

Al and Fe substitution in MgSiO₃ perovskite: An ²⁷Al and ²⁹Si NMR study

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This study involves ²⁷Al and ²⁹Si NMR spectroscopy on ²⁹Si- and ⁵⁷Fe-enriched, Al- and Fe-bearing MgSiO₃ perovskite of nominal composition (Mg_{1-x}Fe_x)(Si_{1-x}Al_x)O₃ (x < 0.05) in order to elucidate the substitutional mechanisms of Al and Fe. Previous ²⁷Al NMR studies have focused on Fe-free, Al-bearing MgSiO₃ perovskite; however, it is known that Fe has a dramatic impact on the incorporation of Al due to a coupled substitution of Al³⁺ and Fe³⁺ [1]. Nonetheless, the exact nature of Al substitution in the presence of iron (i.e. site occupancy of Al³⁺ and Fe³⁺, order/disorder and distribution of the substituting cations, etc...) is incompletely understood. Mössbauer spectroscopy of our samples found bulk sample Fe³⁺/Fe_{total} = 40-60%, indicating that coupled substitution of Fe³⁺ and Al³⁺ occurs to a significant extent. An analysis of ²⁷Al and ²⁹Si signal losses and peak widths with increasing Al and Fe content suggests a strong ordering of Fe³⁺ occurring in Mg²⁺ sites with Al³⁺ occupying adjacent Si⁴⁺ sites. However, particularly at higher concentrations of Al and Fe, it is clear that this coupled substitution is not the only mechanism operating in these samples. This study is an extension of previous work involving natural Fe-bearing pyrope garnet [2] and rare earth orthophosphates and builds on the insights obtained therein.

[1] Frost & Langenhorst (2002) *Earth Planet. Sci. Lett.* **199**, 227–241. [2] Palke & Stebbins (2011) *Am. Min.* in press.

Environmental controls on potential nitrate and sulfate reduction rates in a range of aquatic sediments

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Nitrate and sulfate are two important terminal electron acceptors for anaerobic respiration in littoral sediments. We investigated the environmental factors controlling potential rates of nitrate reduction and sulfate reduction (NRR and SRR) in a range of aquatic sediments. Reaction rates were determined on intact surface sediment slices sampled at 14 sites using flow-through reactors. Nitrate and sulfate were added separately or simultaneously. We used redundancy analysis to assess how environmental factors might control the variability of these rates.

On average, NRR exceeded SRR by one order of magnitude and 9% of the NRR can be accounted for by nitrate-mediated sulfide oxidation to sulfate in the studied sediments. When nitrate and sulfate were supplied simultaneously, the effect of nitrate on SRR was variable, ranging from near complete inhibition to 25% enhancement. Redundancy analysis showed that overlying water pH and salinity were the two most important predictors of variability of sediment potential NRR and SRR under all conditions. However, when nitrate and sulfate were added separately, sulfate concentration in the overlying water and sediment N content were additional factors explaining the variations of potential NRR and SRR. Furthermore, when the two electron acceptors were both present, the potential NRR and SRR were also controlled by sediment arsenic content besides pH and salinity. It suggests that different biogeochemical processes are involved in the N and S cycles in response to separate and simultaneous addition of nitrate and sulfate. These results indicate that controls on elemental cycling in systems subject to S and N pollution are more complex than formerly thought and point to the need to critically reassess the representation of anaerobic respiration kinetics and their interactions in diagenetic models.