

Lithium in kerogen: A source of isotopically light Li in the global geochemical cycle

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Lithium is a critical resource for batteries, therefore understanding its sources is key to identifying economic reserves. Recently, Li-isotopes of marine sediments have been used for interpreting paleo-weathering as an indicator of global climate change. The contribution of Li from organic sources to porefluids is often neglected, therefore this study evaluated the changes in Li-content and isotopic composition of organic maceral groups (vitrinite, liptinite, inertinite) in coal as a function of thermal maturation across two coal seams intruded by dikes. Samples were collected from a single depositional layer in the Vermejo Fm. (Colorado USA) where high-volatile bituminous coal was intruded by a mafic-lamprophyre dike, and from the Dutch Creek No.2 mine where a medium volatile bituminous coal was intruded by a felsic-porphyry dike. Samples were collected across the contact zone and into unmetamorphosed country rock.

The Li-content and isotopic composition ($\delta^7\text{Li}$ ‰) of coal macerals were measured *in situ* by secondary ion mass spectrometry (SIMS). The organic macerals of the unmetamorphosed Vermejo coal (VRo 0.68%) contained $<1\mu\text{g/g}$ Li, however the $\delta^7\text{Li}$ of the vitrinite, which makes up the bulk of these coals, was 18 to 37‰ *lighter* than the metamorphosed vitrinite and coke, indicating that isotopically light Li is released during metamorphism. Unmetamorphosed coal had vitrinite with average $\delta^7\text{Li}$ of $-28.4\pm 1.6\%$ (2σ), liptinite $-15.4\pm 3.6\%$, and inertinite $-10.5\pm 3.7\%$. Organic macerals may release their isotopically light Li at different temperatures.

The Dutch Creek coal (VRo 1.15%) had been heated by burial to ~ 150 °C before felsic dike emplacement and had likely released organo-Li during diagenesis, so there was a smaller range in $\delta^7\text{Li}$. Nonetheless, vitrinite in the unmetamorphosed country rock had $\delta^7\text{Li}$ values 8 to 20‰ lighter than vitrinite and coke in the contact zone, again showing that ^6Li is preferentially released from organics as temperature increases. A negative correlation was observed between Li-contents ($<10\mu\text{g/g}$) and C/Si ratios, indicating that at elevated temperatures Li becomes concentrated in authigenic silicates. Thus, isotopically light Li from organic sources must be considered when using $\delta^7\text{Li}$ of authigenic minerals to interpret past global weathering due to climate change.