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Time Resolved X-ray Diffraction Studies of K, Na, and Li Exchanged (Al,Ge)-GIS

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Introduction: Ion exchange in microporous materials is influenced by many factors and mainly has been explored *ex situ* in a static environment [1]. Recently, time resolved *in situ* X-ray diffraction studies of cation exchange have revealed how materials select and incorporate specific guest species [2,3]. GIS, the material studied here, has shown a high framework flexibility during ion exchange [4] thus allowing the study of an array of guest species.

Methods and Materials: Ion exchange reactions on the starting materials, $K_8Al_8Ge_8O_{32}\cdot 8H_2O$ (K-GIS) and $Na_{24}Al_{24}Ge_{24}O_{96}\cdot 40H_2O$ (Na-GIS) [5], were conducted at ambient conditions in a flow through cell [6]. Samples were placed in a 0.7mm quartz capillary and contained by glass wool plugs. Three 0.03M solutions were prepared with NaCl, KCl, and LiOH. The exchanging electrolyte was placed in a 500mL Nalgene[®] bottle with N_2 gas over pressure to serve as the driving force for the solution. Data was collected at two-minute intervals with a MAR345 imaging plate. Rietveld refinement was used to refine the structure models.

Results: Three ion exchange experiments were conducted: K^+ into Na-GIS, Na^+ into K-GIS, and Li^+ into K-GIS. When K^+ was exchanged for Na-GIS, super-cell reflections of Na-GIS reduced in intensity as K^+ substituted for Na^+ (Fig. 1). After approximately 10% K^+ exchange into the [001] channel of the Na-GIS super-cell, the K-GIS sub-cell began to form. Rietveld refinement showed that after sub-cell formation, Na^+ , K^+ , and H_2O were disordered in the center of the [201] channel making it nearly impossible to distinguish Na^+ from H_2O without constraining H_2O sites. For Na^+ into K-GIS, sub-cell reflections persisted throughout the duration of the experiment. After approximately one hour,

super-cell reflections became apparent. At the end of the ion exchange reaction, only 12% Na^+ exchange for K^+ was achieved. The final experiment was performed to see how a cation smaller than Na^+ would exchange into the K-GIS structure. A model structure solved from a single crystal resulting from 50% *ex situ* Li^+ exchange in the K-GIS, $(Li_4K_4)Al_8Ge_8O_{32}\cdot 8H_2O$, was used for the Rietveld refinement. The onset of the ion exchange reaction was not observed because the flow speed of the electrolyte was too fast and the transition occurred before diffraction data could be collected. No volume changes were observed in either cell during Li^+ for K^+ ion exchange. Ion exchange stopped near the end of the experiment because an impermeable layer, formed by grain packing, ceased solution flow.

Conclusions: Ion exchange experiments for K^+ , Na^+ , and Li^+ into (Al,Ge)-GIS showed that K^+ is the preferred cation to occupy extra-framework positions. Substitution of Li^+ cations in the K-GIS

structure could only achieve 50% exchange, which may be a result of its low coordination geometry, but this was not demonstrated by the time-resolved powder diffraction data.

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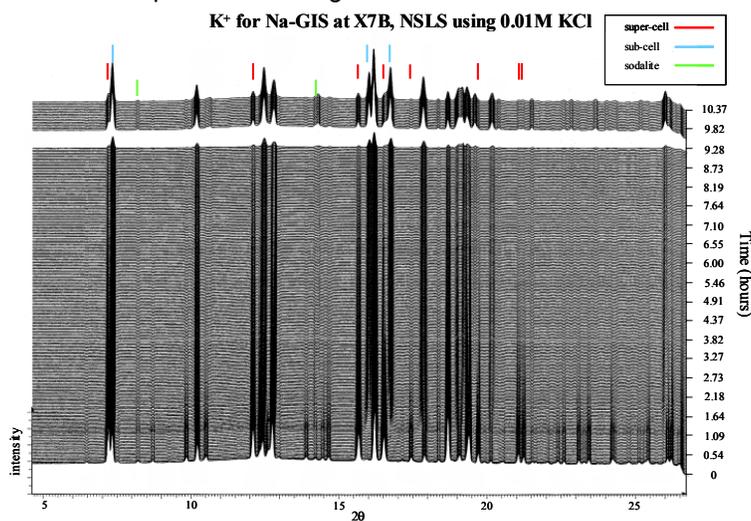


Figure 1. *In situ* XRD patterns of K for Na-GIS ion exchange. Twenty-seven frames were collected during beam dump and refill, no X-rays were hitting the sample. Red markers indicate the disappearance of the observed super-cell reflections. Blue markers indicate the appearance of the sub-cell reflections. Green marks show the SOD reflections.