

## High-temperature behavior of natural ferrierite: In-situ synchrotron X-ray powder diffraction study

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### ABSTRACT

In this paper, we report the results of the first study focused on the thermal stability and dehydration dynamics of the natural zeolite mineral ferrierite. A sample from Monastir, Sardinia [(Na<sub>0.56</sub>K<sub>1.19</sub>Mg<sub>2.02</sub>Ca<sub>0.52</sub>Sr<sub>0.14</sub>)(Al<sub>6.89</sub>Si<sub>29.04</sub>)O<sub>72</sub>·17.86H<sub>2</sub>O; *a* = 19.2241(3) Å; *b* = 14.1563(2) Å; *c* = 7.5106(1) Å, *V* = 2043.95(7) Å<sup>3</sup>] was investigated by thermogravimetric analysis and in-situ synchrotron X-ray powder diffraction. Thermogravimetric data show that H<sub>2</sub>O release begins already in the range 50–100 °C and is complete at ~600 °C. The results of the structure refinements performed in *Immm* space group by Rietveld analysis with data collected up to 670 °C show that ferrierite belongs to the group of zeolites that do not undergo phase transitions. Upon heating to 670 °C, ferrierite behaves as a non-collapsible structure displaying only a slight contraction of the unit-cell volume ( $\Delta V = -3\%$ ). The unit-cell parameter reductions are anisotropic, more pronounced for *a* than for *b* and *c* ( $\Delta a = -1.6\%$ ;  $\Delta b = -0.76\%$ ;  $\Delta c = -0.70\%$ ). This anisotropic response to a temperature increase is interpreted as due to the presence in the ferrierite framework of five-membered ring chains of SiO<sub>4</sub> tetrahedra, which impart a higher structural rigidity along *b* and *c*. Upon dehydration we observe: (1) the gradual H<sub>2</sub>O loss, beginning with the molecules hosted in the 10MR channel, is almost complete at 670 °C, in good agreement with the TG data; (2) as a consequence of the decreased H<sub>2</sub>O content, Mg and K migrate from their original positions, moving from the center of the 10MR channel toward the walls to coordinate the framework oxygen atoms. The observation of transmission electron microscopy selected-area electron diffraction patterns revealed defective crystals with an occasional and moderate structural disorder. Beyond providing information on the thermal stability and behavior of natural ferrierite, the results of this work have significant implications for possible technological applications. These data allow for comparison with the dehydration kinetics/mechanisms of the corresponding synthetic phases, clarifying the role played by framework and extra-framework species on the high-temperature behavior of porous materials with ferrierite topology. Moreover, the information on the thermal behavior of natural ferrierite can be used to predict the energetic performances of analogous synthetic Si-pure counterparts, namely “zeosil-electrolyte” systems, under non-ambient conditions. Specifically, the very high thermal stability of ferrierite determined in this study, coupled with the baric behavior determined in other investigations, suggests that the “Si-FER–electrolyte” system may be an excellent candidate for use as an energy reservoir. Indeed, ferrierite exhibits the so-called “spring behavior,” i.e., upon compression in water or in an electrolyte solution, it converts the mechanical energy into interfacial energy, and—when pressure is released—it can completely restore the supplied mechanical energy accumulated during the compression step.

**Keywords:** Zeolite, ferrierite, thermal behavior, high-temperature synchrotron X-ray powder diffraction, structure refinement, TEM, TGA; Microporous Materials: Crystal-Chemistry, Properties, and Utilizations