Solid state NMR study of oxygen site exchange and Al-O-Al site concentration in analcime

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ABSTRACT

Oxygen isotope exchange between natural analcime and water vapor at low pressure is studied by $^{17}$O NMR, which can distinguish Si-O-Si and Si-O-Al sites and provide information on site specific exchange kinetics and mechanisms. Si-O-Al sites in analcime are found to exchange faster than Si-O-Si sites at lower temperature (400 °C). At higher temperature (500 °C), the exchange rates for the two types of site are similar, suggesting that the exchange process for Si-O-Si has a higher activation energy, as predicted by published theoretical calculations. The overall exchange reaction appears to be controlled largely by reaction at sites, not diffusion. Static $^{17}$O spectra show an anomalously high ratio of Si-O-Si to Si-O-Al sites, suggesting the presence of a few percent of Al-O-Al sites, which are indeed resolved and observed in triple quantum magic-angle spinning (3QMAS) spectra.

INTRODUCTION

The kinetics and mechanisms of oxygen isotope exchange in oxides and silicates are important to many fields. For example, natural mineral assemblages with isotopic compositions out of equilibrium are common, and some isotopic geothermometer temperatures are found to be inconsistent with phase-equilibrium evidence (Cole and Ohimoto 1986; Gregor and Criss 1986). Rates and mechanisms of oxygen isotope exchange between solid silicates and water (as liquid or vapor) may also be relevant to a variety of surface processes, when they reveal information about fundamental steps in reactions. Bulk isotope exchange reactions have thus been extensively studied for their geochemical context, as well as in relation to the activity of aluminosilicate catalysts used in petroleum refinement and in industrial chemical synthesis (Oblad et al. 1953; Saxena and Taylor 1963; Von Ballmoos and Meier 1982).

Most studies of oxygen exchange reactions have been based on macroscopic measurements, which treat whole minerals as single reaction units. However, most minerals have multiple oxygen sites that have different bonding environments. These oxygen sites have different energetics and thus potentially different oxygen exchange characteristics. Independent rates of isotope exchange for different oxygen sites (OH and SO$_4$) have been measured in aluminate using chemical methods (Stoffregen et al. 1994), but this approach is unfortunately not generally applicable to silicates. Increased rates of bulk oxygen isotope exchange in zeolites with higher Al/Si have suggested greater reactivity of Si-O-Al vs. Si-O-Si bonds (van Ballmoos 1981), but such measurements cannot separate out individual rates in a single material. In contrast, because different sites in a crystal or glass can often be easily distinguished by solid state NMR, this technique provides a unique method to study isotope exchange reactions at the microscopic level. In framework aluminosilicates (both crystalline and glassy), for example, $^{17}$O NMR can readily distinguish and quantify oxygen in Si-O-Al, Si-O-Si, and even Al-O-Al linkages (Timken et al. 1986b; Dirken et al. 1997; Xu et al. 1998; Xu and Stebbins 1998b; Stebbins et al. 1999a, 1999b). This method was recently first applied to the kinetics of exchange between water vapor and the zeolite stilbite (Xu and Stebbins 1998a). Because water diffusion is so rapid in zeolites, site exchange kinetics predominated over diffusion and a clear distinction in rates between Si-O-Si sites (relatively slow exchange) and Si-O-Al sites (relatively fast) was observed. Very recently, a small fraction of Al-O-Al sites in stilbite was found to exchange oxygen with water vapor even more rapidly (Stebbins et al. 1999b). However, a relatively narrow range of temperature stability limited the exploration of the relative activation energies for the exchange rates.

Here we extend this approach to the mineral analcime (NaAlSi$_6$O$_{16}$H$_2$O, generally with a slight excess of SiO$_2$). The structure of analcime is well characterized and, once dehydrated, remains stable to surprisingly high temperatures (at least 800 °C) (Taylor 1930; Mazzi and Galli 1978; Line et al. 1995). The structure is also relatively simple, giving NMR spectra that are easier to interpret than those of a phase as complex as stilbite. Its macroscopic oxygen isotope exchange kinetics with water vapor have been studied in detail (Feng and Savin 1993), providing a means of testing spectroscopic conclusions. Analcime is also interesting geologically as a potential candidate for a low-temperature oxygen isotope geothermometer (Carlsson et al. 1985; Karlsson and Clayton 1990). Because the framework and bonding in analcime are similar to those in aluminosilicate zeolite catalysts, site-specific exchange reactions may also shed light on the catalytic activity of different sites.

The natural abundance of $^{17}$O is very low, about 0.04%. To obtain useful $^{17}$O NMR spectra of silicates, this isotope must be exchanged into the sample. In our previous studies of stilbite, an initial large enrichment was accomplished by equilibrating samples with H$_2$$^{17}$O under hydrothermal conditions,