

## **Constraints on aluminum and scandium substitution mechanisms in forsterite, periclase, and larnite: High-resolution NMR**

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### **ABSTRACT**

The incorporation of incompatible Al in forsterite is particularly interesting due to its relevance in Al olivine-spinel geobarometry techniques as well as the proposed influence of Al on upper mantle diffusion and water storage capacity. However, determining the site preference and substitution mechanisms of aluminum in forsterite presents considerable challenge, because the incompatibility of Al in the olivine structure results in correspondingly low Al concentrations. In this work we use solid state nuclear magnetic resonance (NMR) to directly observe Al coordination in synthetic samples from which we can constrain site preferences. We investigate Al in MgO and clinoenstatite to confirm that the forsterite spectra do not contain contributions from these impurity phases. To better interpret our results we used the independent component analysis (ICA) algorithm, SIMPLISMA, which accurately deconvoluted complex NMR line shapes, separating spectral components from known impurities and enabling the identification of unknown spectral components that in some cases we can assign to substituting Al. We additionally investigate Al in larnite, which has a tetrahedral environment similar to that of forsterite and that presents an another ICA test case, and investigate Sc in forsterite and periclase to add context to our Al observations. Our <sup>27</sup>Al and <sup>45</sup>Sc MAS NMR spectra place new constraints on the site preferences of Al in synthetic forsterite, clinoenstatite, periclase, and larnite as well as Sc in forsterite and periclase.

In forsterite, we identified Al in the tetrahedral site and at least three distinct octahedral environments. The overall ratio of contents of AlO<sub>4</sub> to AlO<sub>6</sub> is about 1:3; the excess of the latter suggesting that at least two substitution mechanisms are necessary for Al<sup>3+</sup> incorporation. In some cases the estimated species abundance for observed features are as low as 70 μg/g Al<sup>3+</sup>, but were readily detected by NMR. Also in forsterite, we identified Sc in a single MgO<sub>6</sub> environment. In larnite (also known as belite or C<sub>2</sub>S in cement chemist notation), a single, ordered tetrahedral Al species is detected. In enstatite samples, primarily composed of clinoenstatite, <sup>27</sup>Al NMR spectra look very similar to previous observations of orthoenstatite, likely indicating a similar coupled AlO<sub>6</sub> and AlO<sub>4</sub> substitution. In periclase, Al is observed in an undistorted MgO<sub>6</sub> site with cubic or nearly cubic point symmetry, in addition to a lower symmetry, sixfold-coordinated site. This work provides new insight into incompatible element substitutions mechanism in minerals, in forsterite's case indicating complex behavior involving multiple species despite compositional simplicity.

**Keywords:** Forsterite, periclase, enstatite, larnite, belite, independent component analysis, nuclear magnetic resonance, trace elements, SIMPLISMA