



Boron Isotopic Systematics and Its Significance in Natural Processes: An Overview

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ABSTRACT

In recent years, interest in boron has expanded from microscopic to macroscopic levels, and several studies have contributed to understanding the role of boron in earth and natural processes. The boron isotopic composition provides a unique perspective into the crystallization process in granites, pegmatites, and temperature variations. Boron isotopic studies have been used as a tracer to understand geothermal systems, rivers, rock processes, reconstruction of pH and pCO₂, groundwater pollution, and further help in understanding the changes which have occurred in oceans through geological time. Furthermore, boron isotopes have also been utilized to understand the genesis of ores and understanding subduction processes and as a tracer in groundwater pollution. In plants, it acts as a micronutrient. However, its deficiency and the excessive amount may inhibit the growth of plants, bacteria, and fungi and may also affect the soil and aquatic microflora. Boron maintains and regulates several metabolic pathways, and its quantity above a certain level may prove detrimental to the environment. This overview explains boron isotope variations and their implications in earth sciences and natural processes.

INTRODUCTION

Radiogenic and stable isotopes have been extensively utilized for understanding various phenomena, such as earth systems, paleoclimate, ecology, the hydrologic cycle, biology, and forensic investigations. Over the past few decades, the application of stable isotopes has grown considerably, each with its unique potential for illuminating particular processes (Rasbury & Hemming 2017). Stable isotopes of carbon (¹²C and ¹³C), nitrogen (¹⁴N and ¹⁵N), and oxygen (¹⁶O, ¹⁷O, ¹⁸O) are valuable for retracing oceanic changes and past climatic conditions (Tiwari et al. 2015). Sulfur has four stable isotopes (32S, 33S, 34S, 36S), which are found in rivers, the atmosphere, lakes, and groundwater. The sulfur compounds have been tracked using stable isotopes of sulfate. To understand the sulfur cycle of marine sediments in both the present and past, stable isotopes are a crucial tool (Thode 1963, Jørgensen 2021). Silicon has three stable isotopes (²⁸Si, ²⁹Si, ³⁰Si) and silicon isotope ratios can be used to derive paleoenvironmental information, and in phytoliths may be used in archaeological studies (Leng et al. 2009).

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In 1808, Joseph Louis Gay-Lussac, Humphry Davy, and Louis Jacques Thénard were the first to isolate boron by heating boron oxide with potassium metal (Davy 1808, Gay-Lussac & Thénard 1808). However, the first measurements of boron isotopes in natural materials were made in 1961 (McMullen et al. 1961). Boron with atomic number 5 has an extremely high affinity for oxygen (Lemarchand & Gaillardet 2005). When combined with oxygen, boron invariably forms trigonal and tetrahedral complexes, and boron is primarily found in weakly alkaline as the trigonal B(OH)₃ complex but in strongly alkaline conditions as the tetragonal B(OH)₄ (Baes & Mesmer 1976). Over the past years, many investigations have been conducted to determine whether boron isotopes in carbonates may be used as a proxy for paleo-ocean pH. However, for such usage of boron isotopes, both as sources or as a process proxy, it is necessary to thoroughly characterize the physicochemical processes that govern boron incorporation in carbonates and to quantify the corresponding chemical and isotopic fractionation (Hemming & Hanson 1992, Lemarchand et al. 2002, Lemarchand & Gaillardet 2005). Material science, energy research, and electronics boron have a wide range of applications in chemistry. In medical chemistry, boron is either used as an atom or cluster and in recent days, boron has been used in antibacterial, antifungal, and antiseptic

treatments (Leśnikowski 2016). Boron compounds are employed in nuclear technology, rocket engines as fuel, the manufacture of heat-resistant materials, and high-resistant polymers (Yilmaz et al. 2008). Apart from this, boron isotopes have been used as a geochemical tracer, and their major applications are in the field of ore genesis, sedimentary environments, crustal mantle evolution, subduction-related processes, and cosmochemistry (Foster et al. 2018, Liu & Chaussidon 2018, Marschall & Foster 2018). Boron is important for the assimilation of nitrogen in plants and the growth of roots in nitrogen-fixing plants (Bolaños et al. 1994, Camacho-Cristóbal et al. 2005), boron isotopic composition provides a better understanding of the rate of ocean acidification during periods of warming events (Penman et al. 2014). In this study, we present a short review of the application and significance of boron isotopic systematics for understanding its importance in natural processes.

BORON GEOCHEMISTRY AND GEOCHEMICAL CYCLE

Since 1961, when the boron isotopes were first measured, several research articles have been published on boron isotope geochemistry and its analytical techniques (Spivack & Edmond 1987, Barth 1993, Aggarwal & Palmer 1995, Marschall 2018, Trumbull & Slack 2018, Wang et al. 2019). Boron is a lithophile element having two stable isotopes ^{10}B and ^{11}B , with an abundance of ~20% and ~80%, respectively (Kakihana et al. 1977, Barth 1993, Palmer & Swihart 1996, Foster et al. 2018). The boron isotopes are generally expressed as $\delta^{11}\text{B}$ as,

$$\delta^{11}\text{B}(\text{‰}) = \left[\frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}} - (^{11}\text{B}/^{10}\text{B})_{\text{standard}}}{(^{11}\text{B}/^{10}\text{B})_{\text{standard}}} - 1 \right] \times 10^3$$

And the $^{11}\text{B}/^{10}\text{B}_{\text{standard}}$ is the boron isotopic composition of the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 951 boric acid, which is used in most of the studies, and the value of $(^{11}\text{B}/^{10}\text{B})_{\text{standard}} = 4.04367$ (Catanzaro 1970). Other isotopic reference materials for the isotope ratio of boron are NIST-SRM-952, IAEA-B1, IAEA-B2, and IAEA-B4 (Aggarwal & You 2016). There are over 250 known minerals that contain boron, the most prevalent of which are calcium, sodium, and magnesium salts (Helvacı 2017). Commercially important minerals with boron contents are represented in (Fig. 1). Boron is also found in skarns, calcareous sediments, metasediments, metamorphic minerals, mafic and ultramafic igneous rocks and minerals (Henry & Dutrow 1996). The concentration of boron (ppm) in different rocks is represented in Fig. 2 (a-c).

A significant flux of gaseous B drives the atmospheric component of the global B cycle in the form of boric acid (H_3BO_3) derived from sea salt aerosols (Park & Schlesinger 2002). Exchanges primarily determine the oceanic boron fluxes with the atmosphere; influx and outflux occur mostly due to direct precipitation, dry deposition, and gaseous absorption and outflux through seawater aerosol production (Carrano et al. 2009). By delivering boron from natural and anthropogenic sources via riverine transport, the hydrosphere is the second largest flux to the oceans (Carrano et al. 2009).

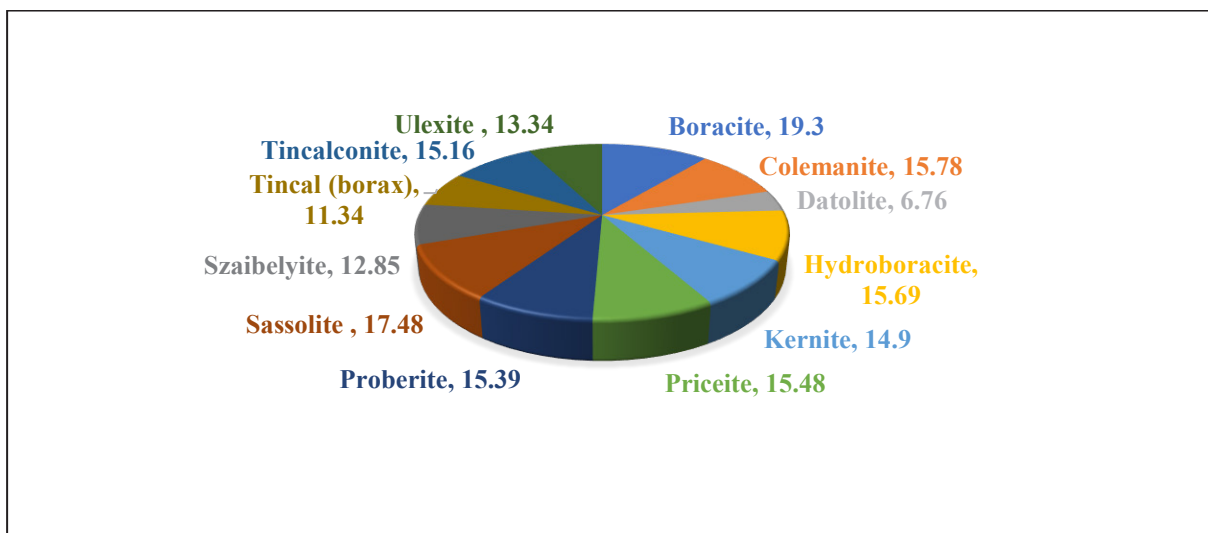
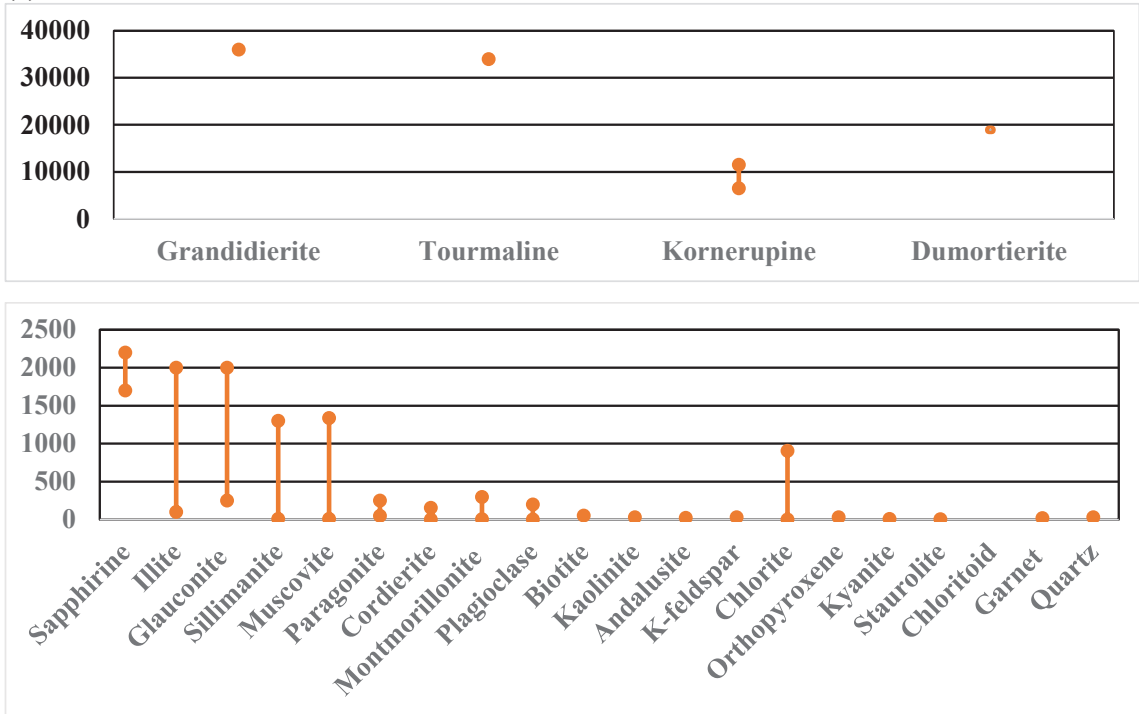


Fig. 1: Percentage of boron in commercially important boron-containing minerals Data source: Lyday (2000).

(a)



(b)

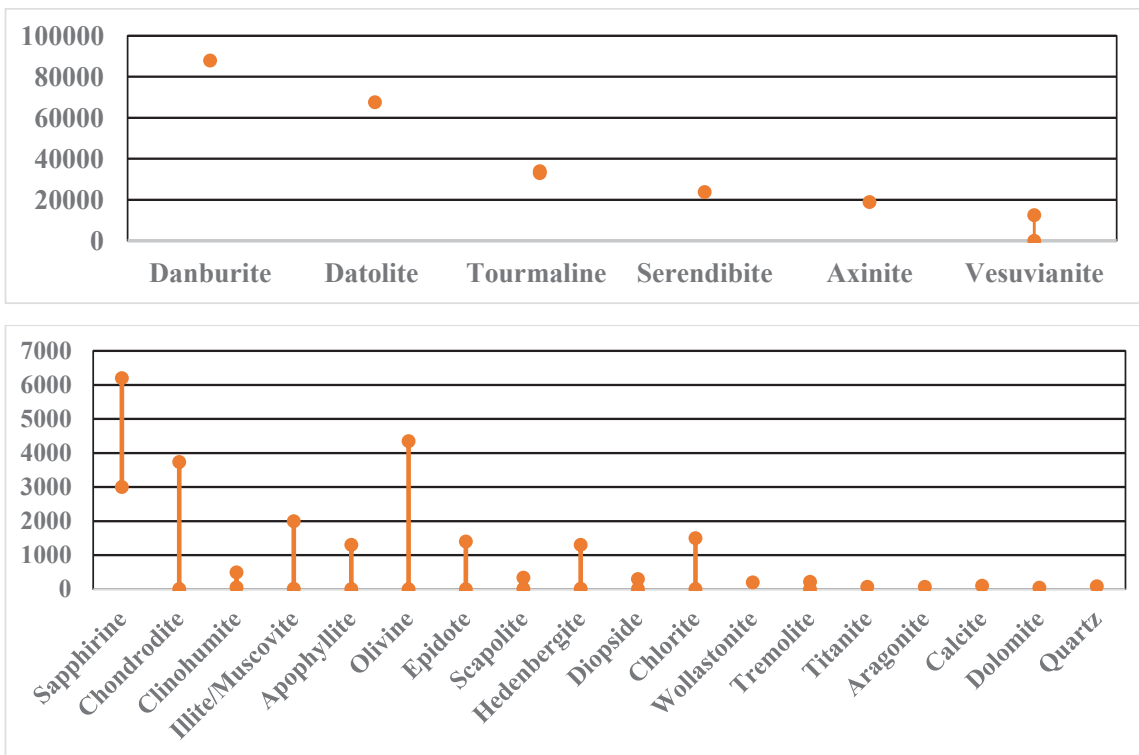


Fig. Cont....

(c)

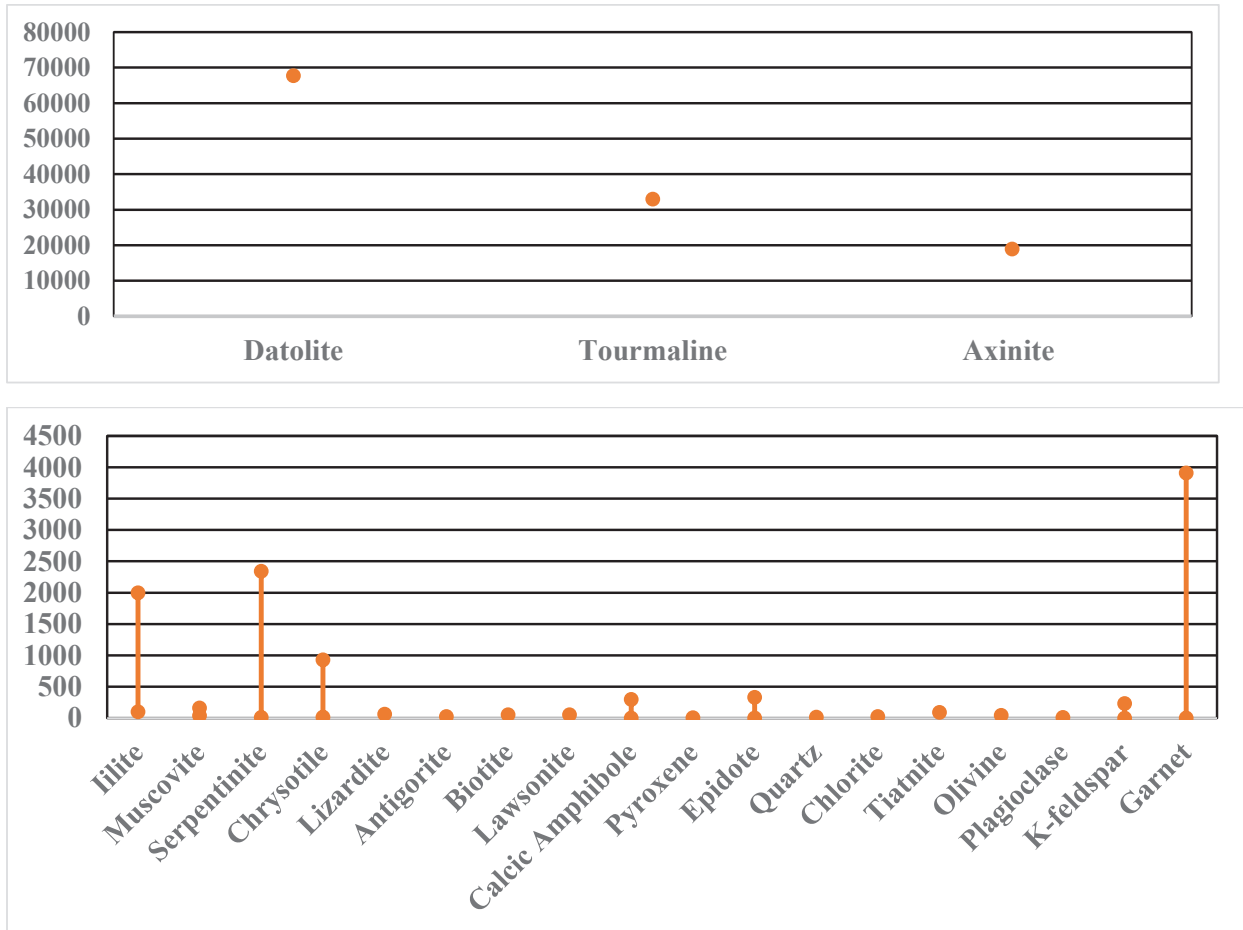


Fig. 2: Range of boron (ppm) in minerals (a) pelitic and psammitic sedimentary and metasedimentary rocks (b) calcareous sediments, metasediments and skarns (c) mafic and ultramafic igneous and metamorphic rocks. Data sources: Henry & Dutrow (1996).

METHODS FOR BORON ISOTOPE DETERMINATION

Mass spectrometry is one of the best analytical techniques that possess unparalleled sensitivity, detecting range, speed, and a plethora of uses, and it also has played a decisive role in understanding the geological processes in the past decades (Jocelyn Paré & Yaylayan 1997, Hoffmann & Stroobant 2007, Joshi et al. 2021, Banerji et al. 2022).

For boron isotope analysis, mass spectrometry is used in various ways, which include: Multi-collector and Inductively coupled Plasma Mass spectrometry (MC-ICPMS) which is relatively fast with high precision and requires a small sample size. However, it is a bit expensive (Aggarwal et al. 2003). Thermal ionization mass spectrometry (TIMS), including negative ion thermal ionization (N-TIMS), has

a higher analytical speed and requires minimal sample preparation. However, limited precision is the disadvantage of this technique (Hemming & Hanson 1994). The advantage of using Positive ionization mass spectrometry (P-TIMS) is that it has a high level of accuracy, whereas the drawback is that the sample should be pure (Aggarwal & Palmer 1995). Secondary-ion mass spectrometry (SIMS) is used in the micro-analysis of boron in various solid rock samples and does not require sample preparation (Chaussidon et al. 1997). Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICPMS) has the benefit of high spatial resolution (Fietzke et al. 2010). A Triple quadrupole-based ICP system (ICP-QQQ) has the advantage of high abundance sensitivity and elimination of interferences (Fernández et al. 2015). High-resolution inductively coupled plasma mass spectrometry (HR-ICPMS) is responsible for fast analysis (Gäbler & Bahr 1999).

BORON ISOTOPES IN THE HIMALAYAN REGION

Geothermal Systems and Rivers

In the Himalayas, Steller et al. (2019) analyzed the boron isotopic and elemental concentrations from diatom-rich sediments of the Puga geothermal system in India and reported $\delta^{11}\text{B} = -41.0\text{‰}$. In Tibetan, geothermal areas $\delta^{11}\text{B}$ values vary from (-16.0 to 13.1‰) and indicate non-marine origin, whereas, in Tengchong geothermal areas in Yunnan province, $\delta^{11}\text{B}$ varies from (-11.8 to 4.2‰) (Lü et al. 2014). The boron isotopic variations in the geothermal system are plotted in Fig. 3.

In the Himalayas, the isotopic composition of the rivers varies greatly up to $\sim 35 \delta^{11}\text{B} \text{‰}$. The huge difference seen in the boron isotopic composition of Brahmaputra and Ganga may be due to the variation in the chemical composition of bedrock and silicate alteration (Rose-Koga et al. 2000). The $\delta^{11}\text{B} \text{‰}$ concentrations in Himalayan rivers are highly variable. Range from -7‰ to 29.4‰ (Rose-Koga et al. 2000) with variable major ion concentrations have differing inputs from various weathered lithologies, including evaporites, carbonates, and silicates. The boron isotopic variation of different river systems is mentioned in Fig. 4.

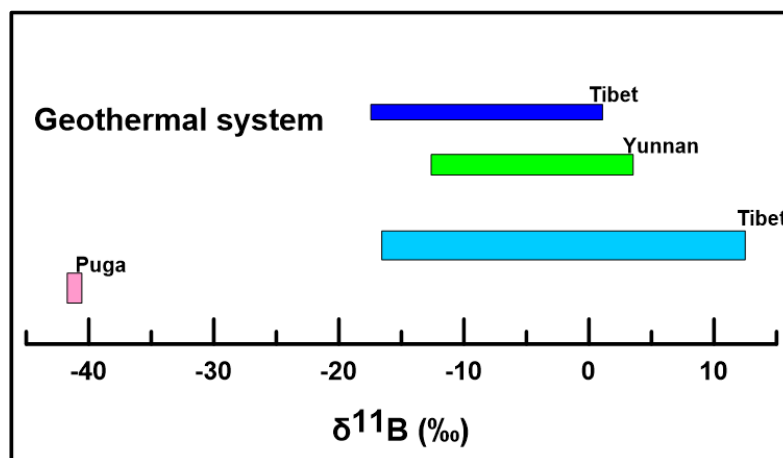


Fig. 3: Boron isotopic compositions in the geothermal system. Data sources Steller et al. (2019), Lü et al. (2014), Zhang et al. (2015).

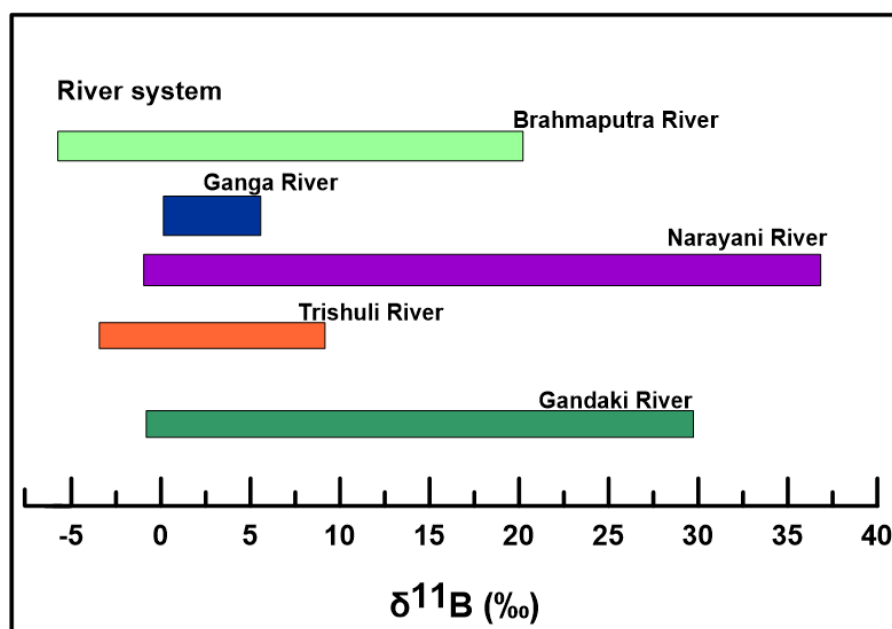


Fig. 4: Boron isotopic compositions of the river system. Data sources (Rose-Koga et al. 2000).

Igneous and Metamorphic Rocks

In the Himalayas, numerous studies on tourmaline boron isotopic and chemical compositions have been used to elucidate the genesis of leucogranite or pegmatites (Yang et al. 2015, Gou et al. 2017, Hu et al. 2018, Zhou et al. 2019, Cheng et al. 2021, Srivastava et al. 2022). In igneous petrology, boron plays an important role as a flux for silicate melts, where it lowers the solidus and liquidus temperatures and the viscosity of the melts (Dingwell 1992, London et al. 2018). In peraluminous granites, boron isotopic composition is determined by the isotopic nature of their source composition (Trumbull et al. 2008). Tourmaline is the most common borosilicate mineral in crustal rocks

analyzed for boron isotopic composition (Samson & Sinclair 1992, Trumbull et al. 2008, Marschall & Jiang 2011, Yang & Jiang 2012). Tourmaline is ubiquitous in igneous and metamorphic rocks in the Himalayas (Henry & Guidotti 1985, Henry & Dutrow 2018), and as it crystallizes at the late stage of magmatic evolution and its abundance in leucogranites makes it an appropriate tracer of source rocks and its genesis (London 1996, Kasemann et al. 2000, Van Hinsberg et al. 2011).

Some researchers inferred that tourmaline-bearing leucogranites are generated by dehydration melting of metasedimentary rocks having either muscovite, biotite, or both (Le Fort et al. 1987, Harris & Massey 1994, Harris et

Table 1: Boron isotopic compositions in the Himalayan region in different systems.

Area	Sample Description	$\delta^{11}\text{B}$ (‰)	References
Puga	Geothermal system	-41.0‰	Steller et al. (2019)
Tibet	Geothermal system	-16.0 to 13.1‰	Lü et al. (2014)
Yunnan	Tengchong Geothermal	-11.8 to 4.2‰	
Tibet	Geothermal waters	-16.57 to 0.52‰	Zhang et al. (2015)
Gandaki River Basin	Riverine	-1.7 to 29.8‰	Rose et al. (2000)
Trishuli River Basin	Riverine	-3.1 to 8.5‰	
Narayani River Basin	Riverine	-1.6 to 36.9‰	
Ganga	Riverine	0.1 to 5.1‰	
Brahmaputra	Riverine	-5.7 to 21.0‰	
Nyalam	Leucogranites (mineral: tourmaline)	-15.1‰ to -14.4‰	Yang et al. (2015)
Conadong, South Tibet	Leucogranites (mineral: tourmaline)	-9.78 to -8.53‰	Zhou et al. (2019)
	Pegmatite	-14.02 to -11.83‰	
LHS, Central Himalayas	Chlorite schist (mineral: tourmaline)	-17.8 ‰ to -13.9‰	Liu et al. (2022)
Main Central Thrust Zone, Central Himalayas	Quartz tourmaline (mineral: tourmaline)	-18.3 to -12.8‰	
GHS, Central Himalayas	Leucogranites (mineral: tourmaline)	-17.2 to -8.2‰	
GHS, Central Himalayas	Leucosomes (mineral: tourmaline)	-11.8 to -10.7‰	
GHS, Central Himalayas	Garnet Amphibolite (mineral: tourmaline)	-16.9 to -13.6‰	
GHS, Central Himalayas	Mica Schist (mineral: muscovite)	-22.4 to -15.4‰	
GHS, Central Himalayas	Leucogranites (mineral: muscovite)	-23.3 to -17.2‰	
Himalayas	Leucogranites (mineral: tourmaline)	-7 to -13‰	Cheng et al. (2021)
Sikkim Himalayas	Pegmatite (mineral: tourmaline)	-13.83 to -12.78‰	Srivastava et al. (2022)
Ama Drime gneiss	Ama Drime Gneiss (mineral: tourmaline)	-17.6 to -14.3‰	Hu et al. (2018)
Majba	Leucogranite (mineral: tourmaline)	-18.9 to -17.4‰	
Quedang	Metapelite (mineral: tourmaline)	-15.3 to -12.5‰	
Malaysian	Leucogranite (mineral: tourmaline)	-16.2 to -8.0‰	
Yardo	Leucogranite (mineral: tourmaline)	-8.4 to -5.4‰	
Conadong Leucogranite	Two-mica granites,	-15.80 to -13.25‰	Fan et al. (2021)
	Muscovite Leucogranite, Biotite -rich granite	-15.38 to -11.90‰	
	Biotite-rich granite (whole rock)	-11.97 to -9.00‰	

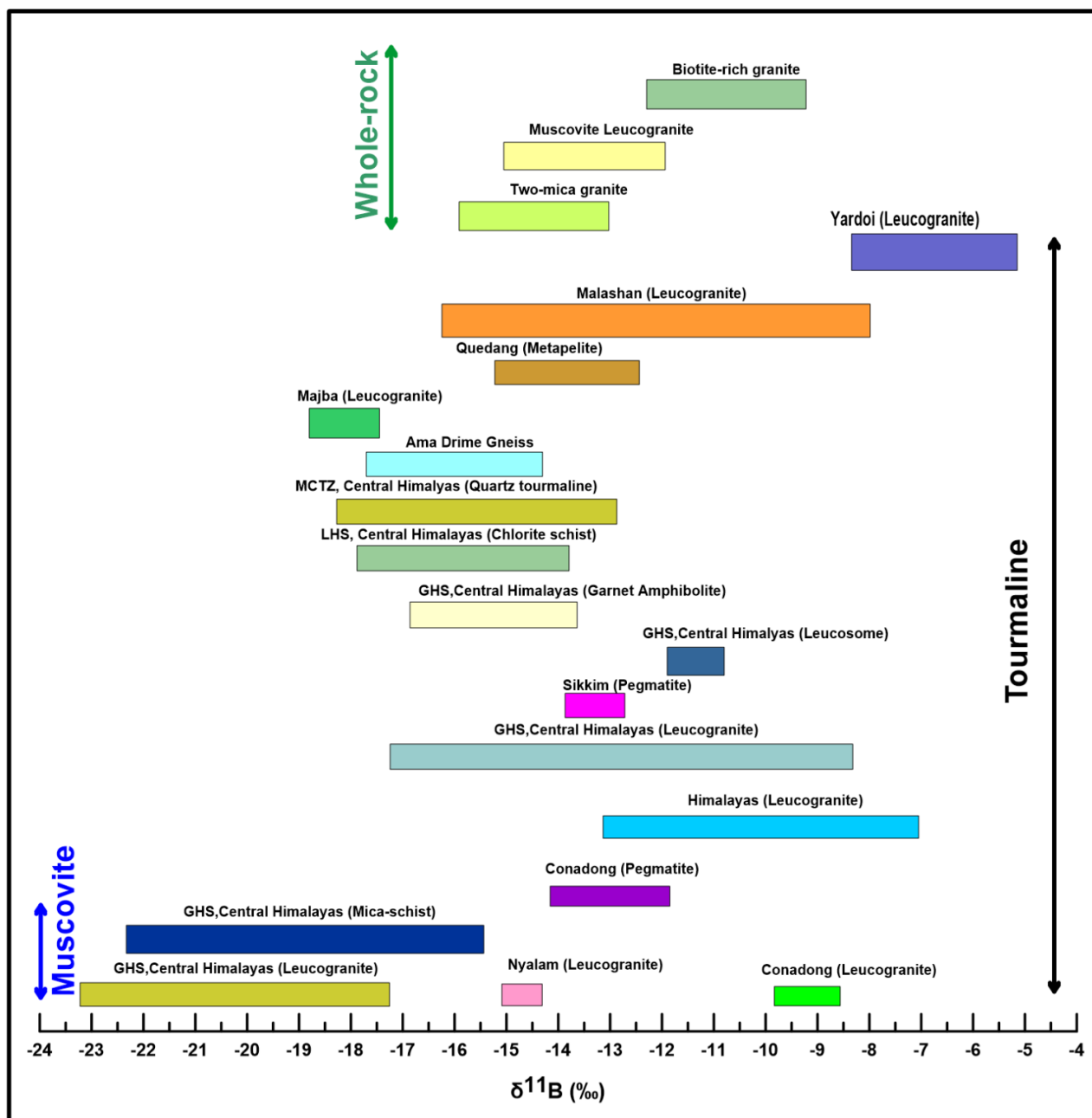


Fig. 5: Boron isotopic composition of tourmaline, muscovite, and whole rock boron isotopic composition in Igneous and metamorphic rocks from the Himalayan region. Data Sources Yang et al. (2015), Zhou et al. (2019), Liu et al. (2022), Cheng et al. (2021), Srivastava et al. (2022), Hu et al. (2018) Fan et al. (2021).

al. 1995, Guo & Wilson 2012) while a few researchers have suggested that Himalayan leucogranites are crystallized from highly fractionated magma (Wu et al. 2015, Zheng et al. 2016). Besides tourmaline, muscovite is also a major boron-bearing mineral in metasedimentary rocks and granites (Nakano & Nakamura 2001, Cheng et al. 2021, Liu et al. 2022). The

boron isotopic compositions of tourmaline and muscovite are represented in Fig. 5. Fan et al. (2021) performed whole rock-boron isotopic compositions for two-mica granite, muscovite leucogranite and biotite granite from the Conadong region represented in Fig. 5. The boron isotopic composition of the Himalayan region in different systems is compiled in Table 1.

BORON ISOTOPES IN EARTH SCIENCES AND BIOLOGICAL PROCESSES

Understanding Subduction Zone Processes

In magmatic processes, boron behaves as an incompatible trace element and is a highly fluid mobile; thus, it acts as a perfect tracer for the role and motion of water during subduction (Palmer 2017). In high-pressure metamorphic rocks, like mantle wedge peridotites boron isotope concentrations have been employed as markers for mass fluxes, mass transfer between the slab and overlying mantle, and element recycling during subduction (Palmer & Helvacı 1997, Peacock & Hervig 1999, Tonarini et al. 2001, Savov et al. 2007, Pabst et al. 2011). The abundance of boron and the isotopic compositions of fluids and lavas from subduction zone environments offer a great deal of information for understanding the mass flux along the present-day convergent boundaries of the earth (Bebout & Nakamura 2003). During serpentinization, boron is readily taken up into serpentine phyllosilicates (Pabst et al. 2011). The abyssal peridotites react with hydrothermal fluids and become serpentinized, due to which serpentine, amphibole, magnesite, and talc are formed due to the reaction of pyroxenes and olivine which are found along spreading ridges and transform faults (De Hoog & Savov 2018). Boron is significantly enriched and isotopically fractionated in subducted sediments, altered oceanic crust, and serpentinized mantle. These materials are among the most effective tools for studying fluid-mediated processes at subduction zones, and the partitioning of boron is independent of melt composition between hydrous fluids and melts (Hervig et al. 2001, De Hoog & Savov 2018). The boron from micas is either purged from the subduction-zone rocks beneath forearcs. Volcanic arcs by metamorphic fluids or is sequestered by developing tourmaline, where the boron can be entrained to even greater depths (Bebout & Nakamura 2003). The deep mantle may recycle a small amount of subducted boron even if ninety percent of subducted boron is recycled back to the surface, and boron has also been used as a tracer to probe into crustal carbonate degassing in volcanic arcs (Savov et al. 2007, Deegan et al. 2016, De Hoog & Savov 2018). In arc-related and granitic magmas, the isotope ratios of boron are sensitive indicators of subduction slab components and fluid-mediated mass transfer during subduction (Palmer 1991, Scambelluri & Tonarini 2012). The amount of boron and its isotopic composition in the altered oceanic crust are greatly influenced by the temperature and water-to-rock ratio at the time of alteration (Ishikawa & Nakamura 1992).

Mineralization

The boron sources and the fluids involved in bentonitization

in marine and non-marine environments are better understood because of the mineralogical, chemical, and isotopic analyses of smectites with variable interlayer cation occupancies from bentonite deposits in different depositional environments (Köster et al. 2019). It is seen that the boron isotope geochemistry of smectites can be used to shed light on the fluids responsible for the development of clay mineral deposits. It also offers a lot of potential for tracing fluids in other environments with authigenic clay minerals, like sedimentary basins and surfaces of crystalline rocks, as well as in artificial settings, like storage facilities for radioactive waste that is very active (Köster et al. 2019). The boron isotopes in tourmaline are useful in depicting sources (Spivack & Edmond 1987) and explicating the fluid processes (Palmer & Swihart 1996; Marschall et al. 2008). The ore-forming processes of tourmaline have been better constrained by mineralogical, chemical, and boron isotopic analyses and provide important insights on petrologic, fluid or magma origin, the evolution of genesis of ore deposits (Marschall & Jiang 2011, Trumbull et al. 2011, Yang & Jiang 2012). The composition of the boron sources mostly determines the $\delta^{11}\text{B}$ value of boron (Palmer & Slack 1989) and the variation in boron isotopes of tourmaline from large sulfide sources also depends on the composition of parent rocks (Jiang 2001). The boron isotopic fingerprints of fluids originating from magmatic-hydrothermal and basin evaporitic sources are very different, and tourmaline in hydrothermal deposits is a great recorder of fluid sources due to its refractory properties. Hence tourmaline boron isotopes can be used as the sources of fluids in iron-oxide copper gold (IOCG) (Xavier et al. 2008, Pal et al. 2010, Van Hinsberg et al. 2011). The use of boron isotopes in investigating mineral resources is a relatively new advancement, and tourmaline is the major mineral studied, particularly in large sulfide deposits and hydrothermal W-Sn associated with granites (Slack 1996).

Erosion and Weathering

The rivers are the main source of boron input into the ocean, while clay minerals are the principal boron sink, and this makes boron, in addition to its ability to trace the pH and ancient seawater, a particularly strong tracer of the weathering/erosion balance of terrestrial surfaces (Gaillardet & Lemarchand 2018). The partitioning of boron into the soluble and solid phases occurs when water and rock interact and can be included in secondary phases like clay minerals and amorphous iron oxyhydroxides, which are liberated into the hydrosphere by the dissolution of primary minerals (Ercolani et al. 2019). It has been suggested that isotopic fractionations occurring during the adsorption of riverine-dissolved boron onto detrital clays are the causes of this

significant $\delta^{11}\text{B}$ enrichment of saltwater relative to ordinary continental crust (Palmer et al. 1987).

Depositional Environment

Depositional environment and secondary enrichments affect the B content of coals from sedimentary basins, and boron has been utilized to estimate the paleoenvironments of coal reserves (Williams & Hervig 2004). Using marine and non-marine evaporite minerals, boron isotopes are useful geochemical tracers to distinguish depositional environments (Bassett 1990). The mineralogy of borates, as well as the pH of the brine borate precipitation, affect the $\delta^{11}\text{B}$ values of borates in the same depositional environment, and the minerals with the same geologic origin are observed to have decreasing $^{11}\text{B}/^{10}\text{B}$ values in the following order Na borates, Na/Ca borate and Ca borates (Oi et al. 1989, Palmer & Helvacı 1997). Apart from this, loess and paleosols also contain clay minerals, and these minerals adsorb boron resulting in boron fractionation (Zhao et al. 2003)

Paleo pH, Paleo Salinity and Paleo CO_2

It is crucial to understand the ranges of pH variations at various time scales to properly comprehend the severity of the environmental issues posed by ocean acidification, and this information is necessary to determine the pH ranges at which marine creatures may survive and further our understanding of how the oceans are absorbing atmospheric CO_2 through its many mechanisms (Pelejero & Calvo 2008). The boron isotope fractionation is a function of pH (Hemming & Hanson 1992, Sanyal et al. 1995, Lécuyer et al. 2002), and the boron isotope ratio of marine biogenic carbonates can be used to reconstruct pH and pCO_2 of seawater, as well as atmospheric CO_2 concentration (Spivack et al. 1993, Palmer et al. 1998, Zeebe & Wolf-Gladrow 2001, Kubota et al. 2015, Martínez-Boti & Marino 2015), it is also used for the reconstruction of pH variations for glacial cycles (Hönisch & Hemming 2005). Foraminifers and tropical corals' boron isotope ratio ($\delta^{11}\text{B}$) has been suggested as a way to measure the pH of seawater, and the long-term climate variability has been constructed using the ($\delta^{11}\text{B}$) pH proxy (Pelejero & Calvo 2008, Anagnostou et al. 2012). Boron isotope measurements have been widely employed as proxies for surface oceanic pH or pCO_2 in foraminiferal calcite and tropical coral aragonite (Hönisch & Hemming 2005, Douville et al. 2006). The surface ocean pH often decreases during increasing atmospheric CO_2 due to CO_2 uptake (Hönisch & Hemming 2005). Borate $\text{B}(\text{OH})_4$ and boric acid $\text{B}(\text{OH})_3$ are the two main dissolved forms of boron in seawater, and relative quantities of each form depend on the pH of the environment, $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4$ are predominant form

under low and high pH respectively (Klochko et al. 2006, Pelejero & Calvo 2008), and contrast to borate, which prefers the lighter isotope ^{10}B , boric acid prefers the heavier isotope ^{11}B and the boron isotope composition of marine carbonate fossils records ancient ocean pH by incorporating only borate in carbonate shells (Rasbury & Hemming 2017). Since boron has ~14-20 million years of residence time in seawater (Lemarchand et al. 2000), most boron research focuses on pre-Quaternary times, however, due to temporal changes of $\delta^{11}\text{B}$ in seawater for these ages, the inferences can be wide-ranging (Lemarchand et al. 2000, Pelejero & Calvo 2008).

The extreme sensitivity of seawater isotope $\delta^{11}\text{B}$ to global weathering and denudation (via rivers) and the significance of boron isotopes in carbonates for reconstructing atmospheric and oceanic CO_2 levels (Gaillardet & Lemarchand 2018). Due to its generally warmer climate, protracted volcanism, and CO_2 emissions, quick ocean acidification events, and other abrupt carbon cycle alterations that occurred in the early Cenozoic of utmost relevance for researching climate sensitivity to carbon system perturbation under greenhouse conditions (Zachos et al. 2008) estimate paleo- CO_2 concentrations for periods older than those accessible from ice cores and to reconstruct surface pH fluctuations on glacial/interglacial, marine carbonate boron isotopic compositions have been used (Sanyal et al. 2000, Palmer & Pearson 2003, Hönisch & Hemming 2005). Due to the proven correlation between pH and partial pressure of atmospheric CO_2 , the boron isotope composition of calcium carbonate shells of marine organisms has the unique potential to record the surface ocean pH and enable the calculation of atmospheric pCO_2 (Rasbury & Hemming 2017).

One of the most pervasive processes that lower water quality and put future water use at risk is salinization. The drinkable freshwater supply is often constrained by groundwater salinization, especially in arid and semiarid regions (Vengosh et al. 1999). The geochemical properties of boron isotopes are used extensively to evaluate a variety of geological processes, including the interaction of water and rock, the sedimentary environment, the genesis of salt lakes and groundwater, wastewater recharging, and the causes of anthropogenic pollution (Vengosh et al. 1994, Widory et al. 2005, Pennisi et al. 2006, Wei et al. 2014, Musashi et al. 2015).

The chemical weathering of evaporites and silicates, along with their mixing with seawater, regulates the amount of dissolved boron in groundwater; however, as a trace element or minor ion, boron is typically present in groundwater in extremely low amounts (Morell et al. 2008). For Mesozoic and Cenozoic clayey strata, the presence of boron is a sign of paleo salinity. However, clay diagenesis affects the boron

content of deeply buried Paleozoic and Ediacaran sediments (Retallack et al. 2020). As marine waters have a larger boron level of 20-50 ppm than freshwater, which has a boron content of only 2 ppm, boron in clays has been employed as a paleo salinity proxy (Walker & Price 1963, Couch 1971). The boron concentration of known marine fossils, such as Ediacaran stromatolites and algae, is substantially higher than that of Ediacaran vendobionts, which is indistinguishable from that of fossil plants and paleosols (Retallack et al. 2020)

Groundwater Contamination

An understanding of hydrogeological processes can be gained by identifying the composition and concentration of boron isotopes, and these isotopes further reveal that evaporite dissolution had an impact on salinization (Vengosh et al. 1994, Bassett et al. 1995, Gómez-Alday et al. 2022). Boron is a useful natural isotopic tracer for identifying the sources of pollution in groundwater systems due to the wide range in the isotopic composition of the boron sources in water resources, both natural (such as seawater, fossil brines, and hydrothermal fluids) and anthropogenic (sewage effluent, boron fertilizers, fly ash leachate, and landfill effluents) (Vengosh et al. 1994, Vengosh et al. 1998). In most river waters, the amount of boron is below 40 µg/L, while high levels of boron are present in rivers draining evaporites due to weathering (Lemarchand et al. 2002, Lemarchand & Gaillardet 2006). As nitrate transformation processes do not affect it, the boron isotope can discriminate between sewage and manure sources (Vengosh et al. 1994, Barth 1998). The investigations have demonstrated a clear difference in $\delta^{11}\text{B}$ values between seawater and terrestrial water (Barth 1993). The ocean water, groundwater, geothermal water and brines have a similar range of $\delta^{11}\text{B}$ (Bassett et al. 1995). Water-rock interactions and the biological cycle of B are the major causes of B isotopic fractionation in regolith and groundwater, whereas adsorption on sediments affects B isotopic fractionation in rivers slightly (Mao et al. 2019). Urban wastewater can be detected in surface water using boron isotopes, and also the source of boron in solution and the origin of the water are determined using the boron isotope composition of the groundwater (Petelet-Giraud et al. 2003, Nigro et al. 2018).

Biological Processes

Boron is an essential plant micronutrient in their metabolic activities (Blevins & Lukaszewski 1998, Pereira et al. 2021). In addition to facilitating vegetative growth and tissue differentiation, boron affects phenolic metabolism, cell wall synthesis, membrane integrity, RNA metabolism, indole acetic acid metabolism, and carbohydrate metabolism (Blevins & Lukaszewski 1998, Camacho-Cristóbal et al.

2005, 2008). The plants absorb boron as boric acid, and its deficiency prevents root growth and leaves expansion (Tanaka & Fujiwara 2008). When plants are deficient in boron, carbohydrates accumulate in the chloroplasts, increasing the rate of pentose phosphate cycle activity and decreasing the Krebs cycle activity (Goldbach 1997). In plants, the research on the first vascular plant, *Zosterophyllum shengfengense*, revealed that boron is primordial, originated in the root system in the terrestrial environment, and is also associated with the biosynthesis of lignin and differentiation of xylem (Lewis 1980, Pereira et al. 2021). The bacteria and fungi strains are affected by boron and boron-containing compounds (Gerretsen & Hoop 1957, Baker et al. 2009, Hunt et al. 2012). As boron protects plants from fungal decay, it is used in the timber industry as a termite and fungus repellent (Kartal et al. 2004) and also prevents infection in white fir *Abir concolor* by *Fomes Annosus* (Smith 1970). Boron further regulates the metabolism of numerous minerals, such as calcium, magnesium, phosphorus, and molybdenum (Wilson & Ruszler 1996). A positive correlation between boron and *Azotobacter* has also been reported (Gerloff 2006).

In cows, treatment of fatty liver (hepatic lipidosis) disease is costly, and researchers believe that borax (sodium borate $\text{Na}_2\text{B}_4\text{O}_7$) helps to prevent fatty liver disease because it helps in significant reductions in serum triglyceride (TG) and very low-density lipoprotein (VLDL) levels (Basoglu et al. 2002, Bobe et al. 2004). When either vitamin D or magnesium nutrition was disrupted in chicks and rats, it was claimed that lack of boron increased the amount of insulin required to maintain plasma glucose concentrations, and boron deficiency has been linked to hyperinsulinemia in vitamin D-deficient mice (Hunt & Herbel 1991, Bakken & Hunt 2003).

Ocean Acidification

The growth of coral skeletons is susceptible to environmental changes and may be adversely affected by ocean acidification (Gagnon et al. 2021). The analysis of boron elemental and isotopic composition of coral aragonite can uncover important information about coral skeletal calcification strategies (Chalk et al. 2021), also evaporites and brines can be traced using boron isotope geochemistry (Palmer & Slack 1989, Vengosh et al. 1991). As alkalinity and total inorganic carbon concentration control the pH of the surface ocean, so does atmospheric CO_2 partial pressure (Spivack et al. 1993, Bröcker & Franz 1998), and the boron isotopic composition of foraminiferal tests may also be affected by pH and isotopic composition (Bröcker & Franz 1998). The speciation process between the borate ion and boric acid pH dependent and isotopically unique, boron isotope variations in biogenic carbonates can be used to determine the pH of

the calcifying medium (Blamart et al. 2007, Rollion-Bard et al. 2011).

CONCLUSIONS AND FUTURE SCOPE

This work includes a short compilation of boron isotopes in various processes, boron-containing minerals, the latest instrumental techniques involved in the measurement of boron, its distribution and applications in nature. In addition to this, it includes a review of boron isotopic variation in the Himalayas in different systems. In conclusion, boron is a highly mobile element with large fractionation between its two isotopes due to their significant mass differences. Compared to other stable isotopes, it is considered the specific geochemical tracer. In the ocean, boron occurs in abundance, is appraised as an essential trace element, and proves extremely beneficial for paleoclimatic studies. In subduction zones, it acts as powerful means of reconnoitering fluid-mediated processes. The role of boron in cell wall stability may have an impact on how well plants and algae resist infection. Altogether, the current level of understanding about the significance of boron has widened some interesting prospects for more scientific and applied research. In the future, boron, due to its highly incompatible nature and reactive nature, can further provide a special tool to test comprehension across various timescales. In plants and agroecosystems, the role of the boron cycle can be sufficiently evaluated as the research in this area is scarce. As per the literature review study in laboratory experiments, calibrated equations are not available for many coral species, and there is a scarcity of knowledge on boron incorporation, which can be further elaborated.

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