Transition metal cation site preferences in forsterite (Mg₂SiO₄) 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 (Mg₂SiO₄), the spectra for synthetic forsterite containing 0.05 to 5% of the Mg²⁺ replaced with Ni²⁺, Co²⁺, or Fe²⁺ 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 (CaMgSiO₄) 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, Ni²⁺ occupies only M1, Fe²⁺ occupies M1 and M2 roughly equally, and Co²⁺ 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 Mn²⁺ (e.g., 0.1%), as well as higher Fe²⁺ 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

INTRODUCTION

Forsterite (Mg₂SiO₄) is the magnesium end-member of olivine, a common mineral found in basaltic rocks and a major constituent of the Earth’s upper mantle (Harris et al. 1967). Significant research efforts have been invested in better understanding transition metal cation incorporation in forsterite, which can potentially refine partition coefficients used in numerous geothermometric and geobarometric methods (Canil 1994; Loucks 1996; Wu and Zhao 2007). The structure of forsterite is well defined in the space group Pbnm, consisting of isolated silica tetrahedra connected by a network of octahedral Mg sites, M1 and M2. The latter provide two unique substitution environments for compatible, divalent transition metal cations, with the M1 site being smaller and more distorted than the M2 site (Brown 1980).

Multiple studies have converged on similar results for the site occupancies of divalent transition metal cations at high concentrations in olivines, providing a foundation for investigation of concentrations that approach minor to trace element levels. The review chapter by Brown (1980) provides a comprehensive summary of the early efforts on this problem. X-ray diffraction has been a primary tool when concentrations are high enough to measurably affect the long-range crystal structure, such as the finding of the strong Ni²⁺ preference for the M1 site (Rajamani et al. 1975). Similarly, Co²⁺ has also been found to prefer the M1 site, though to a lesser degree than the Ni²⁺ preference (Ghose and Wan 1974). Varying results from different methods place bounds on the distribution of Fe²⁺, which is usually found to occupy the two sites almost equally (Brown 1980). These distributions are largely determined by the greater crystal field stabilization energy for the M1 site, although the M2 site is increasingly favored as ionic radii increase (Brown 1980).

Further spectroscopic studies have confirmed and characterized these distributions. An EXAFS study of Ni-bearing forsterite outlined the changes in distribution with temperature and found an M1 site preference as well as a suggestion of clustering of Ni²⁺ into adjacent M1 sites (Henderson et al. 2001). The work of Taftø and Spence (1982) on natural San Carlos olivine samples (approximately 10% Fe₃SiO₄ component), using an electron-microscopic X-ray emission technique, determined that Fe²⁺ entered the two sites almost equally. A Mössbauer study on synthetic crystals with equal concentrations of Mg²⁺ and Fe²⁺ determined that at 500 °C, Fe slightly prefers the M1 site, a preference that increases as temperature rises to 800 °C (Morozov et al. 2006). The Rietveld refinement of Müller-Sommer et al. (1997) on synthetic Co-rich forsterite indicated a distribution of Co²⁺ between the two sites with an M1 site preference. Polarized optical absorption spectroscopy results additionally agree on the M1 preference of this cation (Taran and Rossman 2001). Confirmation of the M2 site preference of Mn²⁺ has been provided by channeling-enhanced X-ray emission spectroscopy (McCormick et al. 1987). The effects of temperature on transition metal site occupancies in olivines have been extensively studied by XRD and other methods for samples typically in the range of about 10 to 50% of the non-forsterite component, and have...