

Geochemical tracing of lithium carbonate production based on stable isotopic compositions

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Driven by the increased demand for clean energy technologies, provenance verification systems based on isotopic, major and trace element compositions are developed to address concerns about the environmental and social impacts of critical mineral and metal supply. However, limited studies have examined their application to refining processes.

In this work, spodumene concentrates (SCs) from two major Australian sources were refined into lithium carbonate (Li_2CO_3) to investigate how refining affects isotopic fingerprints ($\delta^7\text{Li}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$). The SCs were subjected to laboratory-scale calcination, roasting, water leaching, neutralisation, purification, precipitation, bicarbonation and crystallisation, emulating processes to reject chemical impurities practised in industry. The resulting Li_2CO_3 was analysed by MC-ICP-MS and GasBench IRMS. $\delta^7\text{Li}$ increases consistently from SC to Li_2CO_3 , with higher $\delta^7\text{Li}$ in SC (9.7‰) resulting in Li_2CO_3 with higher $\delta^7\text{Li}$ (13.0‰ and 14.2‰) and SC with lower $\delta^7\text{Li}$ (6.5‰) resulting in LC with lower $\delta^7\text{Li}$ (8.9‰ and 10.1‰). The $\Delta^7\text{Li}_{\text{SC-Li}_2\text{CO}_3}$ varies between 2.4‰ and 4.5‰, reflecting minor adjustments in laboratory refining conditions. The data demonstrate the potential of $\delta^7\text{Li}$ as a provenance fingerprint that can trace the origin of SC through refining processes.

$\delta^{13}\text{C}$ of crude Li_2CO_3 ($\delta^{13}\text{C}_{\text{Crude Li}_2\text{CO}_3} = -7.2\text{‰}$ to -7.5‰) is similar for the different SCs and close to the composition of the soda ash used in the refining process ($\delta^{13}\text{C}_{\text{Na}_2\text{CO}_3} = -9.4\text{‰}$ to -9.6‰). Purification of Li_2CO_3 through bicarbonation and re-crystallisation leads to higher $\delta^{13}\text{C}$ in purified Li_2CO_3 ($\delta^{13}\text{C}_{\text{Li}_2\text{CO}_3} = 4.9\text{‰}$ to 6.9‰). $\delta^{18}\text{O}$ of purified Li_2CO_3 , on the other hand, depends on evaporation time during re-crystallisation, ranging from 17.0‰ to 17.5‰ and 23.6‰ to 26.0‰ for 2 and 5 h of evaporation, respectively. Rather than the SC source, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of purified Li_2CO_3 reflect process chemicals and specific refining process parameters, respectively. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in Li_2CO_3 can thus distinguish different industrial refining processes. Stable isotopic compositions of refining products therefore provide a fingerprint that reflects the origin of source materials and the specific refining processes, which, if further developed, can aid in the assignment of ESG credentials such as CO_2 and energy footprints.