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

RYAN J. MCCARTY1,* AND JONATHAN F. STEBBINS1

1Department of Geological Sciences, Stanford University, Stanford, California 94305, U.S.A.

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 27Al and 45Sc 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 AlO4 to AlO6 is about 1:3; the excess of the latter suggesting that at least two substitution mechanisms are necessary for Al3+ incorporation. In some cases the estimated species abundance for observed features are as low as 70 μg/g Al3+, but were readily detected by NMR. Also in forsterite, we identified Sc in a single MgO environment. In larnite (also known as belite or C2S in cement chemist notation), a single, ordered tetrahedral Al species is detected. In enstatite samples, primarily composed of clinoenstatite, 27Al NMR spectra look very similar to previous observations of orthoenstatite, likely indicating a similar coupled AlO4 and AlO6 substitution. In periclase, Al is observed in an undistorted MgO 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

INTRODUCTION

Aluminum is an abundant element in Earth’s mantle, but scarce in olivine, which is a major mineral component of the upper mantle and a common phase in mafic rocks. Despite aluminum’s low concentrations in olivine (typically less than 400 μg/g), the incorporation of incompatible Al3+ into olivine has drawn considerable interest due to its relevance to a geobarometry technique (where Al3+ concentrations in olivine and spinel are used to predict the equilibration pressure) (Wan et al. 2007; Zhang and Wright 2012). 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 27Al and 45Sc 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.

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

In forsterite (Mg2SiO4), the magnesium-rich end-member of olivine, the preferred lattice site of incorporated Al3+ is not obvious. The ionic radius of Al3+ (39–53 pm) and its charge are between those of tetrahedral Si4+ (26 pm) and octahedral Mg2+ (72 pm) (Shannon and Prewitt 1969). Due in part to this mismatch, the solubility of Al3+ in forsterite is limited, with experimental work indicating a practical solid solution around 500 μg/g at temperatures between 1475 and 1390 °C (Grant and Wood 2010). This low concentration limits the usefulness of diffraction methods to determine structural effects, and can pose challenges of sensitivity for spectroscopic approaches. Many prior studies of aluminum in forsterite have involved multi-dopant systems, and suggest a wide variety of Al3+ incorporation mechanisms that are likely influenced by the presence or absence of additional elements (Bershov et al. 1983; Purton et al. 1997; Berry et al. 2008; Coogan et al. 2014), its proposed role in creating 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 27Al and 45Sc 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.

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