



Potential lithium enrichment in pyrites from organic-rich shales

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In order to meet the technological needs of the energy transition, batteries of all scales, particularly those that power electrical vehicles, have become increasingly important. Lithium-ion batteries are in wide use at present, and continued research to improve them has been a focus of energy engineering. This, in turn, has greatly increased the demand for lithium (Li) as a natural resource. While the primary ores of Li (pegmatite, salar brine, and volcanic-associated clay) are generally well-understood, it would be desirable to identify additional Li sources that could be safely and economically exploited. Using material from previous industrial operations (e.g., mine tailings or drill cuttings) as a source of additional Li would be attractive as it would generate little or no new waste material.

Our study was carried out on 15 Devonian shale samples of varying organic richness from wells drilled in the Appalachian basin (USA). Sequential extraction of the samples was performed to measure Li recovery from targeted rock-forming phases, namely the carbonates, Fe-Mn oxyhydroxides, pyrites, and organic matter. The mineralogy of the post-leaching residue was found to be dominated by silicates and anatase, suggesting the target phases were successfully leached out of the whole rock.

Unsurprisingly, the data shows higher whole-rock Li values are observed in samples with a higher total clay content. The lowest whole-rock Li contents correspond to samples having higher contents of total organic carbon (TOC) and pyrite. Unexpectedly, however, samples with relatively lower Li contents (22 ppm) can liberate up to 54% of the total lithium from pyrite alone. Furthermore, we observe a positive correlation between pyrite content and %Li recovery in the pyrite leachate ($r^2 = 0.732$). These initial findings suggest that pyrite in conjunction with organic matter may play a previously unrecognized role in the Li distribution in organic-rich shales. The geochemical processes that might cause Li enrichments associated with pyrite are not well-understood. However, since Li mobility is highly sensitive to small increases in temperature, the very high thermal maturation of the studied shale sequence may have significantly impacted Li remobilization during the smectite-to-illite clay-mineral transformation. The common Li-mineral that can coexist with different phases of FeS is Li_2S at temperatures $\approx 75^\circ\text{C} - 135^\circ\text{C}$. Several reaction mechanisms have been proposed, but there is little known about the rate kinetics and reaction steps involved in Li association with pyrite in shales.

This study suggests the possibility that some Li may be sequestered in pyrite in organic-rich shales. As pyrite is a common mineral in the Appalachian Basin, this has implications for exploiting shale pyrite in the Devonian sequence if the Li proves economically extractable. Drill cuttings from past and current oil and gas operations are a ready material upon which to test the feasibility of this concept.