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REVIEW

Cl, Br, B, Li, and noble gases isotopes to study the origin and evolution of deep groundwater in sedimentary basins: a review

Wanjun Jiang[1,2] · Yizhi Sheng[3,4] · Guangcai Wang[4,5] · Zheming Shi[4,5] · Futian Liu[1,2] · Jing Zhang[1,2] · Donglei Chen[1,2]

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Abstract

Deep groundwater characteristics provide valuable information on oil and gas extraction and evolution of hydrosphere, and nonmetallic and metallic elements in deep groundwater are raising industrial interest. There is therefore a need for a better understanding of the origin and evolution of deep groundwater in large sedimentary basins, e.g., by using non-traditional isotopes. Here, we review the constraints of isotopes of chloride (Cl), bromine (Br), boron (B), lithium (Li), helium (He), neon (Ne), and argon (Ar) on the origin and evolution of deep groundwater in large sedimentary basins. In deep groundwater, δ^{37}Cl ranges from −1.96 to + 2.07‰, δ^{81}Br from −1.50 to + 3.35‰, δ^{11}B from + 1.10 to + 39.99‰, and δ^{7}Li from −1.00 to + 31.80‰. These values either overlap or are different compared to those in freshwater, e.g., meteoric water, river water and shallow groundwater, hydrothermal fluid, seawater, subsurface brine, lake sediment, or mineral. Noble gas isotopes such as ^{3}He/^{4}He, ^{4}He/^{20}Ne, and ^{36}Ar/^{40}Ar are also effective tracers for deep groundwater evolution. Integrating multiple non-traditional isotopes allows to study dissolution, sedimentation, evaporation, and mixing of different waters in deep aquifers.

Keywords Deep groundwater · Non-traditional isotopes · Sedimentary basins · Water–rock interaction

Abbreviations

Cl	Chloride
Br	Bromine
B	Boron
Li	Lithium
He	Helium
Ne	Neon
Ar	Argon
TDS	Total dissolved solids
TIMS	Thermo-ionization mass spectrometer
SIMS	Secondary-ion mass spectrometry
MC-ICP-MS	Multi-collector inductively coupled plasma mass spectrometer
SW China	Southwest China

✉ Yizhi Sheng
shengyz0330@163.com

1 Tianjin Center, China Geological Survey (CGS), Tianjin 300170, China

2 North China Center for Geoscience Innovation, Tianjin 300170, China

3 Department of Geology and Environmental Earth Science, Miami University, Oxford, OH 45056, USA

4 State Key Laboratory of Biogeology and Environmental Geology & MOE Key Laboratory of Groundwater Circulation and Environment Evolution, China University of Geosciences, Beijing 100083, China

5 School of Water Resources and Environment, China University of Geosciences, Beijing 100083, China

Introduction

Most sedimentary strata of large sedimentary basins are rich in petroleum, natural gas, salt minerals, and metal deposits. In the crystalline basement or the sedimentary strata, hundreds and even thousands of meters below the surface, "deep" groundwater with high total dissolved solids (TDS) is commonly formed (Chan et al. 2002; Bagheri et al. 2014a, b; Birkle et al. 2009a, b; Kharaka and Hanor, 2003; Lowenstein et al. 2003; Sheng et al. 2018; Tan et al. 2011; Vengosh et al. 1995; Yu et al. 2013). In the studies of hydrogeochemistry in sedimentary basins, deep groundwater is often referred to as "formation water" (Bagheri et al. 2014a, b; Birkle et al. 2009a, b; Kharaka and Hanor, 2003; Lüders et al. 2010; Millot et al. 2011; Ni et al. 2021; Yu et al. 2013), which often buries in the rock cracks of hydrocarbon reservoirs (Kharaka and Hanor 2003). During the processes of oil and gas resources exploitation, deep groundwater is brought to the surface from the deep aquifer, and thus, it is also called

"produced formation water" or "oilfield brine" (Bagheri et al. 2014b; Boschetti et al. 2020; Fan et al. 2010; Huang et al. 2020; Kharaka and Hanor, 2003; Ni et al. 2021; Phan et al. 2020; Tan et al. 2011; Yu et al. 2013). The enrichment of trace or metallic elements such as K, B, Li, Br, and I in this type of groundwater shows high industrial utilization values and socioeconomic benefits. Meanwhile, the migration and evolution of deep groundwater can aggregate dissolved carbohydrate chemicals, salts, metals, and trace elements into ores (Bagheri et al. 2014a, b; Chan et al. 2002; Tan et al. 2011). Therefore, the study on the source, formation, and evolution of deep groundwater can reveal the subsurface water resources and strata formations (Hanor and Mcintosh, 2006, 2007).

Since the mid- and late-twentieth century, the characteristics of deep groundwater and its role in the hydrocarbon geological processes have attracted widespread attention by geoscientists in the fields of mineralogy, geochemistry, and sedimentology (Carothers and Kharaka, 1978; Fritz and Frape, 1982; Kaufmann et al. 1993). After entering the twenty-first century, researchers began to pay more attention to the circulation and evolution of deep groundwater in large sedimentary basins, such as in China (Cai et al. 2001; Chen et al. 2013, 2014; Li and Cai, 2017; Tan et al. 2011; Yu et al. 2013), Canada (Bottomley et al. 2003; Bottomley and Clark 2004; Leybourne and Goodfellow, 2007; Osselin et al. 2018, 2019; Stotler et al. 2006, 2010;), Russia (Shouakar-Stash et al. 2007b), America (Bouchaou et al. 2008; Shouakar-Stash et al. 2006), Greece (Dotsika et al. 2010), Germany (Lüders et al. 2010), France (Millot et al. 2011), Italy (Barbieri and Morotti, 2003; Barbieri et al. 2005; Boschetti et al. 2011, 2013), Australia (Meredith et al. 2013), and Iran (Bagheri et al. 2014a, b, c).

However, due to the sampling difficulty, the research on the source, formation, and evolution of deep groundwater in large sedimentary basins is still insufficient. Understanding the hydrogeochemical composition in groundwater (formed by water–rock interaction) can help to evaluate the diagenetic history assessment of basins (e.g., mineralization, crustal circulation, fluid flow, and migration) and improve oil and gas reservoir management (Bagheri et al. 2014b; Hanor and Mcintosh, 2007; Yu et al. 2013). Prolonged water–rock interaction processes may significantly change the chemical compositions of deep groundwater. Thus, deep groundwater's source and evolution have always been complicated (Bagheri et al. 2014a, b; Birkle et al. 2009a, b; Kharaka and Hanor, 2003; Lüders et al. 2010).

In recent years, isotopic techniques have been applied to uncover the source, formation, and evolution of groundwater in sedimentary basins (Boschetti et al. 2013; Chen et al. 2014; Jiang et al. 2019; Lüders et al. 2010; Millot et al. 2011; Tan et al. 2011; Yu et al. 2013). Isotopes are a group of chemical elements with the same number of protons but different neutrons, including stable and radioactive isotopes. Although the isotopes of the same element have different mass numbers, their chemical properties are basically the same, while their mass spectrum properties, radioactive transformation, and physical properties are different. The stable isotopes (H, O, C, N, S) existing in the natural environment are the essential elements in the geological, hydrological, and biological systems, and their changes are subject to natural processes (Jiang et al. 2016; Clark and Fritz, 1997). Due to the mass discrepancy, the phenomenon that the isotopes of an element are distributed in different media or coexisting phases with different proportions is defined as isotopic fractionation. As a result of fractionation, the coexisting phases often develop unique isotopic compositions (ratios of heavy to light isotopes) that may be indicative of their sources or the processes that formed them. The isotope geochemistry can be applied to study the distribution, migration, and enrichment of water, nutrients, and solutes in various environmental media (atmosphere, lithosphere, hydrosphere, biosphere, and anthroposphere) (Clark and Fritz 1997).

Entering the end of the twentieth century, with the birth and development of thermo-ionization mass spectrometer (TIMS), secondary-ion mass spectrometry (SIMS), and especially multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), unprecedented high precise determination for isotopic compositions of non-gaseous elements becomes possible (Halliday et al. 1995; Maréchal et al. 1999). This marks the beginning of the era for non-traditional isotope geochemistry (isotopes of elements other than the more traditional H, C, N, O, and S). These isotopes consist of metallic elements (e.g., Li, Mg, K, Ca, Fe, Cu, Cr, Ni, Cu, Zn, and Ba), reactive non-metallic elements (e.g., B, Si, Cl, Se, and Br), as well as some noble gases (e.g., He, Ne, Ar, Kr) (Johnson et al. 2004; Maureen et al. 2009; Richter et al. 2009; Teng et al. 2017, 2019).

The unique characteristics make non-traditional stable isotopes susceptible to fractionation in various physical–chemical processes (e.g., redox reactions, diffusion, evaporation, and condensation) and biological processes (Johnson et al. 2004; Richter et al. 2009; Teng et al. 2017). The non-traditional isotopes have been applied in the studies of groundwater pollution by identifying the sources of solute (Briand et al. 2017; Castorina et al. 2013; Ellis et al. 2002; Jackson et al. 2010; Khaska et al. 2013; Nigro et al. 2017; Novak et al. 2014; 2017; Kaown et al. 2013; Ransom et al. 2016; Vengosh et al. 2005), including formation water-contaminated shallow groundwater environments in oil and gas extraction fields (Bondu et al. 2021; Cao et al. 2020; Darrah et al. 2014; Harkness et al. 2017; Huang et al. 2020; McIntosh et al. 2019; McMahon et al. 2021; Whyte et al. 2021; Warner et al. 2012; Zheng et al. 2017). In addition, the unique chemical properties of non-traditional stable isotopes

are often utilized to track geochemical events and processes (Teng et al. 2019), including magmatic mineralization, geochemical circulation of crust and mantle, and continental weathering (Barnes et al. 2008; Bernal et al. 2014; Chiaradia et al. 2014; Henchiri et al. 2014; John et al. 2010; Millot et al. 2010a; 2010b; Rizzo et al. 2013; Rudnick et al. 2004; Teng et al. 2006, 2019).

However, the application of non-traditional stable isotopes (e.g., Cl, Br, B, Li, and noble gas isotopes) on studying deep groundwater sources and evolution in large sedimentary basins has remained elusive due to the variations and overlaps of isotopic compositions in different media and complex isotopic fractionation mechanisms. In this paper, the research progress of application and development of Cl, Br, B, Li, and noble gases isotopes on investigating the source and formation of deep groundwater in large sedimentary basins is studied. The abundance of these non-traditional isotopes in deep groundwater and other natural reservoirs is summarized based on ~ 300 previously published literature. This paper intends to reference future research on the formation and evolution of deep groundwater and lay a relevant technical foundation.

Implication of non-traditional stable isotopes on deep groundwater studies

Cl isotopes

Background and importance

Under natural conditions, chlorine (Cl) is a soluble element in various water types, and its chemical property is relatively stable since it does not participate in the geochemical evolution of geological bodies. In other words, the redox environment barely affects the transformation of Cl in the waters, as Cl does not form insoluble salts or be absorbed by ion substitution and plants. Two stable isotopes of Cl in nature are ^{37}Cl and ^{35}Cl, with abundance of 75.78 and 24.22%, respectively (Rosman and Taylor, 1998).

Nonetheless, the fractionation of Cl isotopes can be induced by the different migration rates of ^{37}Cl and ^{35}Cl due to their relative mass discrepancy in some physical processes, such as precipitation and dissolution of salt (Eggenkamp et al. 1995; Eastoe et al. 1999; Luo et al. 2012, 2014), evaporation (Luo et al. 2012, 2016; Xiao et al. 1994a, b, 1996), ion filtration (Godon et al. 2004; Kaufmann et al. 1988; Li et al. 2012; Phillips and Bentley, 1987), and ion exchange and diffusion (Beekman et al. 2011; Eastoe et al. 2001; Eggenkamp and Coleman, 2009; Musashi et al. 2004, 2007). With the migration of water bodies, ^{37}Cl stable is primarily enriched in sedimentary environments such as oceans and lakes, which records the evolution of waters flowing through different geological bodies (Warmerdam et al. 1995).

Back to 1980s and 1990s, with the determination of Cl stable isotope fractionation in nature, δ^{37}Cl has been shown as a sensitive tracer in the groundwater migration, changes in paleocene and paleoclimate, the sedimentary environments, element geochemistry, formation of hydrothermal deposits (Banks et al. 2000a, b; Eastoe et al. 1989; Eastoe and Guilbert 1992; Kaufmann et al. 1984a, b, 1987, 1993; Liu et al. 1996), and saline water buried in the deep subsurface (Eastoe and Guilbert, 1992; Eastoe et al. 1999; Kaufmann et al. 1984a, 1988). In the twenty-first century, with the establishment and continuous improvement of high-precision test methods for Cl stable isotopes, Cl stable isotopes have been widely utilized to trace the source of salt in deep groundwater, mixing of different waters, and water–rock interaction (Bagheri et al. 2014b; Boschetti et al. 2011; Chen et al. 2014; Frape et al. 2004; Shouakar-Stash et al. 2007b; Sie and Frape 2002; Stewart and Spivack 2004; Stotler et al. 2010; Yu et al. 2013).

Application of Cl isotopes in deep groundwater studies

The δ^{37}Cl ratios in minerals and water bodies are distinct (Fig. 1). Generally, the δ^{37}Cl values in rocks are positive (greater than 0‰), while the δ^{37}Cl values in some waters are negative. The δ^{37}Cl values in seawater range from −0.76‰ to + 0.94‰, whereas they decrease during the evaporation process of seawater (−0.9 to + 0.2‰, Godon et al. 2004; Kaufmann et al. 1984b). In contrast, the δ^{37}Cl in deep groundwater had a wider range than seawater, ranging from −1.96‰ to + 2.07‰. The values of δ^{37}Cl in river water and shallow fresh groundwater are higher than those in deep groundwater, ranging from −0.4 to + 3.07‰ and −2.13 to + 3.82‰, respectively. The δ^{37}Cl in hydrothermal fluids ranged from −0.4 to 4.32‰.

Based on δ^{37}Cl values, the mid-deep groundwater in the Pliocene–Pleistocene strata in the Gulf Coast Basin is shown to stem from the mixture of primitive seawater and deep underground brine (Eastoe et al. 2001). The suite of isotopic (δ^{37}Cl and δ^{81}Br) and hydrochemical data indicates that the salinity origin of the formation water in a gas reservoir is the evaporated seawater (Bagheri et al. 2014b). Based on hydrogeochemical characteristics and isotopic characteristics including δD, δ^{18}O, δ^{37}Cl, and δ^{81}Br, the formation of deep groundwater in the North China Plain is found to be originated from meteoric waters, and its primary evolutionary process is the evaporation and a mixture of seawater (Chen et al. 2014). Besides, relative to the marine brine and seawater, the high δ^{37}Cl (from + 0.22 to + 0.39‰) in the Oeillal spring water indicates the non-marine origin of deep

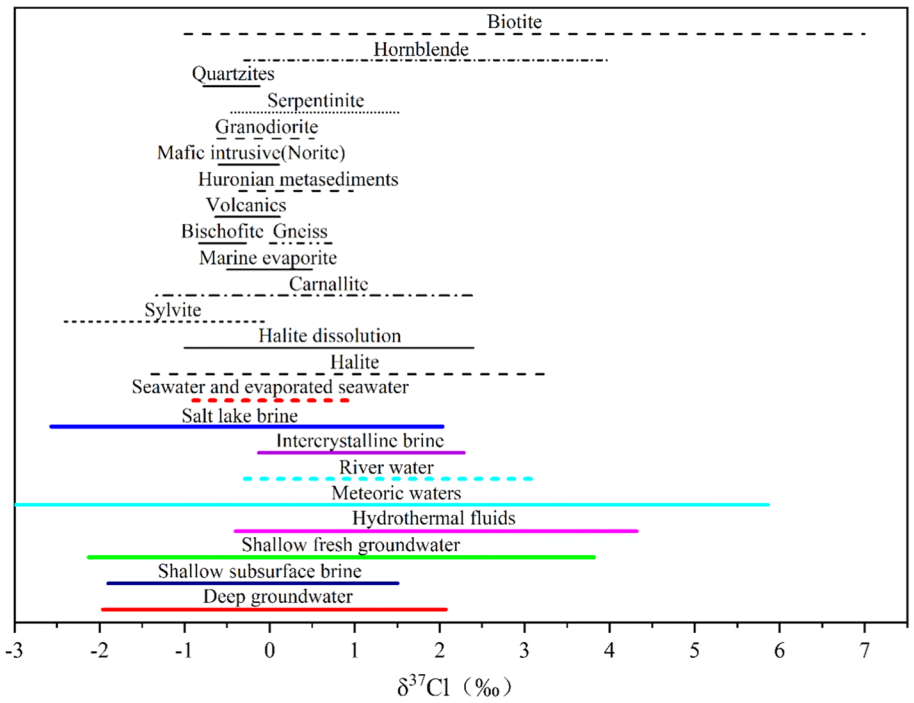

Fig. 1 $\delta^{37}Cl$ values in different water types and rock mineral compositions in nature. References of $\delta^{37}Cl$ are shown in Table 1. The differences in geochemical and specific isotopic compositions between "deep groundwater" and other water types or rock mineral make it possible to be the sensitive indicators and diagnostic indexes for tracing or identifying the origin and evolution of "deep" groundwater in sedimentary basins

water and high-temperature water–rock interaction process, and the Cl isotope ratios of the Oeillal spring water are the result of a water mixing process (Khaska et al. 2015).

Although $\delta^{37}Cl$ values in different geological bodies and water bodies have inconsistent abundance, which can be indicatives of the groundwater sources, their overlaps may obscure the acquisition of precise deep groundwater source information. The overlapping phenomenon may be affected and constrained by different fractionation mechanisms of Cl isotopes, such that integrating Cl isotopes with other isotopes is required to comprehensively study the deep groundwater evolution.

Br isotopes

Background and importance

Bromine (Br) does not exist as a monomer in mineral deposits in nature, while it easily forms water-soluble compounds with alkaline earth metals and enters Cl^-containing rock minerals in the form of isomorphism. The chemical properties of Br are analogous to those of Cl, which is a relatively conservative element in groundwater. Therefore, it is considered an inert element in various hydrochemical and geological processes.

The mass discrepancy between the two stable isotopes of Br, namely ^{81}Br and ^{79}Br (with similar abundance 49.314 and 50.686%, respectively), results in a bond energy difference between the heavy isotopes and light isotopes. As a result, the aggregation and dispersion of different media in the process of physical or chemical reactions can lead to significant fractionation of Br isotopes (Eggenkamp and Coleman, 2009; Stewart and Spivack 2004; Stotler et al. 2010). Similarly, the fractionation of Br isotopes is observed in various hydrogeochemical processes, such as ion diffusion (Eggenkamp and Coleman, 2009), mixing of different waters (Shouakar-Stash et al. 2007b), precipitation and dissolution of salt minerals (Eggenkamp et al. 2011), ion filtration (Phillips and Bentley 1987), and water–rock interaction (Stotler et al. 2010). Therefore, Br isotopes have been utilized to reveal and identify the source, formation, and hydrogeochemical process in deep groundwater (Frape et al. 2007; Shouakar-Stash et al. 2006, 2007a; Stotler et al. 2006).

Application of Br isotopes in deep groundwater studies

Since approximately 99% of Br on the earth exists in seawater, it is generally believed that Br from seawater is the primary natural source of inorganic Br in other environments (Eggenkamp 2014). In the groundwater environment, the primary sources of Br ions are seawater and evaporites (Stotler et al. 2010). $\delta^{81}Br$ values in different geological bodies are illustrated in Fig. 2. The stable isotopic compositions of Br vary significantly across various geological bodies and processes, giving a perspective of incorporating the Br isotopes in deep groundwater study.

To date, the overall variation of Br isotopes in the hydrosphere ranges from −1.5‰ to + 3.35‰ (Fig. 2). The application of Br isotopes in deep groundwater studies is relatively late compared to other stable isotopes. The Br

Table 1 $\delta^{37}Cl$ values in different water types and rock mineral compositions in nature

Types	$\delta^{37}Cl$ ‰	References to the data sources
Deep groundwater	−1.96 to 2.07	Bagheri et al. 2014b; Boschetti et al. 2011; Chen et al. 2014; Eastoe and Guilbert, 1992; Eastoe et al. 1999, 2001; Frape et al. 2004; Kaufmann et al. 1984a, 1993; Khaska et al. 2015; Lavastre et al. 2005; Liu et al. 1996; Liu et al 1997; Palmén and Hellä, 2003; Shouakar-Stash et al. 2006, 2007a, 2007b; Sie and Frape, 2002; Sie, 1999; Stewart and Spivack, 2004; Stotler et al. 2006; 2010; Xiao et al. 2000; Yu et al. 2013; Ziegler et al. 2001
Shallow subsurface brine	−1.9 to 1.5	Chen et al. 2014; Du et al. 2016; Eastoe and Guilbert, 1992; Frape et al. 1998; Kaufmann et al. 1984a, b; Li et al. 2016; Liu et al. 2016; Sie and Frape 2002; Stotler et al. 2010
Shallow fresh groundwater	−2.13 to 3.82	Bassett et al. 1995; Chen et al. 2014; Desaulniers et al. 1986; Eastoe et al. 1989; Eastoe, 2016; Gwynne et al. 2013; Kaufmann et al. 1984a, 1993; Khaska et al. 2015; Lavastre et al. 2005; Li et al. 2012; Li et al. 2016; Liu et al. 1996; Liu et al. 2016; Sie and Frape 2002; Véronique et al. 2005; Xiao et al. 1994a; Zhang et al. 2007
Hydrothermal fluids or geothermal brines	−1 to 4.32	Banks et al. 2000a, 2000b; Bernal et al. 2014; Bonifacie et al. 2005; Cullen et al. 2015, 2021; Kaufmann et al. 1984a; Li et al. 2015; Liu et al. 1996; Pinti et al. 2020; Stefánsson and Barnes 2016; Stefánsson et al. 2017; Xiao et al. 1994a, 2000
Meteoric waters	−3.5 to 5.86	Koehler and Wassenaar, 2010; Xiao et al. 1994a
River water	−0.4 to 3.07	Eastoe et al. 1999; Eastoe et al. 2007; Eastoe 2016; Eggenkamp et al. 1995; Godon et al. 2004; Kaufmann et al. 1984a; Koehler and Wassenaar 2010; Liu et al. 1996, 1997; Xiao et al. 2000
Intercrystalline brine	0.37 to 2.28	Chen et al. 2014; Eastoe 2016; Han et al. 2018; Liu et al. 1994, 1996, 1997, 1999; Luo et al. 2012; Xiao et al. 1994a, 1996, 1997
Salt lake brine	−2.57 to 2.04	
Seawater and evaporated seawater	−0.9 to 0.94	Bagheri et al. 2014b; Chen et al. 2014; Eastoe et al. 1999, 2001; Eggenkamp et al. 1995, 2019a; Godon et al. 2004; Kaufmann et al. 1984a; Richard et al. 2011; Shirodkar et al. 2003; Xiao et al. 2002
Terrestrial evaporates (Halite)	−1.39 to 3.3	Eastoe et al. 1999, 2001, 2007; Eastoe 2016; Eggenkamp et al. 2019a; 2019b; Kaufmann et al. 1984a; Liu et al. 1997; Luo et al. 2012, 2016; Meng et al. 2014; Sharp et al. 2013; Tan et al. 2005a, 2006, 2009; Wang et al. 1995; Xiao et al. 1994b, 1996, 1997, 2000
Halite dissolution	−1 to 2.4	Bagheri et al. 2014b; Banks et al. 2000a, b; Eggenkamp et al. 1995; Eastoe et al. 1999, 2001; Eastoe 2016
Sylvite	−2.41 to −0.03	Tan et al. 2005b; Vengosh et al. 1989; Xiao et al. 1994b;
Carnallite	−1.38 to 2.38	Eggenkamp et al. 2016; Luo et al. 2012, 2014; Xiao et al. 1994b
Bischofite	−0.83 to −0.28	
Marine evaporite	−0.5 to 0.5	Eastoe and Peryt, 1999; Eastoe et al. 2001, 2007; Eggenkamp et al. 1995
Hornblende	−0.3 to 4	Barnes and Cisneros, 2012; Chiaradia et al. 2014; Eggenkamp and Schuiling, 1995; Magenheim et al. 1995; Stewart and Spivack, 2004
Biotite	−1 to 7	Boudreau et al. 1997; Chiaradia et al. 2014; Eastoe and Guilbert, 1992; Willmore et al. 2002
Gneiss	0 to 0.78	Barnes and Sharp, 2006; Barnes et al. 2008; Bonifacie et al. 2008; Chiaradia et al. 2014; Frape et al. 2004; Rizzo et al. 2013; Stotler et al. 2009, 2010
Volcanics	−0.64 to 0.12	
Huronian metasediments	−0.36 to 0.98	
Mafic intrusive Norite	−0.6 to 0.11	
Granodiorite	−0.61 to 0.52	
Serpentinite	−0.45 to 1.52	
Quartzites	−0.78 to −0.12	
Deep groundwater	−1.96 to 2.07	Bagheri et al. 2014b; Boschetti et al. 2011; Chen et al. 2014; Eastoe and Guilbert, 1992; Eastoe et al. 1999, 2001; Frape et al. 2004; Kaufmann et al. 1984a, 1993; Khaska et al. 2015; Lavastre et al. 2005; Liu et al. 1996; Liu et al 1997; Palmén and Hellä, 2003; Shouakar-Stash et al. 2006, 2007a, 2007b; Sie and Frape, 2002; Sie, 1999; Stewart and Spivack, 2004; Stotler et al. 2006; 2010; Xiao et al. 2000; Yu et al. 2013; Ziegler et al. 2001
Shallow subsurface brine	−1.9 to 1.5	Chen et al. 2014; Du et al. 2016; Eastoe and Guilbert, 1992; Frape et al. 1998; Kaufmann et al. 1984a, b; Li et al. 2016; Liu et al. 2016; Sie and Frape 2002; Stotler et al. 2010

Table 1 (continued)

Types	$\delta^{37}Cl$ ‰	References to the data sources
Shallow fresh groundwater	−2.13 to 3.82	Bassett et al. 1995; Chen et al. 2014; Desaulniers et al. 1986; Eastoe et al. 1989; Eastoe, 2016; Gwynne et al. 2013; Kaufmann et al. 1984a, 1993; Khaska et al. 2015; Lavastre et al. 2005; Li et al. 2012; Li et al. 2016; Liu et al. 1996; Liu et al. 2016; Sie and Frape 2002; Véronique et al. 2005; Xiao et al. 1994a; Zhang et al. 2007
Hydrothermal fluids or geothermal brines	−1 to 4.32	Banks et al. 2000a, 2000b; Bernal et al. 2014; Bonifacie et al. 2005; Cullen et al. 2015, 2021; Kaufmann et al. 1984a; Li et al. 2015; Liu et al. 1996; Pinti et al. 2020; Stefánsson and Barnes 2016; Stefánsson et al. 2017; Xiao et al. 1994a, 2000
Meteoric waters	−3.5 to 5.86	Koehler and Wassenaar, 2010; Xiao et al. 1994a
River water	−0.4 to 3.07	Eastoe et al. 1999; Eastoe et al. 2007; Eastoe 2016; Eggenkamp et al. 1995; Godon et al. 2004; Kaufmann et al. 1984a; Koehler and Wassenaar 2010; Liu et al. 1996, 1997; Xiao et al. 2000
Intercrystalline brine	0.37 to 2.28	Chen et al. 2014; Eastoe 2016; Han et al. 2018; Liu et al. 1994, 1996, 1997, 1999; Luo et al. 2012; Xiao et al. 1994a, 1996, 1997
Salt lake brine	−2.57 to 2.04	
Seawater and evaporated seawater	−0.9 to 0.94	Bagheri et al. 2014b; Chen et al. 2014; Eastoe et al. 1999, 2001; Eggenkamp et al. 1995, 2019a; Godon et al. 2004; Kaufmann et al. 1984a; Richard et al. 2011; Shirodkar et al. 2003; Xiao et al. 2002
Terrestrial evaporates (Halite)	−1.39 to 3.3	Eastoe et al. 1999, 2001, 2007; Eastoe 2016; Eggenkamp et al. 2019a; 2019b; Kaufmann et al. 1984a; Liu et al. 1997; Luo et al. 2012, 2016; Meng et al. 2014; Sharp et al. 2013; Tan et al. 2005a, 2006, 2009; Wang et al. 1995; Xiao et al. 1994b, 1996, 1997, 2000
Halite dissolution	−1 to 2.4	Bagheri et al. 2014b; Banks et al. 2000a, b; Eggenkamp et al. 1995; Eastoe et al. 1999, 2001; Eastoe 2016
Sylvite	−2.41 to −0.03	Tan et al. 2005b; Vengosh et al. 1989; Xiao et al. 1994b;
Carnallite	−1.38 to 2.38	Eggenkamp et al. 2016; Luo et al. 2012, 2014; Xiao et al. 1994b
Bischofite	−0.83 to −0.28	
Marine evaporite	−0.5 to 0.5	Eastoe and Peryt 1999; Eastoe et al. 2001, 2007; Eggenkamp et al. 1995
Hornblende	−0.3 to 4	Barnes and Cisneros, 2012; Chiaradia et al. 2014; Eggenkamp and Schuiling, 1995; Magenheim et al. 1995; Stewart and Spivack, 2004
Biotite	−1 to 7	Boudreau et al. 1997; Chiaradia et al. 2014; Eastoe and Guilbert, 1992; Willmore et al. 2002
Gneiss	0 to 0.78	Barnes and Sharp, 2006; Barnes et al. 2008; Bonifacie et al. 2008; Chiaradia et al. 2014; Frape et al. 2004; Rizzo et al. 2013; Stotler et al. 2009, 2010
Volcanics	−0.64 to 0.12	
Huronian metasediments	−0.36 to 0.98	
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Granodiorite	−0.61 to 0.52	
Serpentinite	−0.45 to 1.52	
Quartzites	−0.78 to −0.12	

isotope compositions in natural water were first reported by Eggenkamp and Coleman (2000). They found that the $\delta^{81}Br$ values in 11 deep groundwater samples in the Norwegian shelf ranged from + 0.08‰ and + 1.27‰, establishing the first natural variation range of Br stable isotopes. Since then, more and more studies have used Br isotopes to investigate the sources of deep groundwater. Applications of Br isotopes in deep groundwater in sedimentary basins have been carried out in the North Sea (Eggenkamp and Coleman, 2000), Russia (Shouakar-Stash et al. 2007b), Canada, and Fennoscandia (Frape et al. 2007; Shouakar-Stash et al. 2005, 2007a, b; Stotler et al. 2010), Italy (Boschetti et al. 2011), Iran (Bagheri et al. 2014b), and China (Chen et al. 2014; Du et al. 2016; Yu et al. 2013).

For instance, the groundwaters originated from seawater and evaporated seawater have similar $\delta^{81}Br$ values, ranging from 0.31 to + 0.27‰ (Bagheri et al. 2014b; Boschetti et al. 2011; Eggenkamp and Coleman, 2000; Eggenkamp et al. 2019a, b; Shouakar-Stash et al. 2007b, Shouakar-Stash 2008; Stotler et al. 2010), while $\delta^{81}Br$ values in groundwater originated from halite dissolution, crystalline massifs, and sedimentary structures range from + 0.62 to + 0.88‰, + 0.42 to + 3.07‰, and + 0.09 to + 1.22‰, respectively (Frape et al. 2007) (Fig. 2). The $\delta^{81}Br$ in deep groundwater in different strata in the Williston basin, North America, ranges from

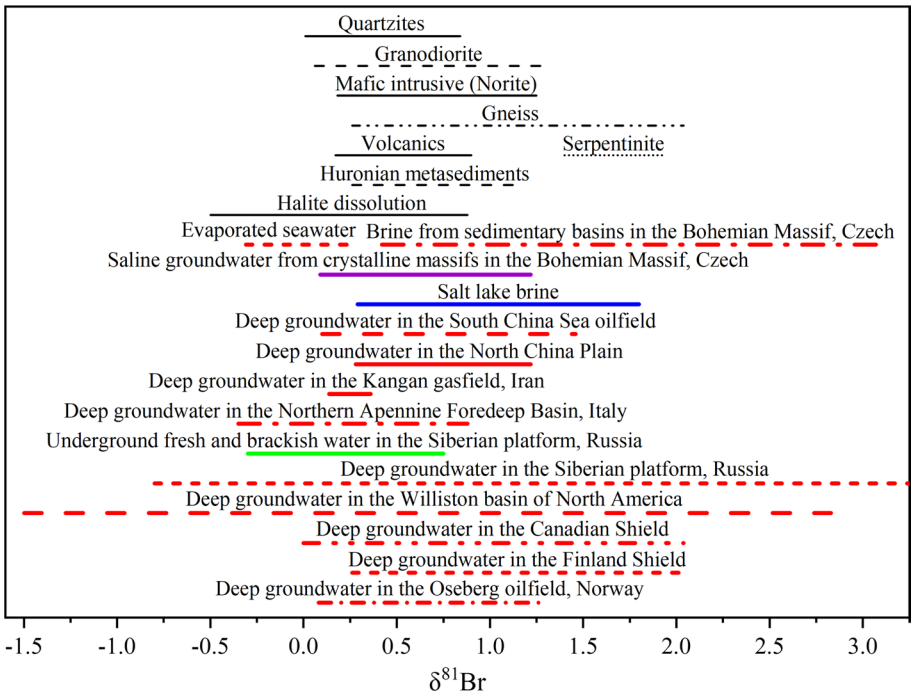

Fig. 2 $\delta^{81}Br$ values in different water types and rock mineral compositions in nature. References of $\delta^{81}Br$ are shown in Table 2. The typical ranges of $\delta^{81}Br$ in different environments vary significantly across various geological bodies and processes

Table 2 $\delta^{81}Br$ values in different water types and rock mineral compositions in nature

Types	$\delta^{81}Br‰$	References to the data sources
Deep groundwater in the Oseberg oilfield, Norway	0.08 to 1.27	Eggenkamp and Coleman 2000
Deep groundwater in the Finland Shield	0.26 to 2.04	Stotler et al. 2010
Deep groundwater in the Canadian Shield	0.01 to 2.04	Frape et al. 2004; Palmén and Hellä, 2003; Pitkanen et al. 1999; Shouakar-Stash et al. 2007a; Sie and Frape 2002, Sie 1999; Stotler et al. 2010
Deep groundwater in the Williston basin of North America	−1.5 to 2.83	Shouakar-Stash et al. 2006
Deep groundwater in the Siberian platform, Russia	−0.8 to 3.35	Shouakar-Stash et al. 2007b
Underground fresh and brackish water in the Siberian platform, Russia	−0.3 to 0.75	
Deep groundwater in the Northern Apennine Foredeep Basin, Italy	−0.35 to 0.88	Boschetti et al. 2011
Deep groundwater in the Kangan gasfield, Iran	0.136 to 0.36	Bagheri et al. 2014b
Deep groundwater in the North China Plain	0.28 to 1.22	Chen et al. 2014
Deep groundwater in the South China Sea oilfield	0.1 to 1.46	Yu et al. 2013
Salt lake brine	0.29 to 1.8	Chen et al. 2014
Saline groundwater from crystalline massifs in the Bohemian Massif, Czech	0.09 to 1.22	Frape et al. 2007
Brine from sedimentary basins in the Bohemian Massif, Czech	0.42 to 3.07	
Seawater and evaporated seawater	−0.31 to 0.27	Bagheri et al. 2014b; Boschetti et al. 2011; Eggenkamp and Coleman, 2000; Eggenkamp et al. 2019a, b; Shouakar-Stash et al. 2007b; Shouakar-Stash 2008; Stotler et al. 2010
Halite dissolution	−0.5 to 0.88	
Huronian metasediments	0.26 to 1.17	Frape et al. 2004; Shouakar-Stash et al. 2005; Stotler et al. 2009; 2010
Volcanics	0.17 to 0.9	
Serpentinite	1.4 to 1.94	
Gneiss	0.26 to 2.04	
Mafic intrusive Norite	0.18 to 1.25	
Granodiorite	0.06 to 1.29	
Quartzites	0.01 to 0.84	

−1.50 to + 2.83‰. The δ^{81}Br values in deep groundwater in the Upper Ordovician strata are more negative, while enriched in deep groundwater in the Upper Devonian strata (Shouakar-Stash et al. 2006). The δ^{81}Br in deep groundwater in Southern Ontario, Canada, ranging from −0.95 to + 2.31‰, suggests that deep groundwater is not affected by the recharge from recent or ancient meteoric waters. The δ^{81}Br values of deep groundwater in the early Silurian sandstone strata are more enriched than those in the middle Silurian carbonate strata, and the groundwater salinity increases with depth. The results indicate the mixing of deep groundwater in the early Silurian strata with brines (relatively low TDS) in the overlying Devonian strata (Shouakar-Stash et al. 2007a).

It is generally believed that physical processes (e.g., diffusion, ion filtration) have similar effects on the isotopic fractionation of Cl and Br (Eggenkamp and Coleman, 2009). The above descriptions show that the combination of Cl and Br stable isotopes can be employed to distinguish the source of deep groundwater salinity, such as halite dissolution and evaporated seawater (Eggenkamp and Coleman, 2000; Shouakar-Stash et al. 2005). For instance, the study on Br and Cl isotopes of deep groundwater in Siberian Platform, Russia, indicates that the natural variation range of δ^{81}Br values is relatively large, ranging from −0.80 to + 3.35‰ (Shouakar-Stash et al. 2007b). The δ^{37}Cl and δ^{81}Br values (ranging from −0.53 to + 0.04‰ and −0.11 to −0.27‰, respectively) indicate that the source of deep groundwater in the Cambrian sedimentary strata is the same as that of the crystalline brine. This study reveals that different groundwater types have different Cl and Br isotope compositions (Shouakar-Stash et al. 2007b).

In addition, the formation and evolution of deep groundwater in the North China Plain have been investigated based on the δ^{37}Cl and δ^{81}Br, and the result indicates that the deep groundwater in Jizhong Depression and Huanghua Depression is derived from meteoric waters (river and/or lake water) (Chen et al. 2014). The δ^{37}Cl and δ^{81}Br values in deep groundwater samples in the South China Sea oilfield (Beibuwan Basin and Zhujiangkou Basin) range from −1.33 to + 0.24‰ and + 0.1 to + 1.46‰, respectively (Yu et al. 2013). The δ^{37}Cl values in deep groundwater in Beibuwan Basin (−0.36‰ to + 0.24‰) are generally higher than those in Zhujiangkou Basin (−1.33 to −0.30‰). In contrast, the δ^{81}Br values of deep groundwater in the Beibuwan Basin (+ 0.10 to + 0.33‰) are relatively depleted compared with those in Zhujiangkou Basin (+ 0.18 to + 1.46‰). These results illustrate that the deep groundwater in Zhujiangkou Basin is greatly affected by evaporation in a relatively closed environment, whereas the primary source of deep groundwater in the Beibuwan Basin may be the halite dissolution by ancient meteoric waters through open fracture structures.

In summary, relative to the Cl stable isotopes, the research of Br stable isotopes is still in the initial stage and lacks comprehensive understanding. The effects of hydrogeochemical processes on Br isotope fractionation in the deep geological environment are still poorly understood. More investigation and research are required to understand the geochemical properties of Br isotopes and the major evolutionary processes affecting their fractionation mechanisms.

B isotopes

Background and importance

Boron (B), as a soluble element, appears mainly in the hydrosphere and upper crust sedimentary rocks (such as marine and lacustrine sediments, oceanic hydrothermal altered basalt, and seawater) and is continuously enriched during the process of migration of natural waters. As such, the B concentration is relatively high in seawater or lakes. Previous studies have shown that B has indicative significance to the sedimentary environments and many geological processes (Deyhle and Kopf, 2001, 2002; Hensen et al. 2004; Hüpers et al. 2016; Kasemann et al. 2004; Millot et al. 2007; Millot and Négrel 2007; Paris et al. 2010; Teichert et al. 2005;). It is an effective hydrogeochemical parameter to identify the water–rock interaction and regional metamorphism (Xiao et al. 1992).

The relative masses of ^{10}B and ^{11}B are significantly different (19.82 and 80.18%, respectively), resulting in the fractionation of B isotopes in different geological bodies and an extensive range of δ^{11}B values in nature (−75 to + 70‰) (He et al. 2013; Xiao et al. 2013). The sources of B stable isotopes are relatively concentrated with few interfering factors, and it is active in the water–rock exchange system (Casanova et al. 2001; Jiang, 2001). Therefore, B and its isotopes geochemistry can trace mixed or exchanged characteristics of the water–rock or different waters during the water circulation processes, facilitating the knowledge on the information of water source and circulation, water–rock interaction, and deposition stage of salt-forming (Cui et al. 2020; Deyhle and Hensen et al. 2004; Hüpers et al. 2016; Huang et al. 2020; Deyhle and Kopf 2001, 2002; Teichert et al. 2005; Zheng et al. 2017). Additionally, the B isotope composition in evaporite and brine has been widely utilized to trace paleosalinity and reconstruct marine and non-marine sedimentary environments (Fan et al. 2015; Liu et al. 2000; Paris et al. 2010; Tan et al. 2011; Vengosh et al. 1991a, b, 1992, 1995; Xiao et al. 1992; Zhang et al. 2013).

In the past 20 years, B isotopic system has been widely used in hydrogeochemical studies, particularly the geochemical behavior and fractionation of B isotopes in salt lakes or deep groundwater (Aggarwal et al. 2000; Hogan and Blum, 2003; Liu et al. 2000; Millot et al. 2011; Ni

et al. 2010; Vengosh et al. 1995) (Fig. 3, Table 3). Generally, B is relatively easy to be dissolved into the liquid phase during water–rock interaction. However, adsorption of B to clay minerals (Meredith et al. 2013; Pennisi et al. 2006; Vengosh et al. 1995; Xiao and Wang 2001; Zheng et al. 2017), co-precipitation with carbonate (Xiao et al. 2008), deposition of evaporite minerals (Liu et al. 2000; Vengosh et al. 1992), and evaporation of brines (Xiao and Wang 2001; Xiao et al. 2007a) result in the fractionation of B isotopes in the groundwater circulation. Thus, the B stable isotopic system has become an effective tool for tracing the source and evolution of deep groundwater (Aggarwal et al. 2000; Barth, 2000; Bouchaou et al. 2008; Casanova et al. 2001; Dotsika et al. 2010; Kloppmann et al. 2001; Lemarchand and and Gaillardet, 2006; Leybourne and Goodfellow, 2007; Meredith et al. 2013).

Application of B isotopes in deep groundwater studies

B is not conservative in groundwater. B contents change as a consequence of water–rock interaction, mixing with waters of different origins, and input of contaminants. If the B concentration in groundwater was originated from water–rock interactions, the $\delta^{11}B$ values of groundwater depended on the B isotope characteristics in the surrounding rocks (such as carbonates, evaporites, granites, and basalts) (Millot et al. 2007; Millot and Négrel 2007) (Fig. 3).

For example, measurements of $\delta^{11}B$ values (+8.7 to +23.1‰) in geothermal reservoirs from the Jiangling Basin, South China, indicate that the hot brines are derived from high-temperature water–rock interactions involving basalt and clastic rocks and recharge of meteoric waters, consistent with the results of traditional δD, $\delta^{18}O$, and $^{87}Sr/^{86}Sr$ isotopes in explaining water–rock interaction processes (Yu et al. 2021). The $\delta^{37}Cl$ (−0.2 to +0.7‰) and $\delta^{11}B$ (−6.2 to −5.9‰) in alkaline–chloride thermal waters in Yellowstone plateau volcanic field show that the water is likely originated from high-temperature leaching of chlorine, lithium, and boron from rhyolite ($\delta^{37}Cl$ and $\delta^{11}B$ values of +0.1 to +0.9‰ and −6.3 to −6.2‰, respectively) (Cullen et al. 2021). Moreover, the residual B in the liquid phase will be enriched in ^{11}B because of the adsorption effect of clay minerals or iron and aluminum oxides along groundwater flow at pH higher than 8, when the anion $B(OH)_4^-$ becomes more enriched. In contrast, ^{10}B preferentially enters the solid or gas phase (Clark, 2015).

The research on B isotopes in groundwater from the crystalline basement in the Alpine fore-land basin shows that the $\delta^{11}B$ values in fresh groundwater (−3.5‰ to 0.6‰) are lower than those in semi-saline groundwater (+6.4 to +17.6‰), while the higher B concentration in the former is related to the leaching of the basement surrounding rock. The B isotope composition in semi-saline groundwater indicates the sources of various crustal fluids (Barth, 2000). Additionally, in the Cornia Plain, the concentration of B in groundwater increases as it approaches the coast, while the isotope ratio persistently decreases. The primary source of B in groundwater and B isotope fractionation are determined by the absorption and desorption of B between the aquifer interstitial material and groundwater (Pennisi et al. 2006). Similarly, the $\delta^{11}B$ (from +44.4‰ to +53.9‰) in saline groundwater from

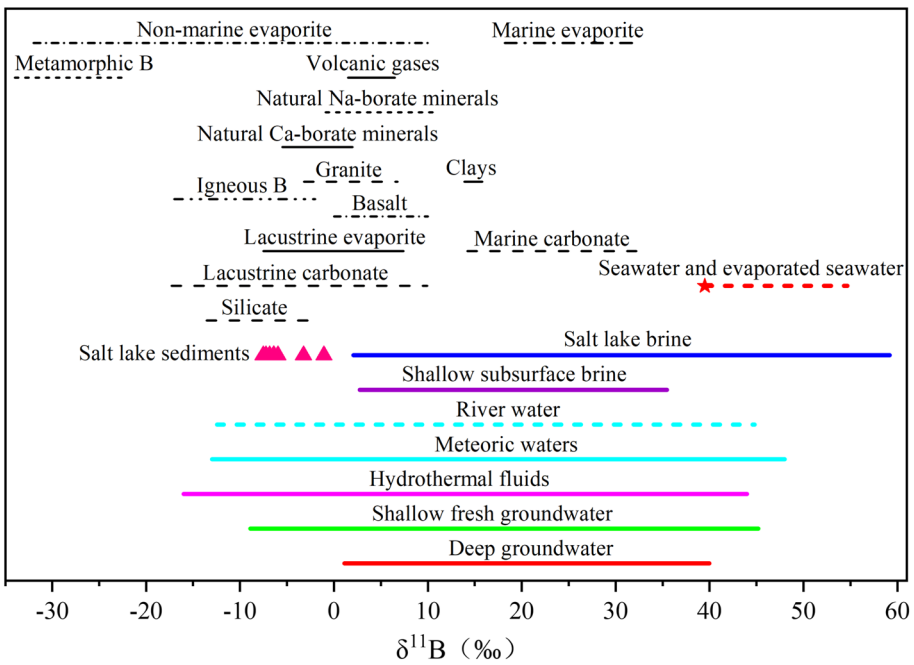

Fig. 3 $\delta^{11}B$ values in different water types or geological bodies in nature. References of $\delta^{11}B$ are shown in Table 3. Compared to the surrounding rock minerals, a wide range of $\delta^{11}B$ values is observed in different water bodies in nature. The $\delta^{11}B$ values in different environments are helpful to identify the origin and evolution of groundwater

Table 3 $\delta^{11}B$ values in different water types or geological bodies in nature

Types	$\delta^{11}B$‰	References to the data sources
Deep groundwater	1.1 to 39.99	Awadh et al. 2018; Boschetti et al. 2020; Cai et al. 2006; Casanova et al. 2001; Deyhle and Kopf, 2001; Harkness et al. 2017; Huang et al. 2020; Innocent et al. 2021a; Land and Macpherson, 1992; Li et al. 2013; Meredith et al. 2013; Millot et al. 2011; Ni et al. 2018; Ni et al. 2021; Phan et al. 2020; Vengosh et al. 1998; Warner et al. 2014; Williams et al. 2001, 2015; Wu et al. 2016; Zheng et al. 2017
Shallow fresh groundwater	−8.9 to 45.19	Barth, 2000; Bouchaou et al. 2008; Cary et al. 2013; Dotsika et al. 2010; Forcada and Evangelista 2008; Harkness et al. 2017; Hogan and Blum, 2003; Huang et al. 2020; Innocent et al. 2021b; Kloppmann et al. 2001; Leybourne and Goodfellow 2007; Louvat et al. 2011; Lü et al. 2014; Ma et al. 2015; Meredith et al. 2013; Millot and Négrel, 2007; Millot et al. 2007, 2011; 2012; Morell et al. 2008; Négrel et al. 2012; Pennisi et al. 2006; Vengosh et al. 1995; Warner et al. 2014; Xiao et al. 2013; Zheng et al. 2017
Hydrothermal fluids	−16.57 to 44	Aggarwal et al. 2000, 2003; Cullen et al. 2021; Dotsika et al. 2010; Elenga et al. 2021; Kasemann et al. 2004; Lu 2014; Lü et al. 2014; Millot et al. 2012; Musashi 1988, 2008; Oi et al. 1996; Palmer and Sturchio, 1990; Pennisi et al. 2000; Stefánsson et al. 2017; Vengosh et al. 1991b, 1994, 1996; Wu et al. 2016; Xiao et al. 1992; Xiao et al. 2013; Yamaoka et al. 2015; Yu et al. 2021; Yuan et al. 2014
Meteoric waters	−13 to 48	Chetelat et al. 2005; Chetelat et al. 2009b; Estelle et al. 2000; Lemarchand and Gaillardet 2006; Lu 2014; Mather and Porteous, 2001; Millot et al. 2010c; Rose et al. 2000; Rose-Koga et al. 2006; Warner et al. 2014; Xiao et al. 1992; Xiao et al. 2013; Yu et al. 2021; Zhao and Liu, 2010
River water	−12.47 to 44.8	Chetelat and Gaillardet, 2005; Chetelat et al. 2009a; Elenga et al. 2021; Estelle et al. 2000; Fan et al. 2015; Lemarchand and Gaillardet 2006; Lemarchand et al. 2000; Louvat et al. 2011; Pennisi et al. 2006; Rose et al. 2000; Vengosh et al. 1995; Xiao et al. 2007b; Zheng et al. 2017
Shallow subsurface brine	2.75 to 35.49	Barth, 2000; Cary et al. 2013; Du et al. 2019; Fan et al. 2015; Han et al. 2016; Kloppmann et al. 2001; Vengosh et al. 1999; Xiao et al. 1992
Salt lake brine	2.06 to 59.2	Du et al. 2019; Fan et al. 2015; Lü et al. 2013; Ma et al. 2015; Sun et al. 1993; Vengosh et al. 1991a, 1991b, 1995; Xiao et al. 1992; Xiao and Wang 2001; Xiao et al. 2013
Seawater	39.5	Foster et al. 2010, 2013; Hogan and Blum, 2003; Louvat et al. 2014; Shirodkar et al. 2003; Spivack and Edmond, 1987; Vengosh et al. 1989, 1992, 1999; Xiao et al. 2007a; Xiao et al. 2013
evaporated seawater	39.5 to 54.7	
Salt lake sediments	−7.54 to −1.06	Xiao et al. 1992; Xiao and Wang 2001
Silicate	−14.65 to −2.8	Wei et al. 2014
Lacustrine carbonate	−17.3 to 9.94	Wei et al. 2014; Zhang et al. 2017
Marine carbonate	14.2 to 32.2	Hemming and Hanson, 1992; Rae et al. 2011; Spivack and Edmond 1987; Vengosh et al. 1994
Lacustrine evaporate halite	−7.54 to 7.43	Du et al. 2019; Fan et al. 2015; Liu et al. 2000; Wei et al. 2014; Zhang et al. 2017
Marine evaporite	18.2 to 32	Bassett 1990; Barth, 1993; Paris et al. 2010; Swihart et al. 1986; Tan et al. 2009; Xiao et al. 2013; Zhang et al. 2013
Non-marine evaporite	−32 to 10.2	Barth, 1993; Bassett, 1990; Du et al. 2019; Fan et al. 2015; Pennisi et al. 2006; Swihart et al. 1986; Vengosh et al. 1994; Wei et al. 2014; Xiao et al. 1992, 2001; Xiao et al. 2013; Zhang et al. 2017
Basalt	0 to 10	Chaussidon and Jambon, 1993; Ishikawa and Nakamura, 1994; Leeman et al. 2004; Pennisi et al. 2000; Spivack and Edmond 1987; Vengosh et al. 1994; Xiao et al. 2013
Igneous B	−17 to −2	Pennisi et al. 2006; Swihart et al. 1986; Vengosh et al. 1994
Granite	−3.2 to 6.8	Jiang et al. 2008; Ishikawa and Nakamura, 1994; Spivack and Edmond 1987; Vengosh et al. 1994; 1995; Xiao et al. 2013
Clays	13.9 to 15.8	Ishikawa and Nakamura, 1994; Spivack and Edmond 1987; Vengosh et al. 1994
Natural Ca-borate	−5.5 to 2.0	Eisenhut et al. 1996; Vengosh et al. 1994, 1998; Xiao et al. 2013
Natural Na-borate	−0.9 to 10.5	
Volcanic gases	1.5 to 6.5	Kanzaki et al. 1979; Oi et al. 1996; Xiao et al. 2013
Metamorphic B	−34 to −22	Pennisi et al. 2006; Vengosh et al. 1994

the Australian hinterland is higher than those in seawater, indicating that the adsorption capacity of clay minerals causes the increase of $\delta^{11}B$ values during the water–rock interaction (Meredith et al. 2013). The $\delta^{11}B$ in formation water is 1.1‰ which is far from the value of seawater, indicating that ancient seawater could not be the source of the formation water from the Dameigou formation in the Northern Qaidam Basin (Zheng et al. 2017).

The $\delta^{11}B$ values in deep groundwater in Fuling Gasfield in the Sichuan Basin, China, range from + 23.9 to + 26.1‰, lower than seawater or evaporated seawater (Huang et al. 2020). The compositions of B isotopes and other isotopes results indicate that the deep groundwater may originate from evaporated seawater and is likely mixed with meteoric waters and undergoes water–rock interactions during the later circulation and evolution (Huang et al. 2020). Similar B isotope compositions in deep groundwater in the Marcellus marine shale formation in the Appalachian Basin, USA (Warner et al. 2014), and the Weiyuan Shale Gasfield in the Sichuan Basin, China, are found (Ni et al. 2018), with $\delta^{11}B$ ranging from + 31 to + 33‰ and + 22.5 to + 33.5‰, respectively. Also, the oilfield water from Jiuquan Basin, Northwestern China, with $\delta^{11}B$ values ranging from + 3.5 to + 39.7‰, is found to be originated from relicts of evaporated seawater and geothermal water undergoing intensive water–rock interactions with the Lower Cretaceous Xiagou Formation (Ni et al. 2021).

In contrast to groundwater, an extensive range of $\delta^{11}B$ values is identified in other geological bodies in nature (Coplen et al. 2002) (Fig. 3). The variation of $\delta^{11}B$ value in meteoric waters is relatively large (−13 to + 48‰). Similar to the concentration of B, it presents a continental effect that gradually decreases from the coast to the interior of the continent (Rose-Koga et al. 2006; Xiao et al. 2007a; Zhao and Liu, 2010). In contrast, the B isotope composition in deep groundwater in large sedimentary basins is more positive (Fig. 3), likely due to the water–rock interactions during the processes of groundwater circulation and evolution. In summary, these results depend on the principle that B isotopic compositions in different geological bodies are inconsistent, and the isotopic fractionations of B in groundwater are tightly linked to the adsorption capacity of clay minerals and other processes.

Li isotopes

Background and importance

Lithium (Li) is an alkali metal element in nature. It is a moderately incompatible element in the process of mantle melting and magma crystallization (Pasvanoğlua and Çelik, 2018) and is widely distributed in the mantle and crust, particularly in the upper crust. Therefore, the concentration of Li is high in both volcanic jets and hydrothermal fluids. The Li element in the river basin is primarily originated from meteoric waters and the weathering products of surface rocks (Clergue et al. 2015; Liu et al. 2015; Pogge von Strandmann et al. 2016, 2017; Wang et al. 2015). Li is leached out of the mineral rocks into the aqueous solution during chemical weathering and migrates to the ocean with the waters and is enriched in marine sediments (Wunder et al. 2006, 2007). The compositions of Li isotopes vary significantly in nature due to the isotope fractionation caused by the mass discrepancy between the two stable isotopes (7.5% ^{6}Li and 92.5% ^{7}Li) (Tomascak et al. 2003; Tomascak 2004; Zhang et al. 2021).

The fractionation of Li isotopes occurs in a series of geological processes, including weathering (Henchiri et al. 2014; Millot et al. 2010a, b; Négrel and Millot 2019; Rudnick et al. 2004; Zhang et al. 2021), metamorphic dehydration (Benton et al. 2013; Marschall et al. 2006; Zack et al. 2003), and magma-surrounding rock interactions (Lundstrom et al. 2005; Teng et al. 2006). Currently, the characteristics of Li isotopes make it a geochemical tracer in continental surface weathering (Dellinger et al. 2015; Teng et al. 2004; 2008; Ushikubo et al. 2008; Vigier et al. 2009; Wang et al. 2015), hydrothermal fluids and ocean crust alteration (Burton and Vigier 2012; Scholz et al. 2009; Vils et al. 2008), plate subduction, and circulation and evolution of crust–mantle materials (Agranier et al. 2007; Chan et al. 2009; Halama et al. 2008; Hamelin et al. 2009; Tian et al. 2015; Wagner and Deloule 2013). Li isotopic system is also employed in the studies of ore deposits (Elliott et al. 2004; Misra and Froelich 2012; Tang et al. 2007; Weber 2013) and high-temperature geochemistry, such as volcanic rocks (Schuessler et al. 2009).

The water–rock interactions result in fractionation of Li isotopes (Burton and Vigier 2012; Richter et al. 2003; Rudnick et al. 2004; Teng et al. 2006; 2009). As a result, ^{6}Li preferentially enters the solid phase, and ^{7}Li enters the liquid phase more easily (Chan and Hein, 2007; Godfrey et al. 2013; Pistiner and Henderson, 2003; Tomascak et al. 2003; Tomascak 2004; Wimpenny et al. 2010a). Hence, the active environmental geochemical properties of Li make it applicable in studying water circulation and evolution (Dellinger et al. 2014, 2015; Henchiri et al. 2014; Lemarchand et al. 2010; Liu et al. 2011; Misra and Froelich, 2012; Wang et al. 2015). Also, Li is enriched in the crustal materials associated with the mantle, and its liquidity is higher than other elements (Chan et al. 2002). These characteristics of Li stable isotopes make it worthwhile for hydrogeology research, especially in studies of deep groundwater in large sedimentary basins (such as basin basement and oilfield brine) (Godfrey et al. 2013; Harkness et al. 2017; Kloppmann et al. 2009; Meredith et al. 2013; Millot et al. 2007, 2010c; Millot and Négrel 2007; Négrel et al. 2010, 2012; Phan et al. 2020; Yu et al. 2013).

Application of Li isotopes in deep groundwater studies

Li isotopes display different compositions in minerals and waters (Fig. 4). The $\delta^{7}Li$ values in rock minerals are lower than those in waters due to the enrichment of heavy isotope ^{7}Li. The $\delta^{7}Li$ values in seawater, ranging from + 29.3

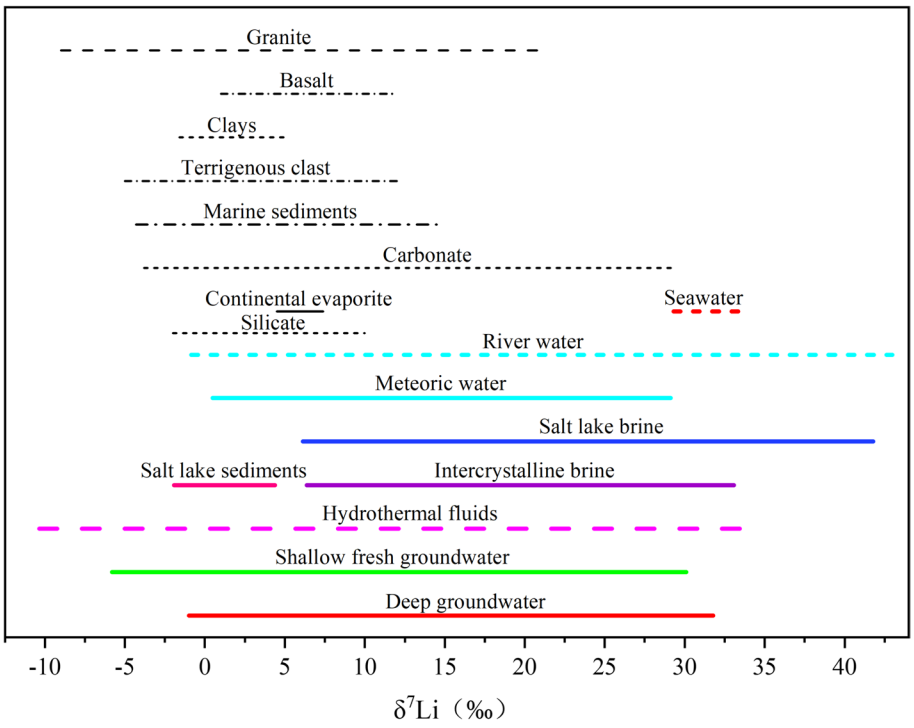

Fig. 4 δ^7Li values in different water types and rock mineral compositions in nature. References of δ^7Li are shown in Table 4. Compared to the surrounding rock minerals, an extensive range of δ^7Li values is observed in different water bodies in nature. It indicates that the isotopic composition of Li in the deep groundwater is dependent upon both the source and subsequent hydrochemical evolution

to 33.4‰, are more positive than those in meteoric waters (+0.49 to +29.13‰) (Fig. 4, Table 4). Additionally, large ranges of δ^7Li are shown in river water, shallow fresh groundwater, salt lake brine, and intercrystalline brine (Fig. 4, Table 4). The δ^7Li values in deep groundwater in sedimentary basins vary from −1 to +31.8‰, lower than seawater (Fig. 4). This is related to a series of prolonged water–rock interactions or evaporation, dilution, and a mixture of different waters in deep sedimentary environments. For instance, δ^7Li in thermal waters in Yellowstone plateau volcanic field ranges from −1.2 to +3.8‰ because Li is incorporated into hydrothermal alteration minerals (Cullen et al. 2021). Additionally, based on the values of δ^7Li (−0.3 to +2.1‰) and δ^{11}B (−8.0 to −8.1‰), Cl, Li, and B in travertine depositing calcium-carbonate thermal waters which discharge in the northern and southern Yellowstone plateau volcanic field are found to be derived from Mesozoic siliciclastic sediments (Cullen et al. 2021).

The reported oilfield waters containing Li are mostly derived from seawater, and even so, quite a few of them have low Li contents (Chan et al. 2002; Millot et al. 2011; Wang et al. 2018a; Huang et al. 2020). For instance, the δ^7Li values range from +18.2 to +30.8‰ in brine in Yellowknife, Northwest Canada, revealing that the source of deep groundwater is seawater. The fractionation of Li isotopes is caused by the adsorption of secondary minerals, resulting in the enrichment of ^{6}Li in secondary minerals and the high δ^7Li values in groundwater (Bottomley et al. 1999). The Li isotopic composition (+17.9 to +26.3‰) in the deep groundwater in the Heletz–Kokhav oilfield, Israel, is lighter than that in seawater, revealing that the groundwater is originated from seawater and undergoes a series of evolutionary processes such as water–rock interactions, evaporation, or dilution (Chan et al. 2002). Additionally, kerogen extracted from oil source rock has been shown to harbor high B and Li with low δ^{11}B and δ^7Li, similar to the composition in pore-filling clay minerals in reservoir rocks, such that it controls low δ^{11}B and δ^7Li in associated oilfield water (Teichert et al. 2020; Williams and Hervig, 2005; Williams et al. 2013).

However, geothermal and/or volcanic associations are the other mechanisms introducing Li into continental basins (Eccles and Berhane, 2011; Kesler et al. 2012; Benson et al. 2017). Much of the world's Li occurs as basinal brines in magmatic units, particularly in continental volcanic arcs (Chen et al. 2020). Past studies have also shown that B and Li released from organic macerals during thermal maturation (Teichert et al. 2020; Williams and Hervig 2005; Williams et al. 2013) can lead to enrichment of elemental B and Li in oilfield water with lower δ^{11}B and δ^7Li relative to the expected chemical and isotopic trajectory of evaporated seawater (Macpherson 2015; Macpherson et al. 2014; Ni et al. 2018; Pfister et al. 2017; Phan et al. 2020; Warner et al. 2014; Williams et al. 2001, 2015). As shown by the δ^7Li values in oilfield waters in the western Qaidam Basin (0.9 to 31.8‰) as well as a comparative study on deep groundwater and other waters (surface water, spring, salt lake brine) in the western Qaidam Basin, China, an association with the marine provenance for the oilfield waters can be excluded

Table 4 δ^7Li values in different water types and rock mineral compositions in nature

Types	δ^7Li‰	References to the data sources
Deep groundwater	−1 to 31.8	Araoka et al. 2014; Bottomley et al. 2003; Capo et al. 2014; Chan et al. 2002; Chapman et al. 2012; Harkness et al. 2017; Innocent et al. 2021a; Li et al. 2021; Macpherson et al. 2014; Macpherson, 2015; Meredith et al. 2013; Millot et al. 2011; Pfister et al. 2017; Phan et al. 2016, 2018, 2020; Rowan et al. 2015; Teichert et al. 2020; Wang et al. 2018a, b; Warner et al. 2014; Williams et al. 2015
Shallow fresh groundwater	−5.81 to 30.1	Boschetti et al. 2013; Godfrey et al. 2013; Harkness et al. 2017; He et al. 2020; Hogan and Blum 2003; Innocent et al. 2021b; Liu et al. 2015; Meredith et al. 2013; Millot et al. 2011; Négrel and Millot, 2019; Négrel et al. 2010, 2012; Pfister et al. 2017; Phan et al. 2016; Pogge von Strandmann et al. 2014; Scholz et al. 2010; Tomascak et al. 2003; Warner et al. 2014; Xiao et al. 1994c
Hydrothermal fluids	−10.36 to 34.8	Bernal et al. 2014; Chan et al. 1993, 1994; Cullen et al. 2021; Foustoukos et al. 2004; Godfrey et al. 2013; Millot and Négrel 2007; Millot et al. 2007, 2010a, 2011, 2012; Pogge von Strandmann et al. 2016; Scholz et al. 2010; Sturchio and Chan 2003; Tomascak et al. 2003; Tomascak 2004; Vigier et al. 2009; Xiao et al.1994c
Intercrystalline brine	6.37 to 27	Araoka et al. 2014; Bottomley et al. 1999; Godfrey et al. 2013; He et al. 2020; Li et al. 2021; Macpherson et al. 2014; Tomascak 2004; Xiao and Qi 1993; Xiao et al. 1994c
Salt lake brine	6.12 to 41.8	
Meteoric water	0.49 to 16.46	Clergue et al. 2015; Millot et al. 2010c; Négrel and Millot 2019; Pistiner et al. 2003; Vigier et al. 2009; Witherow et al. 2010; Xiao et al. 1994c
Seawater	29.3 to 33.4	Choi et al. 2010, 2013; Hogan and Blum 2003; Huang et al. 2010; James and Palmer, 2000a; Li and West 2014; Millot et al. 2004; Misra and Froelich 2009; Misra and Froelich 2012; Moriguti and Nakamura 1998a, b; Nishio and Nakai, 2002; Pogge von Strandmann et al. 2010; Rosner et al. 2007; Scholz et al. 2010; Tomascak et al. 1999; You and Chan, 1996; You et al. 1995
River water	−0.85 to 44	Burton and Vigier 2012; Clergue et al. 2015; Dellinger et al. 2014, 2015; Godfrey et al. 2013; Gou et al. 2019; He et al. 2020; Henchiri et al. 2014; Huh et al. 1998; 2001; Kisakürek et al. 2005; Lemarchand et al. 2010; Li et al. 2021; Liu et al. 2011; Liu et al. 2013, 2015; Millot et al. 2010b; Misra and Froelich, 2012; Négrel and Millot, 2019; Négrel et al. 2010; Pogge von Strandmann and Henderson 2015; Pogge von Strandmann et al. 2006, 2010, 2017; Tomascak et al. 2003; Tomascak, 2004; Vigier et al. 2009; Wang et al. 2015; Wimpenny et al. 2010b; Witherow et al. 2010
Salt lake sediments	−1.94 to 4.4	Godfrey et al. 2013; He et al. 2020; Witherow et al. 2010; Xiao and Qi 1993; Xiao et al. 1994a, b, 1994c
Silicate	−2 to 10	Coplen et al. 2002; Seitz et al. 2007; Sauzéat et al. 2015; Teng et al. 2004, 2008
Continental evaporite	4.5 to 7.4	Araoka et al. 2014; Wang et al. 2015
Carbonate	−3.8 to 29.5	Bouman et al. 2004; Chan et al. 1992, 1994, 2003; Chan and Hein 2007; Godfrey et al. 2013; Halama et al. 2008; James and Palmer, 2000b; Kalderon-Asael et al. 2021; Marriott et al. 2004; Moriguti and Nakamura 1998b; Nishio et al. 2006; Tomascak et al. 2008
Marine sediments	−4.3 to 14.5	Bouman et al. 2004; Chan et al. 1992, 2006; Hoefs and Sywall, 1997; Scholz et al. 2010; You et al. 1995, 2003; Zhang and Chen 1998; Chan and Kastner 2000
Terrigenous clast	−5 to 12	Hoefs and Sywall 1997; Zhang and Chen 1998; Chan and Hein 2007
Clays	−1.6 to 5	Chan and Hein, 2007; Leeman et al. 2004
Basalt	1 to 11.8	Bouman et al. 2004; Chan and Frey 2003; Chan et al. 2009; Elliott et al. 2004, 2006; Godfrey et al. 2013; Hamelin et al. 2009; Kisakürek et al. 2004; Leeman et al. 2004; Liu et al. 2011; Magna et al. 2004; Nishio et al. 2004, 2006, 2007; Pistiner and Henderson, 2003; Ryan and Kyle 2004; Schuessler et al. 2009; Teng et al. 2004, 2006; Tomascak et al. 2008; Tomascak, 2004; Wimpenny et al. 2010
Granite	−9 to 21.2	Bottomley et al. 2003; Bryant et al. 2003; Chan et al. 2006; Dellinger et al. 2014; James and Palmer 2000a; Jeffcoate et al. 2004; Liu et al. 2011; Magna et al. 2010; Misra and Froelich, 2012; Négrel and Millot, 2019; Nishio and Nakai, 2002; Phan et al. 2016; Pistiner and Henderson, 2003; Sauzéat et al. 2015; Teng et al. 2004, 2006, 2009; Tian et al. 2015; Tomascak et al. 2003; Tomascak, 2004; Wang et al. 2018a, b

based on the geological setting (Li et al. 2021). Instead, the source of Li-rich deep groundwater is originated from the dissolution of Li-rich minerals and controlled by various genetic types of water such as residual water from ancient lakes, surface water infiltrating along deep faults, and deep hydrothermal fluids (Li et al. 2021; Wang et al. 2018b).

In contrast, the Li isotopic composition and the brine concentration in Bolivia and northern Chile suggest that the brine source is the weathering products of volcanic

rocks rather than meteoric waters or hydrothermal fluids (Risacher and Fritz 2009). Li isotopic composition in groundwater from the Paleogene–Neogene sandy aquifer in Southwestern France demonstrates that the main controlling factor of Li concentration and isotopic composition is water–rock interactions during groundwater runoff (Négrel et al. 2012). Phan et al. (2016) have shown that the formation water is heterogeneous across the Appalachian Basin due to different degrees of diagenesis. For example, δ^7Li and δ^{11}B in formation water range from + 11.6 to + 11.9‰ and + 29.5 to + 30.1‰ in Marcellus shale gas wells in the Appalachian Basin (Phan et al. 2020), whereas δ^7Li value is ~ + 10‰ in southwestern Pennsylvania (Capo et al. 2014; Chapman et al. 2012; Phan et al. 2016), + 14 to + 15‰ in northcentral Pennsylvania (Phan et al. 2016; Rowan et al. 2015) and ~ + 9‰ in another place in Pennsylvania (Warner et al. 2014).

Because of the limited application of Li isotopes in oilfield water in sedimentary basins so far, the Li enrichment in the deep groundwater studies remains poorly understood, although it is a promising tool for tracing deep groundwater evolution.

Noble gas isotopes

Background

The chemical properties of noble gas, namely helium (He), neon (Ne), and argon (Ar) isotopes, are conservative in the mantle, crust, hydrosphere, and atmosphere (McIntosh et al. 2019). The terrestrial abundance of noble gas with stable isotopic compositions (^{3}He/^{4}He, ^{4}He/^{20}Ne, and ^{40}Ar/^{36}Ar) is relatively low. The primary sources of noble gas compositions in the geological fluids are air (or air-saturated water), crustal, and mantle fluids (Ballentine et al. 2002; McIntosh et al. 2019; Pinti et al. 2013; Wen et al. 2018). However, the isotopic ratios of noble gas vary from different geological reservoirs in nature. Even if a small amount of mantle-derived helium is added to the crustal fluid, it can be easily identified.

The noble gases dissolved in the water are mainly originated from the atmosphere (Winckler et al. 2001), and the ^{3}He/^{4}He, ^{4}He/^{20}Ne, and ^{40}Ar/^{36}Ar in the air are 1.386×10^{-6} (expressed in Ra), 0.318, and 295.5, respectively (Ballentine et al. 2002; Burnard et al. 1997; Gautheron and Moreira 2002; Ozima and Podosek 1983; Pedroni et al. 1999; Pinti et al. 2013; Winckler et al. 2001). The ^{3}He/^{4}He ratio in the crustal source is only 0.02Ra or even lower due to the large amount of radiogenic ^{4}He in the crust, and that in the upper mantle sourced He is higher, ranging from 7 to 9Ra (around 8Ra, Burnard et al. 1997). This is due to the higher ^{3}He prevalent in the mantle and its derived melting products, while is absent in the atmosphere (Ballentine et al. 2002; Hoke et al. 2000; Klemperer et al. 2013; Matsumoto et al. 2018; Pinti et al. 2013; Saar et al. 2005; Sano and Fischer 2013). The ^{4}He/^{20}Ne value in crust and mantle source is 0.2×10^8 (Yatsevich and Honda 1997) and 0.2×10^5 (Graham 2002), respectively. For Ar, the ratio of ^{40}Ar/^{36}Ar in the gas derived from the crust is greater than 295.5 due to the age accumulation effect of radiogenic ^{40}Ar, and its value increases with the age of source rocks. The gases from mantle, especially the upper mantle, has a high ^{40}Ar/^{36}Ar ratio, up to 10^4 (Burnard et al. 1997; Matsuda 1995; Poreda and Farley 1992).

Since they possess inert chemical properties in the mantle, crust, hydrosphere, and atmosphere, noble gas isotopes have been deployed as geochemical tracers of geological fluids (Ballentine et al. 2002; Birkle et al. 2016; Harkness et al. 2017; Pinti et al. 2013; Wen et al. 2018). These chemical properties make them promising trackers to identify the history of migration and evolution of groundwater (Darrah et al. 2014, 2015a, b; Gilfillan et al. 2009; Heilweil et al. 2015; Klemperer et al. 2013; Pinti et al. 2020).

Application of noble gas isotopes in deep groundwater studies

According to ^{3}He/^{4}He ratio (1.27×10^{-5}) and ^{40}Ar/^{36}Ar ratios (as high as 305) in the brine from three depressions along the axis of the Red Sea, a mantle origin of the helium is observed, and mantle-derived ^{40}Ar excesses of up to 3% of the total argon concentration are present in the brines and transported along with the mantle helium signal (Winckler et al. 2001). Additionally, relationships between ^{3}He/^{4}He and ^{40}Ar/^{36}Ar ratios and both δ^{37}Cl and δ^{81}Br in geothermal fluids from production wells in three Mexican fields suggest that geothermal fluid volatiles have three distinct sources (Pinti et al. 2013; 2020): (1) a local crustal source, enriched in radiogenic ^{4}He (R = 1.7–1.9 Ra), and halogens from brines with δ^{37}Cl and δ^{81}Br of + 0.1 and + 0.3‰, respectively; (2) the mantle wedge, with ^{3}He/^{4}He ratios of 6–6.5 Ra, typical of arc volcanism, and δ^{37}Cl and δ^{81}Br of −0.4 and −1.0‰, respectively, typical (for Cl) of fluids derived from the dehydration of serpentinite in the subducting slab; and (3) a mantle source, with ^{3}He/^{4}He ratios of 7.7–8.2Ra, typical of MORBs, and δ^{37}Cl and δ^{81}Br of + 0.9 and + 0.7‰, respectively (Pinti et al. 2013, 2020). Similarly, Wen et al. (2018) show that ^{3}He/^{4}He ratios in geothermal wells and hot springs in the Los Azufres Geothermal Field, Mexico, range from 4.21 to 7.93, pointing to the occurrence of a MORB-type mantle helium component, with contributions of crustal helium up to 53 and 18%.

As the age of the geological body increases, the Ra value gradually decreases with the more radiogenic ^{4}He produced by the radioactivity of uranium (U) and thorium (Th) (^{3}He is almost unchanged) in the course of geological history (Kennedy and van Soest 2006; Pinti et al. 2013;

Solomon et al. 1996; Zhou and Ballentine, 2006). If the recharge source is originated from meteoric waters, the $^3He/^4He$ ratios in the deep groundwater (R-value) will be close to or less than the Ra value. However, if deep groundwater circulates among the crustal rock minerals for a long time, the isotope composition of He in the deep groundwater will be close to the crustal rocks and minerals with a lower Ra value due to the sufficient water–rock interactions. On the contrary, the $^3He/^4He$ ratios in deep groundwater are higher if mixed or recharged by the mantle fluids.

As shown in Fig. 5, the air–mantle–crust mixing model for He and Ne isotopes (the $^3He/^4He$ and $^4He/^{20}Ne$ value) is drawn using atmospheric, crustal, and mantle sources as three end-members. The sources of noble gases in the groundwater can be identified by the model combined with the hydrogeological conditions in the study area. Similarly, the model can trace the sources and compositions of deep groundwater recharge and reveal the water–rock-–gas interactions during the circulation and evolution processes.

The percentage of contribution in different sources (air, mantle, and crust) in the deep groundwater samples can be calculated by solving mixing equations, and the specific equation and solution are as follows:

$$1 = A + M + C$$

where A, M, C denote the percentage of ^4He source from the air, mantle, and crust in the deep groundwater, respectively. The $^3He/^4He$ and $^4He/^{20}Ne$ ratios in air, mantle, and crust are as follows:

$$\left(^3He/^4He\right)_{air} = 1.38 \times 10^{-6},\ \left(^4He/^{20}Ne\right)_{air} = 0.318;$$

$$\left(^3He/^4He\right)_{mantle} = 1.0 \times 10^{-5},\ \left(^4He/^{20}Ne\right)_{mantle} = 0.2 \times 10^{5};$$

$$\left(^3He/^4He\right)_{crust} = 2.0 \times 10^{-8},\ \left(^4He/^{20}Ne\right)_{crust} = 0.2 \times 10^{8}$$

The $^3He/^4He$ ratios in deep groundwater in the North China Plain range from 0.108×10^{-6} to 1.194×10^{-6} (Matsumoto et al. 2018). The additional radiogenic ^3He causes the higher $^3He/^4He$ ratios in deep groundwater. The mixing model results for the He and Ne isotopes in groundwater reveal a mixture of the He components, including air, mantle, and crust. Contributions of each He source (air, crustal radiogenic, and mantle) are quantified by the above solving mixing equations. The ^3He budget of all groundwater samples is controlled by the mantle-derived ^3He (up to 30% of

$$\left(^3He/^4He\right)_{sample} = A \cdot \left(^3He/^4He\right)_{air} + M \cdot \left(^3He/^4He\right)_{mantle} + C \cdot \left(^3He/^4He\right)_{crust}$$

$$\left(^4He/^{20}Ne\right)_{sample} = A \cdot \left(^4He/^{20}Ne\right)_{air} + M \cdot \left(^4He/^{20}Ne\right)_{mantle} + C \cdot \left(^4He/^{20}Ne\right)_{crust}$$

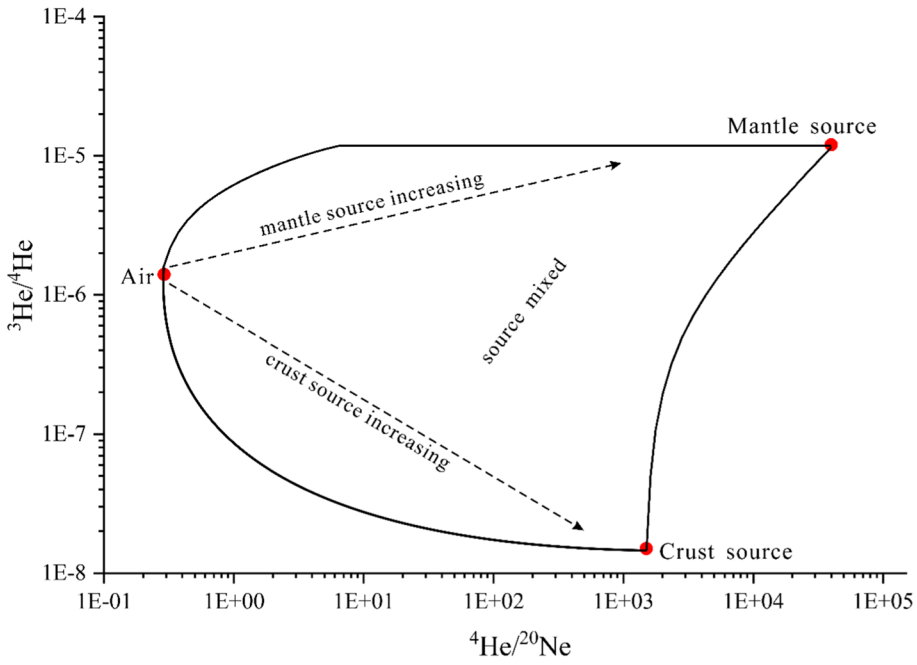

Fig. 5 The air–mantle–crust mixing model of He and Ne isotopes, with mixing lines connecting three end-members. Note that all data can be interpreted as mixing an atmospheric component and a terrigenic component, including crustal and mantle noble gases. The dotted line with arrows represents the trend of contribution by a He mantle-rich component or diluted progressively by the addition of radiogenic He (Crust)

the total) mixed with atmospheric components, and the crustal origin of ^{3}He component within the groundwater samples is negligible. In contrast, most ^{4}He is a predominantly radiogenic source of crustal components and a minor mantle contribution (only up to 6%) (Matsumoto et al. 2018).

Based on noble gas isotopes analysis of groundwater in the Appalachian region, USA, the migration of deep groundwater from deep to shallow and mixing with shallow groundwater over the geologic period is observed (Darrah et al. 2014, 2015a, b). Additionally, in an area for shale gas development in northwestern West Virginia, USA, with the increase of ^{4}He and ^{4}He/^{20}Ne, the ^{3}He/^{4}He ratios in groundwater decrease from 1.021Ra to 0.0166Ra, which is the uniform isotopic composition of crustal resource (Harkness et al. 2017). Similarly, the ^{40}Ar/^{36}Ar ratios in groundwater range from 294.50 to 308.77, reflecting a minor contribution of radiogenic ^{40}Ar. These results suggest that the source of groundwater is a mixture of meteoric waters and an exogenous source of shallow subsurface brines (Harkness et al. 2017). The ^{3}He/^{4}He ratios in two typical deep groundwater are 1.045×10^{-6} and 1.029×10^{-6} in the Paleogene–Neogene strata in western Qaidam Basin, China (Tan et al. 2011), illustrating that the deep groundwater is originated from meteoric waters and undergoes deep circulation and prolonged water–rock interaction processes (Tan et al. 2011).

Integration of multiple isotopes in groundwater studies

To sum up, the stable isotopes of Br and Cl have been used to trace the source of water and salt and the evolution process in deep groundwater, such as water–rock interactions and mixed dilution (Bagheri et al. 2014b; Chen et al. 2014; Eastoe et al. 2001; Richard et al. 2011; Sie and Frape, 2002; Stiller et al. 2009). In contrast, the Li isotope composition of groundwater in the weathering environment does not directly reflect the characteristics of lithology but is controlled by isotope fractionation during the process of water–rock interactions (Lemarchand et al. 2010; Millot et al. 2010b; 2011; Négrel et al. 2012; Pfister et al. 2017; Vigier et al. 2009). The Li isotope composition of waters is mainly controlled by the balance between the transportation of rock weathering products and the formation of secondary minerals in the runoff process. The variation of B isotope composition is caused by different mineral sources, the adsorption or desorption of the mineral phase, and the formation process of secondary minerals (Millot et al. 2007, 2010b, 2010c; Ni et al. 2021; Pennisi et al. 2000, 2006; Vigier et al. 2009; Zheng et al. 2017).

According to the above descriptions, using a single stable isotope is difficult to comprehensively explain the sources and evolution of large-scale groundwater systems, as deep groundwater has diverse sources and the complex characteristics of hydrochemical evolution. Thus, the integration of δ^{37}Cl, δ^{81}Br, δ^{11}B, δ^{7}Li, and noble gas isotopes should be considered as a robust method to trace the source of deep groundwater and identify the main processes controlling the chemical formation and evolution of deep groundwater in basins. Two central issues in deep groundwater studies are yet to be solved: (1) the sources of initial water in deep groundwater and its recharge routes; (2) the sources of salt in deep groundwater and the ways of enrichment for salt, as well as the processes of hydrochemistry evolution.

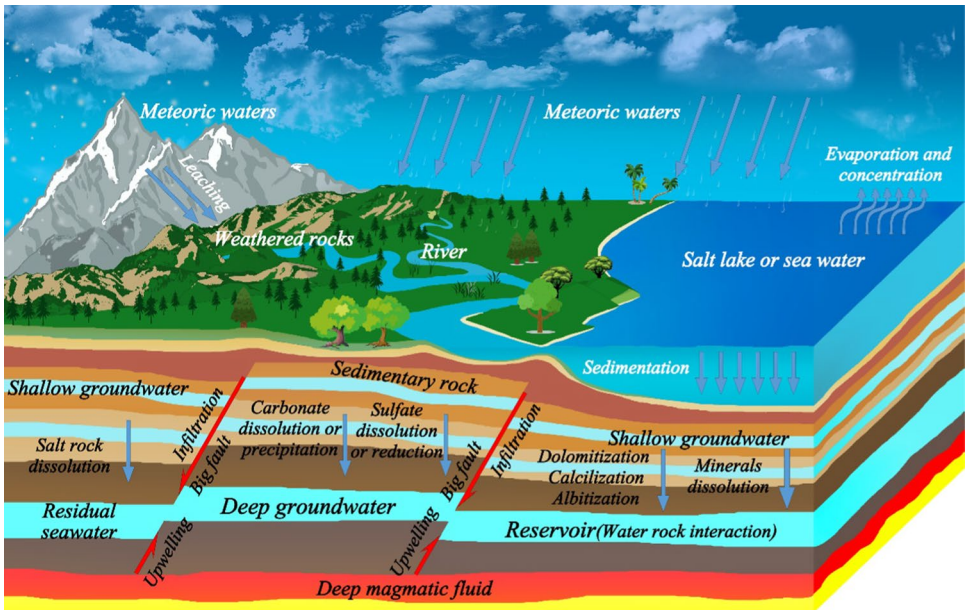

Fig. 6 Conceptual model for the formation and evaluation of deep groundwater in sedimentary basins. The deep groundwater is buried in the deep subsurface aquifer undergoing different geological processes above and beneath it

Source, formation, and evaluation of deep groundwater

Several possible sources of deep groundwater in sedimentary basins are described as follows (Fig. 6): (1) Syngenetic sedimentation water (marine and continental sedimentation water). The residual waters (or connate brines) are trapped and preserved during the formation of sedimentary strata, including residual ancient lake water, ancient seawater, or intercrystalline brines formed by dissolved salts; (2) Sources of meteoric water. It refers to the infiltration recharge by ancient or modern meteoric waters. However, continental sedimentation water also belongs to the origin of meteoric waters, and its age should be equivalent to the geological age of sedimentary strata; (3) Mixed sources. They include the mixing of waters with the same sources but different geological ages or the mixing of waters with different sources and geological ages; (4) Other sources, such as hydrothermal fluids (including waters primarily from the mantle and magmatic water from the residual fluids of magma) or metamorphic water coexisting with surrounding rocks during metamorphism.

The sources of salt in deep groundwater mainly include (1) salt released by weathering from marine or continental evaporite deposits; (2) the leaching of weathered surface rocks in basins; (3) volcanic materials and hydrothermal salts; and (4) the dissolution of sedimentary or crystalline rock reservoirs.

As the deep groundwater contacts with various rocks in the deep sedimentary environment of basins, the compositions of initial waters considerably change under physical, chemical, and biological processes in the complex water–rock interactions, leading to the formation of a complicated system (Kharaka and Hanor, 2003; Birkle et al. 2009a; 2009b; Lüders et al. 2010; Bagheri et al. 2014a; 2014b). The conceptual model for the formation and evaluation of deep groundwater in sedimentary basins include (Fig. 6): (1) dissolution, referring to the dissolution of evaporite minerals, especially halite with the infiltration of freshwater originating from meteoric waters into the salt rock system; (2) sedimentation, referring to the marine or continental sedimentation water trapped and preserved during the formation of sedimentary strata undergoing a series of complex chemical evolutions (e.g., the dissolution and precipitation of minerals and the biological reduction of sulfate) or a series of prolonged strong water–rock interactions (e.g., dolomitization, albitization, and cation exchange); (3) evaporation, referring to the evaporation and concentration of ancient seawater or ancient lake water in the original sedimentary environment to form residual brines with high TDS; (4) membrane filtration. Mudstone or shale in sedimentary basins can act as a weakly permeable geological membrane, resulting in the high TDS in the groundwater trapped on the inflow side of the membrane than that of fluids passing through the membrane; (5) mixing of different waters, including magmatic-derived fluids or mantle source water, seawater, freshwater originating from meteoric waters and connate brine, etc.

Conclusion

Because of the complicated geological and hydrogeological processes in the deep subsurface and the difficulties in the sampling, the formation and evolution of deep groundwater are poorly understood. In recent years, the source, formation, and evolution of deep groundwater have been traced by multi-isotopic techniques. The $\delta^{37}Cl$, $\delta^{81}Br$, $\delta^{11}B$, $\delta^{7}Li$, and noble gas are effective tracers for the source and formation of deep groundwater in large sedimentary basins. Although the distribution of isotopic characteristics in rock minerals and waters is different, there are overlapping isotopic values among different rock mineral or water types, which may cover their accurate source information and reduce their tracking effects. The overlap phenomenon is constraint by the mechanisms of isotope fractionation and is affected by various sources during deep groundwater formation and evolution processes. In most cases, the application of isotopes is only limited to distinguishing groundwater sources that have inconsistent isotope compositions in different geological bodies. Therefore, it is crucial to understand the equilibrium isotope fractionation factors and diffusivity of non-traditional stable isotopes through laboratory experiments, theoretical calculations, and analysis of well-characterized natural samples.

Further efforts are suggested, including the following aspects: (1) Further supplement and improvement for the non-traditional stable isotopic database of natural reservoirs in different geological environments. The fundamental theoretical work on the fractionation mechanism of isotopic tracers during the circulation and evolution processes of deep groundwater should be performed to obtain the geochemical behavior of isotopes and the main factors controlling their fractionation. (2) Comprehensive formation and evolution models of deep groundwater in the background of a specific sedimentary environment should be improved and strengthened based on the characteristics of non-traditional stable isotopes. (3) Comprehensive investigations based on traditional element geochemistry and multiple non-traditional isotopes should be conducted to overcome the one sidedness and limitation of single element and isotope in their respective tracing process.

(4) The chronology of noble gas in deep groundwater can be carried out to reveal the age of the deep groundwater where the noble gases exist. The physical significance of the age is when deep groundwater has undergone water–rock interactions in the sedimentary environment and contains information related to the formation and evolution of deep groundwater.

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Declaration

Conflict of interest Theauthors declare that they have no conflict of interest in this work.

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