



이학석사 학위논문

# Lithium isotopic evidence for enhanced weathering in the Middle Ordovician Taebaeksan basin, Korea

태백산 분지 중기 오르도비스기의 증가한 풍화에 대한 리튬 동위원소 증거

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정제나

## Lithium isotopic evidence for enhanced weathering in the Middle Ordovician Taebaeksan basin, Korea

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#### Abstract

## Lithium isotopic evidence for enhanced weathering in the Middle Ordovician Taebaeksan basin, Korea

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The Ordovician period is known for significant environmental changes in the Paleozoic era, including rapid temperature fluctuations from an early warm climate to a later ice age. Silicate weathering has been proposed as a key factor contributing to this temperature drop, which was intensified by tectonic activity and active volcanism starting in the Middle Ordovician. Silicate weathering plays a crucial role in long-term climate change by consuming atmospheric carbon dioxide, and lithium isotopes have been widely used as indicators of silicate weathering in paleo-environmental studies.

The objective of the thesis is to interpret environmental changes during the Ordovician period using lithium isotopes in the Middle Ordovician carbonate rocks from the Taebaeksan Basin in Korea. In this study, an effective method was developed for analyzing lithium isotopes in carbonate rocks with varying insoluble residue contents from the Duwibong Formation and Jigunsan Formation of the Taebaek Group. A dissolution method was optimized to maximize the extraction of lithium from carbonate minerals while minimizing contamination from silicate minerals. Additionally, a column separation method was established to efficiently separate lithium from samples with high calcium content in the matrix. These methods enable the reconstruction of lithium isotopic ratios of seawater in the Darriwilian. A significant decrease of 10‰ in lithium isotopic ratios was observed during the Middle to Late Darriwilian. A mass-balance model was used to interpret the excursion, and hypothesized a reverse weathering associated with active continental weathering. This study provides additional evidence for increased weathering during the Darriwilian and proposes that reverse weathering may have contributed to the Middle Ordovician climate fluctuation.

Keywords : Lithium isotopes, weathering, climate change, Ordovician, marine carbonate rock, Taconic orogeny Student Number : 2021-29722

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#### Chapter 1. Introduction

The Ordovician period experienced a wide range of climates and fluctuations in sea levels. It is characterized by a transition from a warm climate with sea surface temperatures of approximately 45°C to the later Hirnantian glaciation (Cocks and Torsvik, 2020). Various studies have been suggested to explain this cooling and further onset of glaciation, such as enhanced silicate weathering (Young et al., 2009; Swanson-Hysell and Macdonald, 2017; Conwell et al., 2022) and decreased volcanic outgassing (McKenzie et al., 2016). Active tectonic activity (e.g., Taconic orogeny) started from the Middle Ordovician is considered the most likely cause of increased weathering, which is supported by the global decrease in seawater strontium isotope ratio (87Sr/86Sr) and increase in seawater neodymium isotope ratio (143Nd/144Nd) (Young et al., 2009; Saltzman et al., 2014; Avila et al., 2022; Conwell et al., 2022). The studies suggest that the consumption of atmospheric CO<sub>2</sub> through silicate weathering may have played a role in stabilizing the warm climate during the Early Ordovician and potentially contributed to the onset of the End Ordovician glaciation.

However, the relationship between weathering and cooling during the Middle Ordovician remains understudied. During the Ordovician, there is an overall cooling trend. However, several studies report that during the Middle to Late Ordovician, the decrease in sea surface temperature was slowing down or even showed a brief warming phase (Fig. 1; Trotter et al., 2008; Kidder and Tomescu 2016; Song et al., 2019; Cocks and Torsvik, 2021). Additionally, global carbon cycle models, such as GEOCARBSULF, also show an increase in atmospheric  $CO_2$  (Fig. 1; Saltzman and Edward, 2017). Since strontium and neodymium isotopes are affected by processes other than silicate weathering (e.g., carbonate weathering or regional lithology), new weathering proxy is needed to investigate the specific environment of the Middle Ordovician climate transition.



Figure 1. Combined diagram of the Middle Ordovician environment. (A) Sea Surface Temperature (SST) modified from Song et al. (2019) and Cocks and Torsvik (2021). Temperatures are mean values at one million years interval based on  $\delta^{18}$ O from apatite conodonts. (B) Compiled <sup>87</sup>Sr/<sup>86</sup>Sr record. Data from Young et al. (2009), Saltzman et al. (2014), and Avila et al. (2022). (C) Variations of  $\delta^{13}$ C. T: Tremadocian, D: Dapingian, MDICE: Middle Darriwilian Isotope Carbon Excursion, GICE: Guttenberg Isotope Carbon Excursion. All stage boundaries from Cramer and Jarvis (2020).

Lithium is one of the powerful global weathering proxies (Misra and Froelich, 2012; Dellinger et al., 2015; Kalderon–Asael et al., 2021). Lithium has two stable isotopes, <sup>6</sup>Li and <sup>7</sup>Li with relative abundances of 7.5% and 92.5%, respectively. The isotope composition is expressed in  $\delta$  notation as follows:

$$\delta^{7}Li = \left(\frac{\binom{^{7}Li}{^{6}Li}}{\binom{^{7}Li}{^{6}Li}} - 1\right) \times 1000 \,(\%)$$

Rivers account for approximately 60% of the lithium input flux to the ocean, while the remaining 40% is derived from hydrothermal fluids (Fig. 2; Chan and Edmond, 1988; Hathorne and James, 2006). Lithium is removed from seawater through processes such as marine authigenic clay formation or low– temperature alteration of basalts, with a cumulative fractionation factor of 20‰ and 13‰, respectively (Misra and Froelich, 2012; Coogan et al., 2017). These processes contribute to the relatively high  $\delta^7$ Li value of modern seawater, reported to be 29.5–31.5‰ (Liu et al., 2019; Pogge von Strandmann et al., 2019; Li et al., 2022).

During the water-rock interaction, there is a preferential uptake of light isotope (<sup>6</sup>Li) into secondary minerals, resulting in isotopic fractionation that occurs independently of primary rock dissolution (Pistiner and Henderson, 2003; Penniston–Dorland et al., 2017). Therefore, riverine lithium isotopic composition is controlled by the ratio of primary silicate mineral dissolution to secondary mineral formation, known as 'weathering congruency' (Dellinger et al., 2015). In cases where the rocks undergo congruent dissolution, the river will show a high lithium flux and low dissolved  $\delta$  <sup>7</sup>Li values due to limited secondary mineral formation. Conversely, incongruent weathering results in a low lithium flux and high  $\delta$  <sup>7</sup>Li values due to the preferential uptake of <sup>6</sup>Li by secondary minerals (Penniston–Dorland et al., 2017; Pogge von Strandmann et al., 2017). Therefore, by analyzing lithium isotopes in marine sediments, which reflect the chemical signals of seawater, it is possible to estimate the weathering regime of that time.



Figure 2. The Li budget of the oceans with its sinks and sources.  $F_{Li}$  and [Li] indicate Li flux and concentration, respectively (modified after Pogge von Strandmann et al., 2020; Jeong and Huh, 2023). Data from Huh et al. (1998), Chan and Edmond (1988), Chan et al. (1994), Foustoukos et al. (2004), Hathorne and James (2006), Misra and Froelich (2012), Li and West (2014), Coogan et al. (2017), and Andrews et al. (2020).

Lithium has several key advantages as a silicate weathering proxy. Firstly, lithium is solely affected by silicate weathering, even in carbonatedominated catchment, due to the significantly higher lithium content in silicate minerals (Li/Ca =  $10,000-100,000 \mu \text{ mol/mol}$ ) compared to carbonate minerals (Li/Ca =  $1-100 \mu$  mol/mol) (Dellinger et al., 2020). Secondly, no biological fractionation has been observed during the growth of plants or phytoplankton, ensuring the reliability of lithium as a weathering proxy (Clergue et al., 2015; Pogge von Strandmann et al., 2016). Lastly, the isotopic fractionation factors between seawater and marine sediments are relatively constant (Chan et al., 1992; Marriott et al., 2004a, 2004b; Jeong and Huh, 2023). Also, the residence time of lithium is relatively long compared to other elements (e.g., Neodymium), estimated to be around 1.2 million years (Misra and Froelich, 2012). This enables the interpretation of seawater lithium isotopic ratio as a global signal. For this reason, paleoclimate and paleoenvironment studies aim to reconstruct the past seawater lithium isotope ratio ( $\delta^7 \text{Li}_{\text{SW}}$ ) from the Paleozoic to the Cenozoic. Therefore, this study attempts to interpret the environmental changes in the Middle Ordovician using lithium isotopes as a proxy for silicate weathering.

#### Chapter 2. Method

#### 2–1. Study area

The Korean Peninsula was part of the Sino-Korean Block (SKB), also known as the North China Block, in the Paleozoic (Fig. 3). The SKB was located in the equatorial northeastern peri-Gondwana region in the Early Paleozoic, and sediment deposition occurred in epeiric sea environments. The Taebaeksan basin is located in central-eastern Korea (Fig. 4), and the Joseon Supergroup within it consists of lower Paleozoic successions, which have been extensively studied biostratigraphically (Choi et al., 2004; Lee, 2018; Cho et al., 2021; Lee et al., 2022). The Duwibong Formation and Jigunsan Formation are the upper unit of the Taebaek group, which belong to the Joseon Supergroup (Fig. 5; Choi et al., 2004). T. tangshanensis conodont zone, originating from the Makgol Formation, extends up to the middle part of the Jigunsan Formation, followed by the onset of the *E. suecicus* conodont zone (Fig. 5). Although A. serratus was found in some parts of the upper Duwibong Formation, the starting point of the A. serratus conodont zone could not be clearly determined due to erosion. Therefore, it is reported that the upper part of the Duwibong Formation also belongs to the *E. suecicus* zone (Cho et al., 2021). Using carbon isotope chemostratigraphy, it has been reported that carbon isotope ratios increase until the end of the Duwibong Formation (Bang and Lee, 2020), known as the Middle Darriwilian Isotope Carbon Excursion (MDICE). A negative carbon isotope excursion was also reported below the MDICE (Bang and Lee, 2020), although it may have been influenced by local factors. However, the increasing trend of carbon isotope ratios clearly indicates the trend of the MDICE, but the decreasing trend (i.e., recovery trend) of MDICE has not been observed due to erosion. Based on this evidence, it can be concluded that the Duwibong Formation, Jigunsan Formation, and uppermost Makgol Formation belong to the Middle Darriwilian period. The approximate age of each formation was determined by considering the boundary between *T. tangshanensis* zone and *E. suecicus* zone, which is known to correspond to the middle of Dw2 (Cramer and Jarvis, 2020), located in the middle of the Jigunsan Formation. Additionally, the uppermost part of the Duwibong Formation was set as the end of the *E. suecicus* zone, and the age was calculated based on the height of the sample.



**Figure 3.** The Middle Ordovician paleogeographic map. Red dot indicates the studied section. Paleo-map data from Scotese (2001), PALEOMAP Project.



Figure 4. Map showing the Korean peninsula and studied section. (A) The map shows the location of the Taebaeksan Basin (TB: Taebaeksan basin). (B) Location of the Taebaeksan Basin with studied section (modified from Choi et al., 2005). (C) Geological map of the studied section in southeastern margin of the Taebaeksan Basin. The Studied section are marked by a red box (modified from Choi et al., 2004).

Period	Epoch	Stage	Age (Ma)	Taebaek Group		Period	Stage	Stage slice	Conodont zone	Fm.	
		Hirnantian					458.18 Ma		P.anserinus		
	Late	Katian	445.21					Dw3	P.serra		
		Sandbian	402.70		/			462 Ma			
_			458.18			ian			A.serratus ?	~~~~	$\uparrow$
ciar	<u>e</u>	Dorriwilion		Duwibong Fm.		ovic	ian		E.suecicus	En.	
	lidd	Darriwillari		Jigunsan Fm.		Orde	iwil				Study area
ŏ	≥		469 42	Makgol Fm.		lle (	Jarr	Č M		Jigunsan Fm.	
		Dapingian	471.26		Ν	lido		_			$\downarrow$
	~	Floian	477.08	Makgol Fm.		2		468 Ma	T. tangshanensis		
	Earl		477.00	Dumugol Fm.				-		Makgol Fm.	
		Tremadocian		Dongjeom Fm.			469.42 Ma	DW	?		

Figure 5. The Ordovician time scale and stratigraphic division of the Taebaek group within the Joseon Supergroup are presented (modified from Lee et al., 2022), along with a detailed Darriwilian time scale and biostratigraphic division. Conodont biozone from Choi et al. (2004), Cho et al. (2021), and Lee et al. (2022). All stage boundaries from Cramer and Jarvis (2020). Fm: formation.

#### 2–2. Sample information

This study analyzed  $\delta^7$ Li and trace/major elements from 11 carbonate rock samples of the Jigunsan and Duwibong Formation of the Taebaeksan basin (Fig. 4). The Joseon Supergroup is characterized by shallow platform carbonate rocks with interbedded siliciclastic rocks. Among the groups, the Taebaek group is well-exposed in the Seokgaejae section, located in the Bonghwa County, Gyeongsangbuk-do Province. The Jigunsan Formation has an approximate thickness of 40 m and is composed of layers alternating between dark gray mudstone with interbedded limestone (Fig. 6). The Duwibong Formation is about 45 m thick and consists of light gray and massive limestone with shale (Woo and Chough, 2007). Rock samples were collected at 1 m intervals, and the samples were cut into 1 cm cubic forms, excluding any visible veins, microfossils, and contaminations. Subsequently, the samples were washed with distilled water. Limestone samples were powdered using an agate mortar and dental drilling, selecting only the micrite portion, and stored in glass vials. The powdered samples with high CaCO<sub>3</sub> content (50-90%) were selected and subjected to a geochemical screening procedure (see section 4-1).



Figure 6. Photographs of the Seokgaejae section. (A) Outcrop photograph of Jigunsan and Duwibong Formation. Yellow line indicates a boundary between the two formations. (B) Interbedded limestone of Jigunsan Formation. Photo by Sunhwa Bang. Fm: formation.

#### 2–3. Pretreatment and extraction

This study focused on the selective dissolution of carbonate minerals, given that lithium is significantly more abundant in silicate minerals and has different isotopic composition. The dissolution method employed in this study followed Pogge von Strandmann et al. (2013) and Washington et al. (2020). 200 mg of powdered samples were dissolved in 25 ml of 0.05 M HCl for 1 hour in a 50 ml centrifuge tube, shaking using a vortex mixer and degassing with an ultrasonicator. After centrifugation at 3,000 rpm for 5 minutes, the supernatant of each sample was filtered through an acid–cleaned 0.22  $\mu$  m filter (Steriflip) and collected in a 60 ml Teflon jar. The collected samples were evaporated at 80 °C for 24 hours on a hot plate, redissolved with HNO<sub>3</sub> for ICP–MS analysis and column purification. Prior to use, all the apparatus were thoroughly cleaned with acid and DI water in a clean hood.

Since the samples contain a high concentration of calcium and sodium, a careful verification of the column purification method was necessary to achieve successful separation of lithium. The overall lithium separation process followed Choi et al. (2013). Acid–clean polypropylene columns (BioRad,  $0.8 \times 4$  cm) were packed with 1.8 ml of AG50W–X8 cation exchange resin. The resin was pre–washed with 10 ml of 1.5 M HF followed by 40 ml of 6 M HCl. The columns were then conditioned with 7 ml of HNO<sub>3</sub>-methanol mixture (6 M HNO<sub>3</sub>: methanol = 1:4 v/v), ensuring that

no air bubbles were trapped within the resin. Once conditioned, samples containing approximately 50-150 ng of lithium were dissolved in 1 ml of HNO<sub>3</sub>-methanol mixture and loaded onto each column. Throughout the separation process, the elution speed was maintained below 0.2 ml/min to prevent sodium tailing (Choi et al., 2013). It should be noted that most rock samples contain a significant amount of sodium, which has a distribution coefficient (K<sub>d</sub>) similar to that of lithium (Zhu et al., 2019; Li et al., 2022). Consequently, during the column procedure, it is possible for sodium and lithium peaks to overlap. A high Na/Li ratio (> 2) can affect the measurement of  $\delta^7$ Li due to the space-charge effect, which causes ions with a higher massto-charge ratio to concentrate in the center of the ion beam and force lighter ions toward the outer region (Thomas, 2013). Therefore, samples with a high Na/Li ratio (> 2) were subjected to an additional column process using the same procedure to ensure a low Na/Li ratio. Fig. 7 shows a calibration curve obtained using several samples and reference materials for the separation method. The recovery rate of lithium for all samples was maintained at >99.5 %. Aliquots of each sample were evaporated at 80 °C and prepared in 2 % HNO<sub>3</sub> for isotope analysis.



**Figure 7.** Separation elution curves of Na and Li in the samples and seawater reference material (NASS-7). D43 and J38 are samples from Duwibong and Jigunsan Formation, respectively.

#### 2–4. ICP–MS analysis

In this study, major and trace elements in carbonate fraction of samples, including Li, Na, Mg, Al, Ca, Mn, and Sr were analyzed using the Agilent8900 ICP–QQQ at the Seoul National University (Table 1). To analyze the sample solutions at the 10–100 ppb level, they were diluted by factors of 10 (Al, Na), 1,000 (Mg, Sr, Mn), and 100,000 (Ca). The concentrations were determined using a cation standard concentration curve ranging from 50–300 ppb. The precision for all elements was less than 5%, and the accuracy, which was assessed using geological reference material (GSR–6, limestone), was less than 10%.

#### 2-5. MC-ICPMS analysis

Lithium isotopic ratios were analyzed using Nu Plasma 3, MC– ICPMS at the London Geochemistry and Isotope Centre (LOGIC) (Table 2). A sample–standard bracketing procedure was used with IRMM–016 standard, and each individual measurement had a 50 s of integration time. The 2sd (standard deviation) was calculated based on three repeated individual measurements. The lithium concentration of sample solution was 5 ppb dissolved in 2% HNO<sub>3</sub> which gives a signal intensity of 10–14 V for <sup>7</sup>Li. The total procedure blank for lithium was approximately 15 pg, which is negligible compared to the samples (~20–600 ng). The long–term (twelve months) precision was  $\pm 0.4\%$  (2sd), and the accuracy was checked with  $\delta^7$ Li of seawater (31.11  $\pm$  0.38‰, n=12) (identical to published values).

	CaCO	Li/Ca	Al/Ca	Sr/Ca	Mn/Ca	Mg/Ca
Sample	$CaCO_3$	(µmol/m	(mmol/	(mmol/	(mmol/	(mmol/
	(70)	ol)	mol)	mol)	mol)	mol)
J2-2	65.6	12.1	0.01	1.64	1.64	18.8
J2-17	86.0	22.2	0.01	1.11	3.16	12.5
J38	51.8	50.5	0.03	1.32	4.59	17.9
J45	53.4	33.5	0.03	1.34	3.98	23.7
D3	92.0	8.9	0.01	1.14	1.80	12.8
D9	65.8	32.8	0.03	1.49	1.73	24.9
D21	84.5	14.8	b.d.l.	1.50	0.49	20.0
D33	91.8	6.2	0.01	0.74	2.44	15.7
D43	93.4	16.1	0.01	2.44	0.61	51.8
D27	87.1	33.2	0.01	1.53	4.95	55.0
D40	86.8	20.5	0.03	1.30	0.54	45.5
GSR-6	_	_	0.10	1.98	1.90	32.0

Table 1. Data from the carbonate mineral fractions of the samples and reference material (GSR-6, limestone). B.d.l.: below detection limits.

Sample	Height (m)	$\delta^7$ Li	2sd
J2-2	12.6	19.2	0.9
J2-17	37.5	14.6	0.0
J38	39.0	12.6	0.5
J45	46.0	12.9	0.5
D3	51.0	13.6	0.8
D9	57.0	13.9	0.5
D21	69.0	14.28	0.55
D33	81.0	8.5	1.0
D43	91.0	15.42	0.22
D27	75.0	4.6	0.5
D40	88.0	14.6	0.5
NASS-7		31.0	0.4

Table 2. Lithium isotope ratios of the carbonate mineral fractions of the samples.

#### Chapter 3. Results and discussion

#### 3-1. Results

This study reports lithium isotope ratios from carbonate rock of the Duwibong and Jigunsan Formations in the Taebaeksan basin (Fig. 8). Various geochemical indicators based on elemental data from the leachates were utilized to investigate potential signals of silicate mineral contamination and diagenetic alteration. No correlations ( $R^2 < 0.5$ , p > 0.05, n=11) were found between  $\delta^7$ Li and elemental ratios Al/Ca, Li/Ca, Mg/Ca, Sr/Ca, Mn/Ca, and Mn/Sr in this study (Fig. 9).

If silicate minerals contaminate the carbonate fraction leachates, a negative correlation between Li/Ca and  $\delta^7$ Li would be expected (Pogge von Strandmann et al., 2013, 2019). Most samples had Li/Ca ratios ranging 5 and 50  $\mu$  mol/mol, which is similar to reported values in carbonate minerals (Pogge von Strandmann et al., 2019; Kalderon–Asael et al., 2021). Samples with high Li/Ca ratios (n=3, > 150  $\mu$  mol/mol) are omitted which are not shown in the table. Additionally, Al/Ca ratios used as a threshold for silicate mineral leaching varied among different studies, but this study applied the most conservative value (0.3 mmol/mol; Washington et al., 2020; Wei et al., 2023). All samples show Fe/Ca and Mn/Ca ratios below 0.02 mol/mol and 5 mol/mol, respectively, indicating no or minimal contribution of Li from Fe/Mn hydroxides (Pogge von Strandmann et al., 2013; Dellinger et al., 2018;

Cao et al., 2022).

To account for the potential for post-depositional diagenesis in paleo marine carbonates, this study employed Mn/Sr and Sr/Ca ratios as indicators of diagenetic alteration, given that diagenesis could lead to a decrease in Sr/Ca and an increase in Mn/Sr (Korte et al., 2005; Van Geldern et al., 2006). The Mn/Sr ratios of all leachates were lower than the accepted cutoff value (4) mol/mol) of Mesozoic study (Cao et al., 2022). The average Mn/Sr ratio was  $1.79 \pm 1.26$  mol/mol, which is higher than that of modern carbonate rocks (Pogge von Strandmann et al., 2019) but lower than the Middle Paleozoic values (Sproson et al., 2022). Kim et al., (2021) reported the high <sup>87</sup>Sr/<sup>86</sup>Sr values in the Cambrian Formations of the Taebaek group, possibly due to the interaction with the hydrothermal fluid derived from the intrusive granite. Therefore, although the studied Formations are different, it is possible that the samples were influenced by post-depositional process. However, even considering that, 10% of negative lithium isotopic excursion is quite large, and the correlation between Mn/Sr and  $\delta^7$ Li was low, suggesting that the excursion could reflect the changes in paleo-seawater chemical signals. Additional isotopic studies in this section using <sup>87</sup>Sr/<sup>86</sup>Sr are needed for further interpretations. Average Sr/Ca ratio was  $1.46 \pm 0.4$  mmol/mol, which is higher than that of diagenetic carbonate (Korte et al., 2005; Pogge von Strandmann et al., 2019) and there was no correlation between Sr/Ca and

#### $\delta^7$ Li (R<sup>2</sup> $\langle$ 0.2).

In summary, geochemical screening using elemental data indicated that there is a negligible influence of non-carbonate phases and diagenesis on the marine lithium isotopic trend.



Figure 8. Lithium and carbon isotope records from the Duwibong and Jigunsan Formation.  $\delta^{13}C_{carb}$  data from Bang and Lee (2020).



Figure 9. Cross-plot of  $\delta^7$ Li vs. element ratios for the carbonate mineral fractions of the Duwibong and Jigunsan Formation samples.

#### 3–2. Reconstruct seawater $\delta^7$ Li from carbonate rock

In the studied section, the most notable characteristic of the lithium isotope trend is a significant drop of approximately 10% at MDICE (Fig. 10). Subsequently, the value recovered to its previous level. As mentioned in the section 3–1, it has been confirmed that the lithium isotope ratio values were not affected by other processes such as silicate mineral leaching or diagenesis. To interpret the isotopic values of carbonate in terms of paleo-seawater value, it is necessary to examine the primary minerals (Dellinger et al., 2020). It is widely known that during the Ordovician period, there was a widespread occurrence of calcite precipitation in shallow marine environments, rather than aragonite precipitation (Palmer and Wilson, 2004). Moreover, the samples exhibit lower Sr/Ca ratios compared to modern aragonite values (Sr/Ca ~10 mmol/mol, Kalderon-Asael et al., 2021), indicating that the primary minerals of the samples were calcite. Additionally, the low Mg/Ca ratios ( $\langle 100 \text{ mmol/mol} \rangle$  further suggest that the samples were not affected by dolomitization (Dellinger et al., 2020; Cao et al., 2022). Considering these factors, a fractionation factor of 5.5  $\pm$  1.3% is used to convert the isotopic values of calcite to those of seawater. This value was derived from modern bulk carbonate rock samples (Pogge von Strandmann et al., 2021; Cao et al., 2022).

However, it is possible that the lithium isotopic ratios of the samples reflected more of a continental signal rather than a global oceanic one, considering that the Taebaek section was part of the epeiric sea (Bang and Lee, 2020). Nevertheless, a relative sea level was low during the Jigunsan Formation, and it increased to its highest point during the Duwibong Formation (Kwon et al., 2006). Therefore, the 10‰ of lithium isotopic excursion though to be a plausible feature, as the Highstand systems tract of Duwibong Formation has a higher possibility of reflecting global oceanic chemical properties compared to previous Formations. Analysis of other section of the Taebaeksan Basin or records from other continents is needed for a more detailed interpretation.



Figure 10. Seawater  $\delta^7$ Li at the Middle Darriwilian. Gray line indicates  $\delta^{13}$ C (Bang and Lee, 2020). Red band means the exhumation of Taconic arcs at the tropics (Swanson–Hysell and Macdonald, 2017), and gray band means Middle Darriwilian Isotope Carbon Excursion (MDICE). LDNICE: Lower Darriwilian Negative Isotope Carbone Excursion.

#### 3–3. Mass-balance model for lithium isotopes

This study used a probabilistic mass-balance modeling to investigate the possible causes driving the changes in lithium isotope ratios in seawater (Kalderon-Asael et al., 2021). Basically, model utilized a mass balance equation proposed by Li and West, 2014.

$$F_{Riv} + F_{HT} = F_{AOC} + F_{MAAC}$$
 ----- (1)

$$F_{Riv} \times \delta^{7} Li_{Riv} + F_{HT} \times \delta^{7} Li_{HT} = f_{AOC} \times (F_{Riv} + F_{HT}) \times (\delta^{7} Li_{SW} - \Delta^{7} Li_{AOC}) + f_{MAAC} \times (F_{Riv} + F_{HT}) \times (\delta^{7} Li_{SW} - \Delta^{7} Li_{MAAC}) - (2)$$

Equations are composed of fluxes and isotopic ratio for each reservoir (e.g., river, seawater, hydrothermal flux, etc.), which are summarized in Table 3.  $f_{AOC}$  and  $f_{MAAC}$  indicate the proportion (from 0 to 1) between the lithium output through altered oceanic crust (AOC) and marine authigenic alumino–silicate clay (MAAC) ( $f_{AOC} + f_{MAAC} = 1$ ). Lithium transfer in the ocean is known to dependent on temperature (Chan et al., 1992). At high temperatures, Li is rapidly leached from basalt through interactions with hydrothermal fluids, a process known as hydrothermal input flux (referred to as  $F_{HT}$  in this study). However, at low temperatures (< 150 °C), lithium is removed from the seawater and incorporated into the crust, acting as a output flux of lithium from the ocean (referred to as  $f_{AOC}$  in this study). This is also called low–temperature (off–axis) basalt alteration (Chan et al., 1992; Brant et al., 2012).

MAAC is formed during the reverse weathering, which release  $\text{CO}_2$  to the ocean-atmospheric system. At the modern ocean, AOC is dominant outflux (~90%) of lithium which has a cumulative fractionation factor of 13%. MAAC has a higher fractionation factor (20%) but contributes only 10% to the total output flux (Fig. 11; Chan et al., 1992; Misra and Froelich, 2012; Li and West, 2014). Eq. 1 signifies the balance between the input and output of lithium flux within the marine system. Eq. 2 represents a mass-balance equation derived from Eq. 1, incorporating the isotopic compositions of lithium for each reservoir. The riverine lithium isotopic ratio ( $\delta^7 Li_{Riv}$ ) is calculated with  $\delta^7$ Li of primary rock ( $\delta^7$ Li<sub>rock</sub>) and the fractionation factor between water and secondary minerals ( $\Delta^7 Li_{sec}$ ). The model used the modern  $\Delta^7 \text{Li}_{\text{sec}}$  value which is 17‰. Equations below represent the changes in riverine lithium isotope value due to isotopic fractionation during the continental weathering.

$$\delta^7 Li_{Riv} = \delta^7 Li_{rock} - \Delta^7 Li_{sec} \times \ln(f) \quad (3)$$

$$\delta^7 Li_{Riv,0} = \delta^7 Li_{rock} - \Delta^7 Li_{sec} \times \ln(f_0) \quad (4)$$

$$F_{Riv} = F_{Riv,0} \times (1 + (f - f_0)) \quad ----- \quad (5)$$

f and  $f_0$  denote the fraction of lithium that is incorporated from the original rock to secondary minerals in the current time step and the preceding time step, respectively. The lithium flux parameter in Eq. 5 can be obtained by rearranging Eq. 3 and Eq. 4.

The  $\delta^7 \text{Li}_{sw}$  values of the samples ( $\delta^7 \text{Li}_{this study}$ ), determined with a  $5.5 \pm 1.3\%$  carbonate fractionation factor (excluding one outlier in Pogge von Strandmann et al., 2019), were used to make the data boundaries for the model. Basically, the model generated a set of parameters ( $F_{Riv}$ ,  $\delta^7 Li_{Riv}$ ,  $f_{AOC}$ ,  $f_{MAAC}$ ,  $\Delta^7 Li_{AOC}$ ,  $\Delta^7 Li_{MAAC}$ ) within the specified limits (Table 3) and calculated  $\delta^7 \text{Li}_{sw}$  with mentioned equations. If calculated  $\delta^7 \text{Li}_{sw}$  fell within the designated boundaries ( $\delta^7$ Li<sub>this study</sub> ±1.3‰, standard deviation of carbonate fractionation factor), corresponding values for each parameter were plotted on the graph. This process was repeated 1,000 times at each time step (every 1,000 years) using Monte Carlo simulation (Fig. 12). The model results figure demonstrates the possible range of parameters that can satisfy the given lithium isotopic ratio of seawater ( $\delta^7 Li_{this study} \pm 1.3\%$ ) through probabilistic calculations. Although the hydrothermal flux increases with time by up to three times the modern value in this study (Avila et al., 2022), running the model with a constant hydrothermal flux did not alter the overall trend of the results. It should be note that the obtained results do not represent unique solutions, but rather present the parameter values that have a high possibility of explaining the lithium cycle. The steady-state mass balance diagram of lithium based on the model presented in Fig. 11.

Table 3. Parameters used in the mass balance model described in section 4–3. Modern values from Chan et al. (1992), Huh et al. (1998), Misra and Froelich (2012), and Li and West (2014). Model range of the hydrothermal flux from Avila et al. (2022).

Symbol	Description		
$F_{\mathrm{Riv}}$	Riverine input flux		
$\mathbf{F}_{\mathrm{HT}}$	Hydrothermal input flux		
$F_{AOC}$	Altered oceanic crust output flux		
$F_{MAAC}$	Marine authigenic clay formation output flux		
$\delta^7 \mathrm{Li}_{\mathrm{riv},0}$	Riverine lithium isotope value for previous time step		
$\delta^7 \mathrm{Li}_{\mathrm{riv}}$	Riverine lithium isotope value		
$\delta^7 { m Li}_{ m HT}$	Hydrothermal lithium isotope value		
$\delta^7 Li_{SW}$	Seawater lithium isotope value		
$\delta^7 Li_{rock}$	Primary rock lithium isotope value		
$f_{\scriptscriptstyle  m AOC}$	Proportion of lithium removed through altered oceanic crust		
$f_{\scriptscriptstyle \mathrm{MAAC}}$	Proportion of lithium removed through marine authigenic clay		
$\Delta^7 Li_{AOC}$	Difference between seawater and altered oceanic crust due to isotopic fractionation		
$\Delta^7 Li_{MAAC}$	Difference between seawater and marine authigenic clay due to isotopic fractionation		
$\Delta^7 Li_{sec}$	Difference between river and secondary mineral due to isotopic fractionation during continental weathering		

Table 3. (continued).

Symbol	Modern Value	Model range
$F_{Riv}$	$10 \ge 10^9 \text{ mol/yr}$	$2-50 \ge 10^9 \text{ mol/yr}$
$F_{HT}$	5.2 x 10 <sup>9</sup> mol/yr	Increasing logarithmically from modern value to x3 modern value
$F_{AOC}$	13.7 x 10 <sup>9</sup> mol/yr	Equal to input fluxes
$F_{\text{MAAC}}$	1.5 x 10 <sup>9</sup> mol/yr	Equal to input fluxes
$\delta^7 \mathrm{Li}_{\mathrm{riv},0}$		0 – 30 ‰
$\delta^7 \mathrm{Li}_{\mathrm{riv}}$	23‰	0 – 30 ‰
$\delta^7 { m Li}_{ m HT}$	6.3‰	Unchanged
$\delta^7 { m Li}_{ m SW}$	31‰	Analyzed value from this study
$\delta^7 \mathrm{Li}_{\mathrm{rock}}$	1.5‰	Unchanged
$f_{ m AOC}$		0 – 1
$f_{ m MAAC}$		0 - 1
$\Delta^7 Li_{AOC}$	13‰	10-25‰
$\Delta^7 Li_{MAAC}$	20‰	1-25‰
$\Delta^7 Li_{sec}$	17‰	Unchanged



Figure 11. Steady-state mass balance of lithium cycle. (A) modern ocean (Chan et al., 1992; Huh et al., 1998; Misra and Froelich, 2012; Li and West, 2014) and (B) the ocean during the Middle Darriwilian based on the model results. Note that these are not unique solutions but show the changes of each lithium reservoir.



Figure 12. Density heat map of lithium isotope mass-balance results (modified from Kalderon-Asael et al., 2021). Each panel indicates the density of the parameters that successfully match the designated lithium isotopic ratio range of seawater. A detailed explanation of each parameter is in the main text. As the color goes from blue to black, the lighter color, indicates the higher counts per bin.

#### 3–4. Weathering regime during the Middle Darriwilian

Based on the model results, the lithium isotope excursion of ~10‰ at the Middle Darriwilian may require significant changes in weathering regime and global lithium cycle relative to modern Earth (Fig. 11). The most possible lithium cycle parameters that can explain the Darriwilian seawater lithium isotope data are low riverine  $\delta^7$ Li (~6‰) and high marine authigenic clay formation (~90%) with muted isotope fractionation ( $\Delta^7$ Li<sub>MAAC</sub>=~3.5‰). These are very different value from the modern  $\delta^7$ Li<sub>Riv</sub> (~23‰), F<sub>MAAC</sub> (~10%), and  $\Delta^7$ Li<sub>MAAC</sub> (~20‰).

A Taconic orogeny, which was a large arc-continent collision started about 495 Ma in Iapetus Ocean and the Appalachian margin of Laurentia, has been suggested to be associated with Ordovician cooling (Young et al., 2009; Jagoutz et al., 2016). The Taconic arcs which migrated towards the equator, reached the tropics (0°–10°S) during the Early Ordovician and began to undergo exhumation from 465 Ma (Fig. 1; Swanson–Hysell and Macdonald, 2017). This process led to an increase in weatherability due to the exposure of massive fresh mafic rocks to the tropical climate. The dissolution rates of minerals decrease in order of olivine > Ca–plagiocalse >pyroxene > Na–plagioclase > K–feldspar > muscovite > quartz. Basalts, composed mainly of plagioclase, pyroxene, olivine, and glass, undergo rapid and highly congruent weathering due to their higher dissolution rates compared to K-feldspar and quartz (Kump et al., 2000). Increased weathering during the Middle Ordovician was suggested by previous research using isotopic weathering proxies such as strontium (<sup>87</sup>Sr/<sup>86</sup>Sr) (Young et al., 2009; Avila et al., 2022) and neodymium (143Nd/144Nd) (Swanson-Hysell and Macdonald, 2017; Conwell et al., 2022). The increased exposure of weatherable rock resulted in congruent weathering (i.e., few secondary minerals formed), which subsequently reduced riverine lithium isotopic ratio. Although the mechanisms of the modern Earth may not have applied in the same way during the Paleozoic, the relationship between weathering regime and the lithium isotopes has been demonstrated in previous research spanning from the Paleozoic (Pogge von Strandmann et al., 2017; Sun et al., 2018; Wang et al., 2021; Cao et al., 2022) to the Mesozoic (Pogge von Strandmann et al., 2013; Lechler et al., 2015) and Cenozoic (Misra and Froelich, 2012; Pogge von Strandmann et al., 2021). Therefore, the enhanced weathering resulting from the intense Taconic orogeny and volcanic activity in the Middle Darriwilian likely altered the weathering regime towards congruent weathering, potentially leading to a reduce in the seawater lithium isotopic ratio. This mechanism - decreased riverine lithium isotopic ratio due to exposure of fresh rocks - is also observed in research on the Permian-Triassic boundary, which suggested ~12‰ lithium isotope negative excursion resulting from large igneous province, the Siberian Trap (Sun et al., 2018).

The model results, however, indicate that not only the changes in the input flux of lithium but also the output flux, which includes processes such as authigenic clay formation or alteration of oceanic crust, contributed to the lithium isotopic excursion. Silica uptake through biosilicification during the Ordovician is a 'radiolarian and sponge control', relative to a 'diatom control' of modern ocean. Since the radiolarian and sponge are less efficient silicifiers compared to diatoms, the silica uptake rate would have been lower than that of the modern ocean (Conley et al., 2017). Additionally, the increased in continental weathering may have supplied more amorphous aluminosilicate and cations (e.g., Mg<sup>2+</sup>, K<sup>+</sup>) to the seafloor, leading to the abundant and rapid formation of marine authigenic clay (Dunlea et al., 2017). If massive clay covered ridge flanks, it would have resulted in a decrease of lithium output flux through the alteration of oceanic basalts (Li et al., 2014). All these processes subsequently contributed to the muted isotopic fractionation of MAAC and AOC (Kalderon-Asael et al., 2021; Cao et al., 2022). The model results also indicate that approximately 90% of  $f_{\rm MAAC}$  with low  $\Delta^7 {\rm Li}_{\rm MAAC}$ (~3.5‰) and  $\Delta^7 \text{Li}_{AOC}$  (~10‰) relative to the modern ocean. Therefore, this study suggests that there was a possibility of reverse weathering during the Middle Ordovician. A reverse weathering during the Permian-Triassic boundary also reported in shallow platform carbonate near the North China Block (Cao et al., 2022), which indicates that the  $\delta^7$ Li<sub>sw</sub> recorded in carbonate possible to reflect the global signal. However, this study is unable to determine

whether reverse weathering was predominantly active in a specific ocean or if it occurred in all oceans. Further lithium isotopic study conducted in different continents are needed to gain more accurate understanding of the weathering cycle in Darriwilian.

Carbon dioxide released into the atmosphere as a result of reverse weathering could have potentially influenced the perturbation of sea surface temperature during the Middle Ordovician (Fig. 1). This process could also possibly explain the increased pCO<sub>2</sub> calculated in the GEOCARBSURF model or the brief warming phase proposed by previous studies (Fig. 1; Kidder et al., 2010; Kidder and Tomescu, 2016). The recovery of  $\delta^7 \text{Li}_{sw}$  values following the lithium isotope excursion indicates a shift in weathering regime of the river back to the incongruent weathering. When the river become oversaturated because of the active congruent weathering, the secondary minerals are formed in the modern Earth. This process subsequently leads to an increase in the riverine  $\delta^7$ Li (Pogge von Strandmann and Henderson, 2015). This mechanism has also been applied in a study on the Early Mesozoic (Lechler et al., 2015), where the excursion recovered in short timescale (~100 kyr). This suggests that the rapid recovery of lithium isotopic excursion through the oversaturation of river can be applicable not only to the modern but also to older timescale as well. Additionally, it is possible that the residence time of lithium was relatively short during the Darriwilian due to the higher

seafloor spreading rate compared to the modern ocean (Avila et al., 2022). Therefore, the sharp excursion of  $\delta^7 \text{Li}_{sw}$  observed in the studied section can be explained by the changes in the weathering regime between congruent and incongruent weathering.

#### 3-5. Conclusion

In this study, the Middle Ordovician carbonate rocks of the Taebaeksan basin have been studied for lithium isotopes. The lithium isotope ratio of seawater, which exhibited approximately 20-25‰ during the Early to Middle Darriwilian, showed a negative excursion of 10% during the Middle to Late Darriwilian. The stochastic mass-balance model suggests that the lithium isotope excursion was probably caused by the increased exposure of fresh mafic rock resulting from the exhumation of Taconic arcs in tropics and active volcanism. The estimated riverine lithium isotopic ratio of that time is estimated to be around 6‰, indicating congruent weathering. However, the model also suggests an increased formation of marine authigenic clay with muted fractionation between seawater, indicating the reverse weathering. This study provides additional evidence for increased weathering during the Darriwilian and proposes that reverse weathering may have contributed to the slowdown of Ordovician cooling.

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### 국문초록

오르도비스기는 고생대에서 가장 뚜렷한 환경 변화를 보이는 시기 중 하나로, 초기의 따뜻했던 기후에서 후기의 빙하기까지 급격한 온도 변화가 특징적이다. 이러한 온도 하강의 원인으로 오르도비스기 중기부터 활발했던 지각운동과 화산활동 등으로 인해 증가한 규산염 광물의 풍화가 제시되고 있다. 규산염 광물의 풍화는 대기중 이산화탄소를 소모하여 장기적인 기후 변화를 조절하는 주요 기작 중 하나이며, 리튬 동위원소는 이러한 규산염 광물의 풍화 지시자로서 많은 고환경 연구에서 활용되고 있다. 본 학위 논문에서는 우리나라 태백 분지의 중기 오르도비스기 탄산염암을 이용한 리튬 동위원소 연구를 통해 오르도비스기 환경 변화에 대해 해석하는 것을 목표로 하고있다. 이 연구에서는 조선누층군의 두위봉층, 직운산층을 대상으로 불용해성 자여물 함량이 서로 다른 탄산염 암석으로부터 효과적으로 리튬 동위원소를 분석할 수 있는 방법을 시험하였다. 규산염 광물에 의하 오염을 방지하면서 동시에 미량원소인 리튬을 최대한 확보할 수 있는 용해법을 확인하였으며 칼슘과 소듐의 함량이 높은 시료의 용해액에서 효율적으로 리튬을 분리해내는 컬럼 분리법을 확립하였다. 이를 통해 다리윌리안(Darriwilian) 시기 탄산염암에서 당시 해수의 리튞 동위원소비를 복원할 수 있었다. 중기-후기 다리윌리안 시기에서 리튬 동위원소 비 값의 큰 감소폭(10%)이 나타났으며, 이를 바탕으로 한 질량 균형 모델(mass-balance model)을 통해 당시 활발했던 대륙 풍화와 함께 동반된 역풍화(reverse weathering) 작용을 가설로 제시하였다.

**주요어 :** 리튬 동위원소, 풍화, 기후변화, 오르도비스기, 해양 탄산염암, Taconic orogeny **학 번 :** 2021-29722

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