

Time-Resolved Diffraction Studies of Ion Exchange: K^+ and Na^+ Exchange into Synthetic Aluminogermanate Molecular Sieve with the Gismondine Topology

A.J. Celestian¹, J.B. Parise^{1,2}, C. Goodell¹, A. Tripathi³, and J. Hanson⁴

¹Stony Brook University, Department of Geosciences; ²Stony Brook University, Department of Chemistry; ³Texas A&M, Department of Chemistry; ⁴Brookhaven National Laboratory, Department of Chemistry

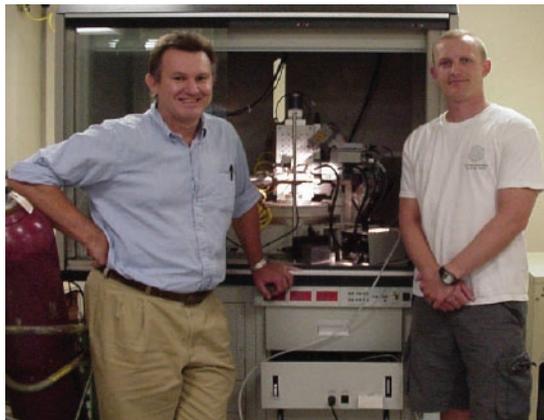
Time-resolved in situ x-ray diffraction was used to determine how ions are exchanged in the potassium (K^+) and sodium (Na^+) forms of the aluminogermanate molecular "sieve" (AlGe-GIS) with the topology of the gismondine (GIS) family of zeolite minerals. The AlGe-GIS structure is of particular interest due to its highly flexible framework and its use in industrial processes. This study illustrates the ion site-selective exchange pathways that are created during the substitution process and also determines possible ion exchange mechanisms. Bond valence calculations indicated that the preferred charge-balancing cation in the GIS structure is K^+ , due to its larger framework bonding coordination. Experiments were conducted at beamline X7B.

Zeolites are nanoporous minerals built from a fully corner-shared framework of tetrahedra. In the gismondine (GIS) family of zeolites, the synthetic aluminogermanate (AlGe-GIS) framework is composed of aluminum (Al^{3+}) and germanium (Ge^{4+}) ions, resulting in a net negative (-1) charge for every Al^{3+} ion in the framework. Therefore, extra-framework cations must be incorporated to charge-balance the structure and maintain electro-neutrality (**Figures 1** and **2**). These extra-framework cations are found in the large channels of the zeolitic framework and can be substituted for other cations. Due to the size, shape, and composition of the zeolitic channels, these materials behave as molecular "sieves" that selectively absorb and desorb cations – a property often used in environmental and industrial applications.

The information obtained from time-resolved *in situ* x-ray diffraction measurements enables us to directly follow the ion exchange process. The exchange of potassium ions (K^+) into Na-AlGe-GIS proceeded to 90% ($\pm 1\%$) completion within the time frame of the experiment (**Figures 3** and **4**). During the first 10% of K^+ substitution, K^+ only entered the [-101] channel (**Figures 1** and **4**) of the Na-AlGe-GIS structure. After 10%, exchange site-specific substitution could no longer be followed. In the reverse exchange (Na^+ into K-AlGe-GIS; data not shown), a gradual growth of the Na-AlGe-GIS phase was observed and stopped after approximately 10% substitution (**Figure 4**) in the time frame of the experiment. Site-

specific ion exchange was not observed during the substitution of Na^+ into K-AlGe-GIS.

The affinity of the GIS framework for the K^+ ion can be explained through bond valence analysis. In K-AlGe-GIS, K conducts most of its bond valence electrons to the O^{2-} framework



Authors (left to right)
John Parise and Aaron Celestian

BEAMLINE X7B

Funding

National Science Foundation Division of Materials Research

Publication

A.J. Celestian, J.B. Parise, C. Goodell, A. Tripathi, and J. Hanson, "Time Resolved Diffraction Studies of Ion Exchange: K^+ and Na^+ Exchange into (Al, Ge) Gismondine (GIS) $Na_{24}Al_{24}Ge_{24}O_{96}\cdot 40H_2O$ and $K_8Al_8Ge_8O_{32}\cdot 8H_2O$," *Chem. of Mat.*, **16(11)**, 2244-2254 (2004).

Contact information

Aaron J. Celestian
Center for Environmental and Molecular Sciences, Department of Geosciences, Stony Brook University

Email: aaron.celestian@stonybrook.edu

(approximately 51% of its total valence), thus achieving direct framework charge balancing. In Na-AlGe-GIS, Na⁺ conducts most of its bond valence electrons through interstitial water molecules (approximately 71% of its total valence). This effectively reduces the amount of direct charge balancing that Na⁺ can accomplish and results in a less stable bonding configuration relative to the K⁺ bonding environment.

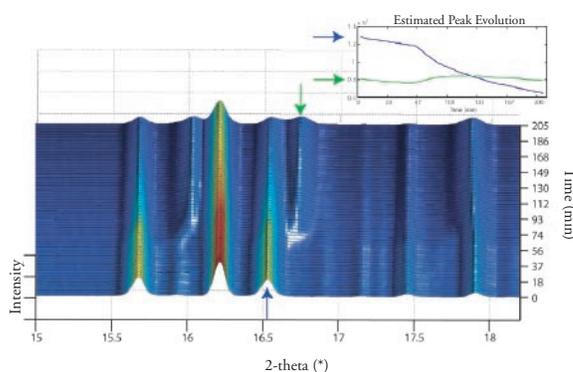


Figure 3. In situ time resolved diffraction patterns (selected 2-theta range shown for clarity). Each diffraction pattern is collected for 60 sec with 2.5 min between each pattern. The onset of ion exchange is seen approximately 60 min from the start of the experiment. New peak growth at 2-theta 16° and 16.75° indicate the K-AlGe-GIS phase forming. Top right insert shows the Iterative Targeted Transformation Factor Analysis (ITTFA), which follows peak position and intensity over all the diffraction patterns. ITTFA serves as an indicator of when subtle changes in the diffraction patterns occur and identifies those patterns for subsequent structure refinements.

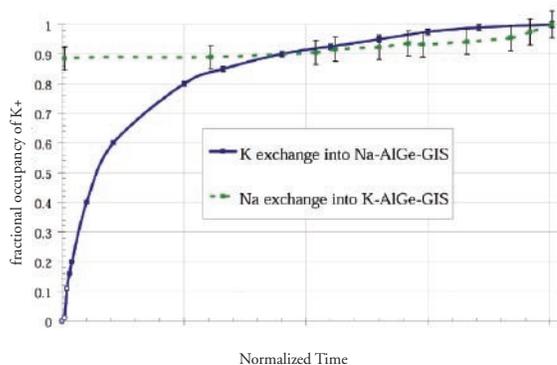


Figure 4. Plot of K⁺ occupancy as a function of time during forward and reverse ion exchanges in AlGe-GIS. Open circles represent structure refinements where site-specific occupancies were refined. Time is normalized due to different experimental time frames.

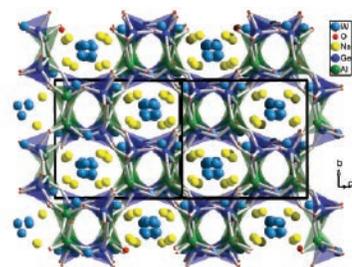


Figure 1. Crystal structure of Na-AlGe-GIS Na₂₄Al₂₄Ge₂₄O₉₆•40 H₂O in the C2/c space group. The 8-member ring channel is filled with Na⁺ (yellow) and water molecules (blue). Unit cell drawn in black. View is down the [-1 0 1] direction.

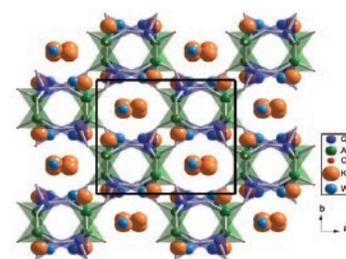


Figure 2. Crystal structure of K-AlGe-GIS K₈Al₈Ge₈O₃₂•8H₂O in the I 2/a space group. The 8-member ring channels are filled with K⁺ (orange) and water molecules (blue). The unit cell is drawn in black. View is down [0 0 1].