American Mineralogist, Volume 111, pages 446–460, 2026

Molecular-level insights into mechanisms of Li enrichment and occurrence in natural clay-bauxite

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ABSTRACT

This study reveals that the intricate sediment compositions, with Li-rich samples characterized by layered clays and layered or needle-like bauxite minerals, form distinct mineral transformation patterns. Mineral co-transformation lags behind the enrichment of Li. AlOOH formed via the desilicification of Li-kaolinite may inherit Li occurrence sites, whereas the transformation of kaolinite to illite potentially leads to the Li loss through K-Li substitution. The Li enrichment shows no selectivity for K, but exhibits a strong coupled enrichment relationship with Al, Mg, and Fe, resulting in dioctahedral minerals transforming into trioctahedral AlMgLiOH. The structure alterations result from inner-complexation of hexa-coordinate Li, differing from previous reports, where Li is bound to the Al-O/OH pseudo-hexagonal cavities (□) of kaolinite and/or AlOOH, exhibiting a more negative ^{7}Li NMR chemical shift of –0.3 ppm, forming Li_2O, LiOH, and LiF species. The Li enrichment mechanism induced by the reaction of structural OH results in varied acid-base feedback, particularly favoring stronger F-OH substitutions in alkaline samples, which facilitate the retention of Li in ultimate weathering products. ^{19}F NMR results indicate that F bonds with mineral structures to form Al-Al-□ and Mg-Al-□ configurations, exhibiting negatively shifted splitting peaks due to Li enrichment in the cavity, which disappear upon Li removal. Notably, Li in natural minerals remains significantly unaffected at ambient temperature and even in 200 °C-HCl solution but is crucially removed by 200 °C-H_2SO_4, with a leaching efficiency as high as 97.17% while dissolving fewer minerals, highlighting a more eco-friendly method for Li and mineral recovery.

Keywords: Li occurrence, mineral co-transformation, clay/bauxite sediments, ^{7}Li and ^{19}F NMR, eco-friendly Li recovery