test (with the exception of one analytical point of the FE-SEM data set). However, it has to be considered that the estimated Mg value slightly exceeds (0.92 and 1.09 a.p.f.u. by FE-SEM and SEM data, respectively) the limit value found by Gualtieri *et al.* (1998). In addition, in the present sample, Ca does not occur and probably this could justify the greater amount of Mg, that is the only available divalent cation.

Therefore, although Mg is not one of the most abundant EF cations, the referring limit has to be re-evaluated, since from a structural point of view, the erionite cage could host a higher Mg content.

Cation mobility and thermal stability

To monitor the mobility of the various cation species inside erionite cages, the dehydration dynamics and thermal stability of a sample of erionite-K is reported and, to conclude, preliminary results on exchange mechanism between simulated lung fluid solution and a sample of fibrous erionite will be presented.

The dehydration dynamics and the thermal stability have been investigated, at a fine temperature scale, in the 303-1253 K thermal range by *in situ* X-ray powder diffraction.

A general depletion of the Ca1, Ca2, and K1 sites is counterbalanced by an increase of the K2 *s.s.* The observed reduction of the site scattering at the K1 site has been explained by invoking the "internal ion exchange" mechanism, which has been monitored *in situ*.

The Mg cations, located at the Ca1 site, are transitory distributed in the 400-500 K thermal range among a few undetected, low-occupancy, sites before diffusion toward the remaining cation sites. The complete depletion of the various water molecule sites occurs in the 413-573 K thermal range, the only exception being OW7 that shows significant *s.s.* up to the structural breakdown.

The exchange mechanism between fibers and simulated lung fluid is mainly related to a partial chemical variation, involving the lost of Mg from erionite cages.

This finding has been confirmed by the structural investigation carried out on erionite after the reaction with ALF-solution. The depletion of the Ca1 site, partially occupied by Mg, was in agreement also with that determined from the analysis of thermal stability of the erionite-K sample, that indicate the easier mobility of Mg in Ca1 site with respect to Na and K, because of its coordination exclusively occurring with water molecules. On the other hand, in the case of an erionite-Na, small changes in term of Na content were expected because of the ALF-solution composition, mainly consisting of sodium cations.

The most relevant finding is related to the dissolution of the erionite rather than its chemical variations. After a reaction time of 48 h, *ca.* one half of the sample has been completely dissolved due to acidic *p*H of the ALF-solution. This clearly indicates that, if no other factors occur, the erionite fibers in contact with lysosomal fluid, will be totally destroyed.

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