

SPECIAL COLLECTION: OLIVINE

Transition metal cation site preferences in forsterite (Mg_2SiO_4) determined from paramagnetically shifted NMR resonances‡

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ABSTRACT

In marked contrast to the single, narrow ²⁹Si MAS NMR resonance for pure forsterite (Mg_2SiO_4), the spectra for synthetic forsterite containing 0.05 to 5% of the Mg^{2+} replaced with Ni^{2+} , Co^{2+} , or Fe^{2+} display between 4 and 26 additional, small, paramagnetically shifted peaks that are caused by interactions of the unpaired electron spins on the transition metal cations and the nuclear spins. Analyses of these relative peak areas, their numbers, and comparison of their positions to those in spectra of synthetic monticellites (CaMgSiO_4) containing similar levels of transition metals, allows at least partial assignment to the effects of cations in either the M1 octahedral site only or to both M1 and M2 sites. More detailed analyses indicate that in forsterite, Ni^{2+} occupies only M1, Fe^{2+} occupies M1 and M2 roughly equally, and Co^{2+} occupies both M1 and M2 in an approximately 3:1 ratio. These findings for low concentrations agree with expectations from previous studies by other methods (e.g., XRD) of olivines with much higher transition metal cation contents. However, even low concentrations of Mn^{2+} (e.g., 0.1%), as well as higher Fe^{2+} contents (e.g., in natural San Carlos olivine) can broaden NMR peaks sufficiently to greatly reduce this kind of information content in spectra.

Keywords: Forsterite, olivine, NMR, transition metal cations, paramagnetic shift, site preference