



## Solid state multinuclear NMR study of iron species in natural and modified clinoptilolite from Tasajera deposit (Cuba)

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### Abstract

The present study has been conducted to elucidate the Fe-sites in natural clinoptilolite, and the possibility to produce a reversible replacement of these atoms in the zeolite framework. In order to achieve these results we have tried to introduce iron in clinoptilolite structure after the almost total extraction of the natural iron species. A sample of the purified natural clinoptilolite from Tasajeras deposit, Central region of Cuba, was modified by a hydrothermal treatment with orthophosphoric acid. Iron exchange forms of the orthophosphoric zeolite were obtained using  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  solutions. The modified zeolites were studied by multinuclear magnetic resonance ( $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$  MAS NMR and  $^{129}\text{Xe}$  NMR). Other analytical techniques as Electron Paramagnetic Resonance, X-ray diffraction, Mössbauer and Infrared spectrometry, volumetric measurements and chemical analysis by Induced Plasma Coupled spectroscopy were used to support the results of NMR studies. The presence of iron species with tetrahedral and octahedral coordination in the structure of a natural clinoptilolite has been confirmed. The influence of iron in tetrahedral coordination in the thermal stability of the clinoptilolite structure was also confirmed.

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### 1. Introduction

The positions of iron atoms in a natural zeolite has been studied and discussed by different authors [1–4]. The discussion has focused on the iron atoms presence in the zeolite structure replacing isomorphically silicon or aluminum atoms. Vessalini [1] has reviewed the subject of possible Fe-sites in natural zeolites and noted that three hypotheses have been advanced in the literature:

- Fe substitutes Al in the framework.
- Fe is present as an extra-framework cation, bound or not to framework oxygen.
- Fe is structurally related to impurities such as hydroxides or oxides.

The presence of tetrahedral  $\text{Fe}^{3+}$  coordinated in the structure of natural clinoptilolite has been explained as an isomorphic substitution of Si or Al [2] and later confirmed using Mössbauer spectrometry [3]. The authors have established that “iron was found as high-spin  $\text{Fe}^{3+}$  in the place of aluminum in framework tetrahedral sites and in extra-framework octahedral sites as free  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ; high-spin  $\text{Fe}^{2+}$  is in octahedral coordination

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