

Lithium isotopes in Phanerozoic brachiopod shells: Implications for the continental weathering flux

Literature study by Natalie Gaspers

Lithium as a geochemical tracer

Lithium has two naturally occurring stable isotopes, ${}^6\text{Li}$ (7.52%) and ${}^7\text{Li}$ (92.48%)[1]. The large relative mass difference between the two isotopes (~16%) is the reason why Li strongly fractionates in many low-temperature geochemical processes [2]–[5]. Due to its ionic radius (0.78 Å) which is similar to that of Mg^{2+} (0.72 Å), Al^{3+} and Fe^{2+} (0.77 Å), Li^+ can substitute for these ions in crystal lattices of mafic silicate minerals [4][6]. Thus, Li behaves as a moderately incompatible element during igneous processes. Furthermore, Li is relatively uniformly distributed in the Earth's crust [7], is a subordinate component in biological, hydrological and atmospheric cycles [3][7] and, therefore, it can be used as a novel tracer for continental weathering and climate changes.

Lithium in the oceans

The residence time of Li in the oceans (~1.2 million years, [8]) is substantially longer than the ocean mixing time (~1000 years, [8]). Lithium is therefore evenly distributed vertically and laterally throughout the oceans both in concentration (~180 ppb) and isotopic composition ($\delta^7\text{Li}_{\text{SW}} = 31 \text{‰}$)[8]–[11].

Two primary sources of Li into the oceans are rivers and hydrothermal fluxes [2][4]. Since rivers transport the products of continental weathering to the oceans and Li is very abundant in silicate weathering products substituting for other elements, these weathering/alteration processes exert an important control

on the Li isotope composition of seawater providing a wide range in concentrations and isotope ratios of weathering products [3]. However, this influence on seawater is controlled by the weathering susceptibility of the parent rock type, the formation of secondary minerals and the weathering rate [3][4][10][14]. Hydrothermal vent fluids (>350°C) are isotopically very distinct from rivers but “only slightly fractionated from their source” [8] but, at the same time, Li concentrations are highly enriched over that of seawater [8].

The most important sinks for Li in the oceans are (i) the formation of marine clays which removes preferably ${}^6\text{Li}$, MAAC (marine authigenic aluminosilicate clays) formation [8], and (ii) biological and inorganic carbonate precipitation [2]. Through the formation of clays and seafloor alteration the seawater is driven toward isotopically heavier compositions, and without these active processes, the ocean would be an

$$\delta^7\text{Li} \text{ (‰)} = \left[\left(\frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{sample}} / \left(\frac{{}^7\text{Li}}{{}^6\text{Li}} \right)_{\text{L-SVEC}} - 1 \right] \times 1000$$

Fig.1: Calculation of $\delta^7\text{Li}$ based on the L-SVEC secondary reference standard [12][13].

exact mirror of the riverine input [8]. On the other hand, carbonate precipitation only requires low levels of Li, since the Li concentrations in carbonates are mostly below 1 ppm [2][4][15].

Lithium in brachiopods

Marine carbonates have the potential to serve as a proxy for seawater composition as a whole and through the incorporated Li for continental weathering in particular. In order to compile a record of the past and recent $\delta^7\text{Li}$ in the oceans, foraminifera shells [8][15]–[17], scleractinian corals [2] and belemnites [18] were measured in several studies. However, only one foraminifera-based record is available for the Cenozoic (Fig.2, [8]), a record for the whole Phanerozoic era has not yet been obtained. Vital effects on $\delta^7\text{Li}$ have not been observed, although the species dependent variations can be large [2].

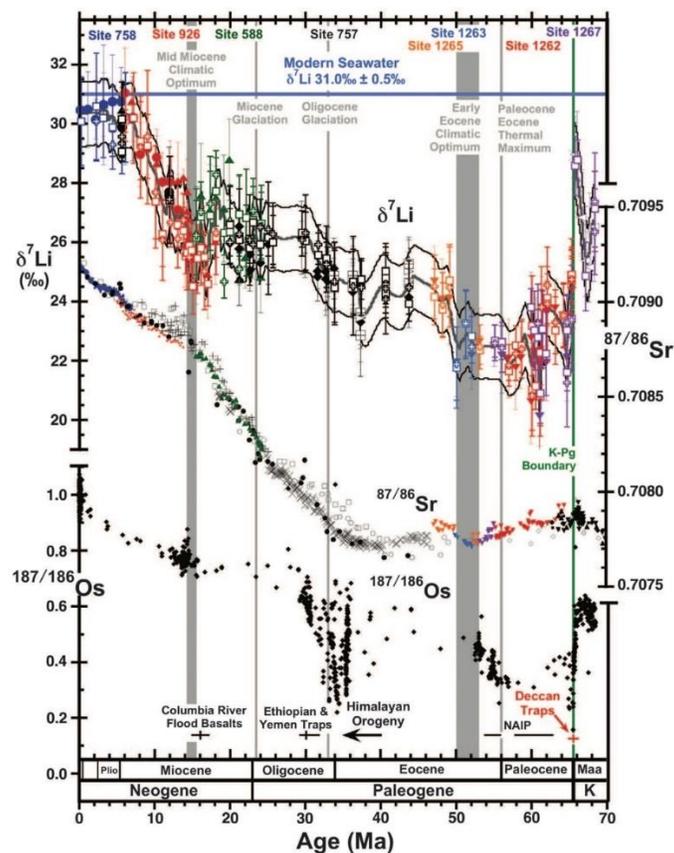


Fig. 2: Late Cretaceous to Holocene Li isotope record based on foraminifera shells by [8].

For this study, brachiopods were selected which may be considered as carbonate archive, because this group represents one of the oldest evolved groups, already present in the Early Cambrian oceans, i.e. the beginning of the Phanerozoic [19]. Furthermore, brachiopods are considered to be less sensitive to diagenesis due to their shell mineralogy (low-Mg calcite) [20] and thus, they should presumably be a suitable archive for the Phanerozoic seawater composition. This study will be among the first to measure Li isotope ratios on brachiopods, while only Li/Ca ratios have been analyzed so far showing an inverse correlation of Li/Ca and growth temperature of the specimens [21].

Lithium and the continental weathering flux

Lithium can be used as a tracer for the continental flux because silicate rocks cover a very narrow range of $\delta^7\text{Li}$ values (unaltered MORB: 3-5‰; continental crust ~0‰ [22]–[26]) compared to rivers transporting the dissolved load of weathered continental crust (6-42‰; [4][5][14][22][27][28]). Since lithium is almost totally incorporated in silicate rocks, $\delta^7\text{Li}$ is almost entirely dependent on weathering of silicate rocks even in carbonate-dominated environments [14][29]–[31]. However, the $\delta^7\text{Li}$ of rivers relies not exclusively on the composition of the bedrock, but also strongly on the formation of secondary minerals in the water column. The reason for this is the preferential incorporation of ^6Li in secondary minerals driving the riverine $\delta^7\text{Li}$ to heavier values [3][14][29]. Thus, $\delta^7\text{Li}$ of rivers “reflects mixing between two end-member solutes: one formed by primary silicate mineral dissolution (with low $\delta^7\text{Li}$ and high [Li]) and the other related to secondary mineral formation (with high $\delta^7\text{Li}$ and low [Li])” [29].

Since the continental weathering flux directly influences the global climate, the estimation of weathering rates in the past and present is very important. The most significant climate-driving process, that needs to be considered regarding Li, is weathering of Ca-Mg silicates [32]. This occurs during the chemical weathering on land where minerals convert the atmospheric carbon dioxide to hydrogen carbonate ions which, along with metal ions, are transported to the oceans by rivers and groundwaters where they are removed via precipitation of calcium carbonate [32]–[34]. Records of seawater chemistry should therefore help determining the importance of continental weathering on the global climate and since Li provides information about both, weathering processes and fluxes, it may be the perfect tracer for this.

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