Exchangeable elements forms in river surface sediments and their influence for migration process of typical elements: a case study from the Nalenggele River basin, Qaidam Basin

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Abstract

The occurrence of elements in sediments is significant to show the migration process of typical elements and their influence mechanism. The terminal salt lake regions of the Nalenggele River basin in Qaidam Basin is an important salt lake resource area rich in Li, K, B in the Qinghai-Tibet Plateau. But, the occurrence fraction of these important resource elements in the migration process is still poorly understood, which hinders the further understanding of the enrichment rule of resource elements in the salt lake area. In this paper, the occurrence states of typical elements (K Li B Ca Mg) in surface sediments of different hydrological environments in the Nalenggele River basin were studied based on the sequential extraction experiments. The results show that the exchangeable elements forms are different in different hydrological environments, which reflects the control of different geological processes on the distribution of exchangeable species of resource elements, including salt mineral precipitation, clay mineral adsorption and Fe-Mn oxide adsorption. In particular, the high content of exchangeable Li in the water-soluble fraction and Fe-Mn oxide fraction in the sediments of runoff plot and salt lake regions in study area indicates that the adsorption of Fe-Mn oxides and the precipitation of salt minerals may play an important role in Li isotope fractionation, besides the adsorption of clay minerals in general. Overall, this study has important implications for understanding the migration process of resource elements in the Nalenggele River basin.

1. Introduction

With the further study of element migration-enrichment process, people gradually realize that this process is not only related to element content, but also has important influence on element existence form. Different existence forms determine that elements will undergo different physical-chemical processes, and macroscopically show different geochemical behaviors (Ure et al., 2002) However, it is not easy to obtain accurate results because of the complex existence forms of elements, various control factors and limited measurement methods (Ure et al., 2002; Bacon and Davidson., 2008) Tessier et al. (1979) put forward sequential extraction method in the process of studying the occurrence state of heavy metals in sediments. The heavy metals in sediments were extracted by different extractants with different extraction intensities, and divided into corresponding occurrence states, and excellent application results were obtained. This method has been widely used in various research fields since then. However, due to the lack of standards for extractants and steps in the extraction process, there are many controversial results (Bacon and Davidson., 2008). Therefore, in the 1990s, the European Community (EU) proposed the BCR sequential extraction method, which provided a relatively reliable standard procedure for sequential extraction experiments (Rauret et al., 2000). It has become commonly used sequential extraction scheme, and in the first few steps of extraction process, the phase state (water soluble fraction, acid soluble fraction, Fe-Mn oxides fraction, organic fraction) is weaker than the residual fraction (Ure et al., 2002;Bacon and Davidson., 2008), indicating that the elements in these phases have stronger mobility, which could effectively reflect a series of effects of sediments on the geochemical behavior of elements in water during the interaction.
The Qaidam Basin has become the richest lithium brine resource and the highest degree of development area after decades of exploration on the Qinghai-Tibetan Plateau (Zheng et al., 2016; Li., 2020; Liu et al., 2021; Miao et al., 2022) which is the second largest lithium brine resource distribution area in the world (Munk et al., 2016; Liu et al., 2021). There are four major lithium-rich salt lakes, West Taijinaier Lake, East Taijinaier Lake, Yiliping Lake, and Senie Lake, which is the famous K and B resource area as well (Zhang, 1987; Miao et al., 2022; Gao et al., 2023). As one of the regions with the best lithium resource endowment in China, the source of lithium has attracted a lot of attention and different scholars have given different views (Zhang, 1987; Zhu et al., 1989; Zheng et al., 2016; Miao et al., 2022). At present, it is most widely accepted that the lithium in the terminal salt lakes mainly comes from the Kunlun Mountain hot spring and is recharged by the Nalenggele River (Yu et al., 2013; Li, 2020; Miao et al., 2022). According to previous investigations, the systematic understanding of salt lake evolution (Miao et al., 2022), salt mineralization and hydrological cycle model (Xu, 2015; Li, 2020) has been preliminarily established. However, with the deepening of the study, it is gradually found that there is a large amount of Li loss in the process of salt lake recharge from the mountain mouth of Nalenggele River (Li, 2020). Previous studies have found that the loss of this part of resources is closely related to the adsorption of clay minerals in sediments (Li, 2020). However, clay minerals are not the only minerals in the sediments, and the influence of other components on the resource is not clear. In addition, the effects of sediment on the migration processes of other elements except Li in the Nalenggele River basin are also poorly understood.

In this paper, we will study the surface sediments of the Nalenggele River basin by sequential extraction experiments to investigate the variation characteristics and the influencing factors of different fraction elements (K, Ca, Mg, Li, B, Sr). At the same time, in order to deepen the understanding of geochemical behavior of typical elements in the process of migration, Gansen and Dazaohuo river are selected as study contrast regions, in which the former is a weak stagnant water region with slow flow velocity (Xu, 2015; Miao et al., 2022; Gao et al., 2023), while the latter is a low Li content basin dominated by epigenetic weathering (Xu, 2015; Miao et al., 2022; Gao et al., 2023). Finally, the migration process of typical elements in surface sediment of Nalenggele River basin is systematically discussed and improves the understanding of the factors that control the migration process of typical elements.

2. Geologic setting

Qaidam Basin is located in the northern Tibetan Plateau (Fig. 1) with an average altitude from 2600 to 3000 m (Zhang, 1987; Yu et al., 2013; Miao et al., 2022). It is surrounded by the Qilian Mountains, the Eastern Kunlun Mountains and the Aljun Mountains, which altitudes all over 3500m (Zhang, 1987; Yu et al., 2013; Miao et al., 2022). The average annual rainfall in the basin is 16.09-189.73mm, but annual sunshine is over 3000 hours and evaporation is 1973.62-3183.04mm(Xu, 2015). Therefore, the climate of the Qaidam basin is extremely dry, which leads to the formation of many salt lakes (Zhang, 1987; Xu, 2015; Li, 2020; Miao et al., 2022). In addition, under the influence of compressive and twisting fracture, the depocenter in the basin had many changes in the Mesozoic. First, it was in Yiliping in the Eocene-Oligocene, second moved northeast in the Oligocene–Miocene, then to the southeast in the late Miocene-Pliocene, and last to the terminal Li-rich salt lakes (Li, 2022).
Nalenggele River is the largest internal river in the Qaidam Basin and the source of the terminal salt lakes region (Yiliping Lake, West Taijinaier Lake, East Taijinaier Lake, and Senie Lake) which is 435km long and the annual runoff is 12.9 x 108 m³/a with a drainage area of 21898 km² (Zhang, 1987; Tang et al., 2014; Miao et al., 2022). Its upstream is the Honghui River, which is predominantly fed by glaciers, meltwater of high mountains and hot springs (Xu, 2015; Li, 2020) and Chulakealagan River is predominantly fed by precipitation, glaciers and snow meltwater (Xu, 2015; Li, 2020). From entering the basin to the terminal Li-rich salt lakes, Nalenggele River water is closely associated with groundwater (Zhang, 1987; Zhu et al., 1989; Yu et al., 2013; Tan et al., 2012; Miao et al., 2022). It mainly recharges groundwater in the Kunlun Mountains and groundwater overflows in the FSAF (The first-stage alluvial fan) which one part flows into the East Taijinaier River with the runoff of the East Taijinaier River and another part forms the Wutumeiren River that flows eastward to Senie Lake (Li, 2020; Miao et al., 2022; Li et al., 2022; Gao et al., 2023). Because of the Nabei uplift barrier, the East Taijinaier River flows northward to form SSAF (The second-stage alluvial fan), where part of the river recharges groundwater and the other part enters the terminal Li-rich salt lakes (Xu, 2015; Li, 2020; Miao et al., 2022).

Yiliping, West Taijinaier and East Taijinaier salt lake are arranged in the NW-SE direction, which is the same direction as the main tectonic line in the basin (Zhang, 1987). Ganseng area is located on the west side of the Nalenggele River, which is mainly a spring formed by groundwater gushing out and the water velocity is slow (Miao et al., 2022; Gao et al., 2023) and the Dazaohuo River is located on the east which is formed by mountain meltwater, precipitation and groundwater recharge (Miao et al., 2022; Gao et al., 2023), neither river has a hydraulic connection with the Nalenggele River (Zhang, 1987; Miao et al., 2022; Gao et al., 2023). In surface sediments, the content of sand gradually decreased and the silt clay increased from the Kunlun Mountains to the terminal salt lake (Li, 2020; Li et al., 2022); the order of clay mineral content is illite, illite/smectite, chlorite and kaolinite, indicating that the regional weathering type is mainly physical weathering (Li, 2020; Miao et al., 2022); the salt minerals are mainly calcite and dolomite from the Kunlun Mountain to FSAF and the content of gypsum, halite, aragonite and polyhalite increases from SSAF to the terminal salt lakes (Miao et al., 2016; Li et al., 2022).

3. Materials and methods

3.1 Sampling and Preliminary Experiment

Sediment samples from 8 sites, including Kunlun Mountains, FASF, Wutumeiren River, Ganseng, Dazaohuo River, Yiliping Lake, West Taijinale Lake, East Taijinaier Lake (Fig. 1). The samples were dried until the sample weight did not change and ground to under 74µm, the instruments used in the sequential extraction experiment were cleaned with dilute nitric acid and dried.

After a long period of development, sequential extraction experiments formed two mainstream extraction schemes which are named Tessier and BCR (Tessier et al., 1979; Rauret et al., 2000; Bacon and Davidson, 2008). At present, BCR is most widely used, because it has a simple process, strong maneuverability and strong contrast between different regions (Wang et al., 2005). In general, researchers could mix the
extraction agent with the sample by shaking for 16 h at 25°C to allow the extraction agent to react fully with the sample (Rauret et al., 2000). But, some researchers proposed to make the extraction agent fully react with the sample through ultrasonic oscillation recently (Matong et al., 2016; Alan and Kara, 2019). Thus, it is necessary to determine which method that sufficiently mixes the extraction agent with the sample is the most suitable for this experiment, before formally starting the sequential extraction experiment.

A preliminary experiment was carried out to compare the effect of the two mixed methods in the experiment. Step 1: Three samples (1.6 ± 0.01g) were randomly selected and each sample was evenly divided into two groups. Then add 40ml of deionized water to the sample in a 50ml centrifuge tube. Step 2: The first group of the centrifuge tube was manually shaken and left for 16h at 25°C. The second group was shaken for 30 minutes by the ultrasonic apparatus (40kHz) at 25°C. Step 3: Centrifugation was used to separate the liquid from the solid residue at 3000g for 30 minutes. The supernatant liquid was transferred into reagent bottles by pipette after suction filtration through a millipore filter (2.2µm). The results (Fig. 2A) indicate that the extraction effect of the two methods is close, but the ultrasonic extraction efficiency is higher. Thus, the ultrasonic is used to accelerate the extraction efficiency in the sequential extraction experiment.

Frequency and temperature are the most important parameters in the process of ultrasonic oscillation. Recent studies have shown that the ultrasonic frequency of 20-80kHz mainly affects the physical form of clay minerals and 150-2000Hz will lead to obvious chemical changes (Chatel et al., 2015) and it is only 40KHz in this experiment. Thus, it would not damage the mineral structure and has little effect on the experimental results. But, the effect of temperature on the experimental results is not clear, thus in order to determine the optimal temperature of ultrasonic oscillation, two samples (3.2 ± 0.01g) were randomly selected and each sample was divided into four groups with temperatures of 30°C, 40°C, 50°C and 60°C. The experimental steps are consistent with the previous experiment and the results indicate that the temperature changes could not influence the extraction results of Li and B (Fig. 2B). Therefore, the ultrasonic oscillation parameters are set to 40kHz, 60°C and 30min.

### 3.2 Sequential extraction experiments

In the study area, evaporation is strong, which leads to precipitation of soluble salt minerals (Zhang, 1986; Li, 2020; Miao et al., 2022), thus the water-soluble extraction is the first step (Rauret et al., 2000). Residual elements are in the crystal lattice of insoluble minerals such as silicates which is not the focus of this study, therefore the step of residual fraction extraction is canceled and the residual lithium content is represented by subtracting the whole rock content of lithium from the total extracted lithium. The details of sequential extraction experiments are shown in Table 1. The operation of each step and the configuration of each extraction agent are in accordance with the standard requirements (Tessier et al., 1979; Rauret et al., 2000) and all experimental works were completed at Qinghai Salt Lake Research Institute, Chinese Academy of Sciences (ISLCAS).
<table>
<thead>
<tr>
<th>Step-target fraction</th>
<th>Extraction agent</th>
<th>Extraction condition</th>
</tr>
</thead>
</table>
| Step 1- water-soluble fraction | Add 40ml of deionized water in a 50ml conical bottom centrifuge tube | • Close with screw cap and keep tightly closed, shaking by ultrasonic apparatus for 30min at 60°C and 40kHz  
• Centrifuge at 3000g for 30 min,  
• supernatant liquid was transferred into a reagent bottles by pipette after suction filtration through a millipore filter(2.2µm).  
• Wash residue and screw cap with 20 mL of water, shaking by ultrasonic apparatus for 30min at 60°C and 40kHz  
• Centrifuge at 3000 rpm for 15 min, decant washing solution |
| Step 2- acid-soluble fraction | Add 32ml of 0.11mol/L CH$_3$COOH into residue from step 1 | • Close with screw cap and keep tightly closed, shaking by ultrasonic apparatus for 30min at 60°C and 40kHz  
• Centrifuge at 3000g for 30 min,  
• supernatant liquid was transferred into a reagent bottles by pipette after suction filtration through a millipore filter(2.2µm).  
• Wash residue and screw cap with 20 mL of water, shaking by ultrasonic apparatus for 30min at 60°C and 40kHz  
• Centrifuge at 3000 rpm for 15 min, decant washing solution |
| Step 3- Fe-Mn oxides fraction | Add 30ml of 0.5 mol /L NH$_2$OH.HCl into residue from step 2 | • Close with screw cap and keep tightly closed, shaking by ultrasonic apparatus for 30min at 60°C and 40kHz  
• Centrifuge at 3000g for 30 min,  
• supernatant liquid was transferred into a reagent bottles by pipette after suction filtration through a millipore filter(2.2µm).  
• Wash residue and screw cap with 20 mL of water, shaking by ultrasonic apparatus for 30min at 60°C and 40kHz  
• Centrifuge at 3000 rpm for 15 min, decant washing solution |
### 3.3 Analytical methods

The major elements (K, Ca, Mg) and the trace elements (Li, Sr, B) were measured by Inductively Coupled Plasma emission spectroscopy (ICP-MS) at Qinghai Salt Lake Research Institute, Chinese Academy of Sciences (ISLCAS), and the analytical precision is better than ±15%. The whole rock content of lithium was measured by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) according to the standard procedures (Rehkämper et al., 2001) at the Analytical Laboratory Beijing Research Institute of Uranium Geology (ALBRIUG) and the analysis accuracy is less than 10%.

### 4. Results

#### 4.1 Water-soluble fraction

The major (K, Ca, Mg) and trace elements (Li, Sr, B) content in the water-soluble fraction is presented in Table 2. K, Ca and Mg content ranged from 1.58 to 28.2mg/L, 8.13-115mg/L and 1.03-55.15mg/L, Li, Sr and B content ranged from 0.002 to 0.636mg/L, 0.085-1.58mg/L and 0.050-1.99mg/L and the proportion of water-soluble fraction elements in the experimental extraction fraction followed the order of B-49.2%, K-38.1%, Li-19.6%, Mg-5.8%, Sr-6.3%, Ca-2.5% (Fig. 3). The elements content are different, but the regional variation curve is parallel (Fig. 3; Fig. 5). Meanwhile, the variances of the different elements are obtained after Logarithmic normalization (Table.2), Li variance is significantly higher than other elements which may be caused by the high content of Li in the salt lake region and it could indicate that there are some special factors to make exchangeable Li enter the water-soluble fraction easily.
<table>
<thead>
<tr>
<th>Extraction fraction</th>
<th>Location</th>
<th>K(mg/L)</th>
<th>Ca(mg/L)</th>
<th>Mg(mg/L)</th>
<th>Li(mg/L)</th>
<th>Sr(mg/L)</th>
<th>B(mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-soluble</td>
<td>KLM(n = 3)</td>
<td>1.662</td>
<td>8.135</td>
<td>1.035</td>
<td>0.005</td>
<td>0.085</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>FASF(n = 9)</td>
<td>1.585</td>
<td>11.453</td>
<td>1.557</td>
<td>0.008</td>
<td>0.152</td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td>Wutumeiren River(n = 8)</td>
<td>1.893</td>
<td>9.031</td>
<td>1.136</td>
<td>0.010</td>
<td>0.124</td>
<td>0.073</td>
</tr>
<tr>
<td></td>
<td>West Taijinai Lake(n = 3)</td>
<td>9.059</td>
<td>22.685</td>
<td>19.213</td>
<td>0.223</td>
<td>0.656</td>
<td>1.345</td>
</tr>
<tr>
<td></td>
<td>East Taijinai Lake(n = 3)</td>
<td>8.494</td>
<td>55.390</td>
<td>7.182</td>
<td>0.224</td>
<td>0.801</td>
<td>0.774</td>
</tr>
<tr>
<td></td>
<td>Yiliping(n = 1)</td>
<td>28.210</td>
<td>115.145</td>
<td>55.155</td>
<td>0.636</td>
<td>1.064</td>
<td>1.993</td>
</tr>
<tr>
<td></td>
<td>Ganseng(n = 2)</td>
<td>6.105</td>
<td>47.603</td>
<td>11.445</td>
<td>0.012</td>
<td>1.583</td>
<td>0.138</td>
</tr>
<tr>
<td></td>
<td>Dazaohuo River(n = 2)</td>
<td>2.317</td>
<td>9.141</td>
<td>1.535</td>
<td>0.002</td>
<td>0.182</td>
<td>0.097</td>
</tr>
<tr>
<td></td>
<td>σ²</td>
<td>0.180</td>
<td>0.169</td>
<td>0.372</td>
<td>0.746</td>
<td>0.207</td>
<td>0.361</td>
</tr>
<tr>
<td>Acid-soluble</td>
<td>KLM(n = 3)</td>
<td>2.133</td>
<td>454.044</td>
<td>16.750</td>
<td>0.010</td>
<td>0.896</td>
<td>0.010</td>
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<td>FASF(n = 9)</td>
<td>2.278</td>
<td>577.135</td>
<td>22.709</td>
<td>0.018</td>
<td>1.992</td>
<td>0.030</td>
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<td>Wutumeiren River(n = 8)</td>
<td>2.780</td>
<td>531.087</td>
<td>24.439</td>
<td>0.017</td>
<td>1.338</td>
<td>0.020</td>
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<td></td>
<td>West Taijinai Lake(n = 3)</td>
<td>4.176</td>
<td>1215.447</td>
<td>81.423</td>
<td>0.092</td>
<td>8.540</td>
<td>0.727</td>
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<td>East Taijinai Lake(n = 3)</td>
<td>3.669</td>
<td>1004.021</td>
<td>65.184</td>
<td>0.065</td>
<td>11.039</td>
<td>0.416</td>
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<td>Yiliping(n = 1)</td>
<td>1.894</td>
<td>1030.291</td>
<td>74.099</td>
<td>0.066</td>
<td>10.290</td>
<td>0.603</td>
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<td>Ganseng(n = 2)</td>
<td>2.883</td>
<td>1367.799</td>
<td>40.668</td>
<td>0.019</td>
<td>18.148</td>
<td>0.178</td>
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<td>Dazaohuo River(n = 2)</td>
<td>4.308</td>
<td>730.563</td>
<td>25.403</td>
<td>0.014</td>
<td>2.266</td>
<td>0.052</td>
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<tr>
<td></td>
<td>σ²</td>
<td>0.016</td>
<td>0.028</td>
<td>0.062</td>
<td>0.118</td>
<td>0.213</td>
<td>0.455</td>
</tr>
<tr>
<td>Extraction fraction</td>
<td>Location</td>
<td>K (mg/L)</td>
<td>Ca (mg/L)</td>
<td>Mg (mg/L)</td>
<td>Li (mg/L)</td>
<td>Sr (mg/L)</td>
<td>B (mg/L)</td>
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<td>----------</td>
</tr>
<tr>
<td>Fe-Mn oxides fraction</td>
<td>KLM (n = 3)</td>
<td>1.633</td>
<td>30.937</td>
<td>10.440</td>
<td>0.053</td>
<td>0.090</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>FASF (n = 9)</td>
<td>2.201</td>
<td>120.549</td>
<td>29.811</td>
<td>0.076</td>
<td>0.296</td>
<td>0.036</td>
</tr>
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<td>Wutumeiren River (n = 8)</td>
<td>1.451</td>
<td>70.089</td>
<td>21.421</td>
<td>0.069</td>
<td>0.139</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>West Taijinaler Lake (n = 3)</td>
<td>6.701</td>
<td>582.802</td>
<td>201.871</td>
<td>0.496</td>
<td>3.547</td>
<td>1.003</td>
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<td>East Taijinaier Lake (n = 3)</td>
<td>2.681</td>
<td>469.507</td>
<td>111.608</td>
<td>0.196</td>
<td>3.267</td>
<td>0.329</td>
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<td></td>
<td>Yiliping (n = 1)</td>
<td>1.986</td>
<td>478.415</td>
<td>139.740</td>
<td>0.246</td>
<td>3.716</td>
<td>0.538</td>
</tr>
<tr>
<td></td>
<td>Ganseng (n = 2)</td>
<td>2.774</td>
<td>747.983</td>
<td>77.035</td>
<td>0.107</td>
<td>8.869</td>
<td>0.095</td>
</tr>
<tr>
<td></td>
<td>Dazaohuo River (n = 2)</td>
<td>2.733</td>
<td>95.893</td>
<td>55.808</td>
<td>0.083</td>
<td>0.176</td>
<td>0.108</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$</td>
<td>0.036</td>
<td>0.230</td>
<td>0.170</td>
<td>0.096</td>
<td>0.553</td>
<td>0.413</td>
</tr>
<tr>
<td>Organic fraction</td>
<td>KLM (n = 3)</td>
<td>1.435</td>
<td>6.607</td>
<td>5.789</td>
<td>0.022</td>
<td>0.031</td>
<td>0.006</td>
</tr>
<tr>
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<td>FASF (n = 9)</td>
<td>1.473</td>
<td>5.458</td>
<td>6.738</td>
<td>0.030</td>
<td>0.031</td>
<td>0.013</td>
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<td>Wutumeiren River (n = 8)</td>
<td>1.576</td>
<td>3.818</td>
<td>6.008</td>
<td>0.028</td>
<td>0.194</td>
<td>0.007</td>
</tr>
<tr>
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<td>West Taijinaler Lake (n = 3)</td>
<td>3.658</td>
<td>7.446</td>
<td>18.340</td>
<td>0.118</td>
<td>0.066</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>East Taijinaier Lake (n = 3)</td>
<td>2.087</td>
<td>6.217</td>
<td>7.964</td>
<td>0.054</td>
<td>0.115</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>Yiliping (n = 1)</td>
<td>1.033</td>
<td>2.651</td>
<td>4.969</td>
<td>0.028</td>
<td>0.041</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>Ganseng (n = 2)</td>
<td>3.172</td>
<td>31.832</td>
<td>22.620</td>
<td>0.059</td>
<td>0.200</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>Dazaohuo River (n = 2)</td>
<td>2.482</td>
<td>4.987</td>
<td>13.935</td>
<td>0.044</td>
<td>0.057</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>$\sigma^2$</td>
<td>0.031</td>
<td>0.088</td>
<td>0.055</td>
<td>0.050</td>
<td>0.095</td>
<td>0.111</td>
</tr>
</tbody>
</table>

4.2 Acid-soluble fraction
As illustrated in Table 2, K, Ca and Mg content ranged from 1.89 to 4.30mg/L, 454-1367mg/L and 16-81mg/L, Li, Sr and B content ranged from 0.010 to 0.092mg/L, 0.896-18.1mg/L and 0.010-0.727mg/L and the proportion of acid-soluble fraction elements in the experimental extraction fraction followed the order of Ca-75.3%, Sr-73.9%, Mg-34.0%, K-24.9%, B-22.3%, Li-10.8% (Fig. 3). The variation of elements content in acid-soluble and water-soluble fractions is generally similar but the curve of former is smoother than latter (Fig. 5). In parallel, The variances of the different elements are obtained in the same way as the water-soluble fraction (Table.2). K, Ca and Mg variances are small which is consistent with supersaturated precipitation of carbonate minerals over the entire region (Li, 2020; Miao et al., 2022) and the variance of the trace elements (Li, Sr, B) is large because of the increase in elemental content of the salt lake region.

4.3 Fe-Mn oxides fraction

Through the data of Fe-Mn oxides fraction in Table 2, K, Ca and Mg content ranged from 1.45 to 6.70mg/L, 30.9-747mg/L and 10.4-201mg/L, Li, Sr and B content ranged from 0.053 to 0.496mg/L, 0.090-8.86mg/L and 0.019-1.00mg/L and the proportion of Fe-Mn oxides fraction elements in the experimental extraction fraction followed the order of Mg-49.0%, Li-48.8%, Ca-22.9%, B-21.4%, K-19.8%, Sr-18.9% (Fig. 3). In this fraction, the content of Li has markedly increased by an order of magnitude, Ca is dramatic decline and other elements have without significant change compared to the previous fraction. Equally, the variation trend of element content has not significantly changed in the whole study area (Fig. 5) except for Sr, which may be mainly influenced by the sample from Ganseng (Table.2).

4.4 Organic fraction and Li content of Residual fraction

The major (K, Ca, Mg) and trace elements (Li, Sr, B) contents in the organic fraction are presented in Table 2. K, Ca and Mg content ranged from 1.03 to 3.65 mg/L, 2.65-31.8mg/L and 4.96-22.6mg/L. Li, Sr and B content ranged from 0.022 to 0.118mg/L, 0.031-0.200mg/L and 0.006-0.083mg/L and the proportion of organic fraction elements in the experimental extraction fraction followed the order of Li-18.0%, K-16.2%, Mg-9.4%, B-4.5%, Sr-2.4%, Ca-0.7% (Fig. 3). The element content of the Organic fraction is very poor than other fractions (Fig. 5), the model has been changed that the salt lake region has higher element content than other regions and the variance of elements is small (Table.2).

Li content of residual fraction (Kunlun Mountains = 20.5mg/L, FASF = 24.9mg/L, Wutumeiren River = 21.9mg/L, West Taijinaier Lake = 61.4mg/L, East Taijinaier Lake = 34.8mg/L, Yiliping = 40.7mg/L, Ganseng = 23.7mg/L, Dazaohuo River = 24.0mg/L) is obtained by subtracting the whole rock content of lithium from the total extracted lithium and the variances is 0.024.

5. Discussion

5.1 Distribution characteristics and control factors of different fraction elements
From the Kunlun Mountains to the FASF and Wutumeiren River, it belongs to the runoff area of Nalenggele Rive where hydrodynamic conditions are strong (Xu, 2015), its water element content is not as high as the salt lake regions (Fig. 4) and the overall environment is similar to Dazaohuo River (Xu, 2015). The hydrodynamic conditions of salt lake regions are weak and has obvious salt mineral precipitation (Xu, 2015; Miao et al., 2022; Gao et al., 2023). The surface water of Ganseng is formed by underground springs, and the water flow is relatively slow (Gao et al., 2023). Thus hydrological environment is more similar to salt lake regions. In this study, experimental results show (Fig. 3; Fig. 5) that the variation of exchangeable elements content in surface sediments shows approximately the same regularity as that of hydrological environment in this region which most obvious one is that the contents of different phase elements in runoff sediments are generally lower than salt lake regions (Miao et al., 2022). Therefore, combining the above research, it is speculated that the following reasons lead to. Firstly, This may be due to the fast water flow velocity in runoff area, short interaction time between water and sediment, and low element content in water, which could not make elements in water fully contact with sediment (Stumm et al., 1992; Xu, 2015; Li, 2020). Secondly, sediment grain size in runoff area is coarse, clay mineral content is low, and element fixation ability is much weaker than salt lake regions (Stumm et al., 1992; Li et al., 2022). Finally, the most important point is that the precipitation of salt minerals in runoff area is weaker than salt lake regions (Li, 2020; Miao et al., 2022). Although the hydrological environment of Gansen area is similar to the salt lake regions (Xu, 2015; Miao et al., 2022; Gao et al., 2023), the element content of water is very low (Miao et al., 2022), only slightly higher than runoff area. Therefore, the element content of different fractions of sediments in Gansen area is generally located between salt lake regions and runoff area. The contents of elements in different fractions of sediments mostly show high anomaly, due to the special hydrological environment in salt lake regions. However, because salt lakes are in different evolution stages, there are still slight discrepancy in the contents of elements in different fractions. Yiliping has entered the end of salt lake evolution (Li, 2020; Miao et al., 2022), most of the area has become dry salt flat; while East and West Taijinaier Salt Lake still receives the recharge of Nalengele River, the brine is relatively abundant (Li, 2020; Miao et al., 2022), and a large number of elements still exist in the brine, thus the contents of different fractions elements in the sediments of East and West Taijiner Salt Lake are generally lower than Yiliping. Therefore, the element contents in different sediment fractions in the study area are obviously affected by hydrological environment.

In addition, The uneven distribution of different elements in different phases is also obvious (Fig. 5). For example, Ca, Mg, Sr and B are mainly distributed in one or two fractions, and this distribution pattern that does not change with the region is more likely to be determined by the properties of the elements. The content of Ca is high in the study area water (Miao et al., 2022) and the carbonate minerals saturation index are greater than 0 such as calcite and dolomite (Li, 2020), which is the probably main reason for Ca, Mg mainly exist in acid-soluble fraction. Ca and Sr may be isomorphic because the ionic radius (Sr$^{3+}$=11.2nm; Ca$^{2+}$=11.8nm) of these two elements is close (Liu et al., 2016) that is the reason why Sr mainly exists in acid soluble fraction. Fe-Mn oxides fraction is another main fraction of Mg that could be due to the isomorphism of Mg$^{2+}$ with Fe$^{2+}$ and Mn$^{2+}$ (Liu et al., 2017). B mainly exists in water soluble fraction, which is consistent with previous studies that B is easily adsorbed by clay minerals, Fe-Mn
oxides and other solids in the process of migration (Debure et al., 2018). The main phase states of K and Li will change with the different regions in the study area, but they mainly exist in one phase state in the regions with similar environment. Thus, it is speculated that besides the properties of elements, environmental changes will also affect the occurrence of elements. Generally, K is easy to precipitate with halite and carnallite in salt lake, and these minerals basically belong to soluble minerals (Zhang, 1987), hence the content of water-soluble K is relatively high in salt lake regions; however, there is no large amount of halite and carnallite precipitation in runoff area (Li, 2020), and the precipitation of carbonate minerals in the whole study area is relatively significant, as a result, K is mainly distributed in acid-soluble fraction in runoff area. The most interesting is Li, which mainly occurs in Fe-Mn oxides fraction in runoff area and in water soluble fraction in salt lake regions. Although B has many similar chemical properties with Li (Liu et al., 2017), the different occurrence states in sediments still indicate that Li still has its own unique characteristics in the process of interaction between water and sediments. Therefore, this interesting phenomenon requires further discussion.

5.2. Model of occurrence of Li and B in sediments

B and Li have many similarities in chemical properties, for example they are both lithophile elements, mainly distributed in the crust surface, easy to migrate with fluids (Liu et al., 2017), which leads to many similar geochemical behaviors of B and Li. However, in this study, the distribution of B and Li in different phases showed obvious differences, indicating that the factors controlling the occurrence of B and Li in sediments were not the same. Li mainly exists in Fe-Mn oxides in runoff area (Fig. 3; Fig. 5) and the trace elements usually enter Fe-Mn oxides with coprecipitation, adsorption, surface complex formation, ion exchange, and penetration of the lattice (Chao and Theobald, 1976; Shuman, 2018). While Li does not precipitate with Fe-Mn oxides which is more favored to enter the fluid phase and with +1 oxidation state (Tomascak et al., 2016), it may be possible for Li to enter the clay minerals and coprecipitate with Fe-Mn oxides (Jiang, 2008). In addition, adsorption of Fe-Mn oxides could be divided into chemisorption and physical adsorption (Li, 2001). But, the physical adsorption could not exist in the Fe-Mn oxides fraction which is easily damaged by water molecules, thus, chemisorbed Li is more likely to exist in the Fe-Mn oxides fraction which could not be displaced by H⁺ (Jiang, 2008). Meanwhile, it could be possible for exchangeable Li to enter the structure of Fe-Mn oxides, for example, Li is usually present in the form of (Al, Li)-OH octahedra (Fig. 6) in Lithiophorite (Post and Appleman, 1994). In addition, Li could enter the Fe-Mn oxides fraction through surface complex formation and ion exchange during long time contact with sediments in theory (Nielsen et al., 2005; Kim et al., 2008). Hence, all of these ways could be the model of the occurrence of Li in the Fe-Mn oxides fraction. But chemisorption and coprecipitation which could not require a long time and a stable environment (Stumm et al., 1992) is probably the main model of the occurrence of Li in Fe-Mn oxides fraction.

Traditionally, Li in the water-soluble fraction is mainly thought to be adsorbed by solid particles such as clay minerals (Fig. 7). But in this study, Li content in the water-soluble fraction has increased significantly in salt lake regions than other positions (Fig. 4; Fig. 5) and the differences in the type of clay minerals are slight between different regions (Li et al., 2022). Meanwhile, from the hydrological environment, the
runoff area environment is turbulent, not as stable as the environment in salt lake regions and Gansen, but the Li content in water-soluble fraction in runoff area is lower than salt lake regions and similar to Gansen (Xu, 2015; Miao et al., 2022; Gao et al., 2023). Therefore, the adsorption of clay minerals and hydrological environment are not the key factors for elevated Li content in water-soluble fraction in salt lake regions. In addition to the above differences, the biggest discrepancy between salt lake regions and runoff area is the precipitation of salt minerals (Xu, 2015; Miao et al., 2022; Gao et al., 2023). Though, the concentration of Li in brine is not high enough to precipitate sulfate or carbonate (Li, 2020; Ma et al., 2016), it is theoretically possible for Li to be carried from water into sediments with the precipitation of other salt minerals (Garcia et al., 2020). Previous studies have shown that the most important salt minerals in salt lake regions are halite, followed by sulfate minerals and carbonate minerals (Li, 2020). Among them, halite is often mixed with many impurities and is easily soluble in water (Zhang, 1987), which may be one of the sources of water-soluble Li. In addition, in combination with the low content of Li in acid solution, it can be found that Li is not easily carried out with the precipitation of carbonate minerals, and the solubility of carbonate minerals in water is not high (Zhang, 1987). At the same time, sulfate minerals precipitated from salt lakes, such as gypsum and polyhalite, mostly contain crystal water and are easily soluble in water (Zhang, 1987; Li, 2020). Therefore, it is also possible that Li enters the water-soluble fraction through crystal water. Similarly, the effect of salt mineral precipitation on B occurrence is also worth discussing. In the runoff area, only dolomite, calcite, aragonite and magnesite are in saturated precipitation state, and B could be adsorbed on the surface of carbonate in the form of $\text{B(OH)}_4^-$ (Yang et al., 2018), which indicates that the adsorption of carbonate minerals is one of the factors affecting the occurrence of B in water solution. Although the proportion of water-soluble boron in salt lake regions decreased, the content of water-soluble boron was still significantly higher than other areas, that is, which means that the content of water-soluble boron increased with the increase of salt mineral types and quantities. It is further proved that the precipitation of salt minerals has an important effect on boron entering into water soluble state in sediments.

Generally speaking, Li and B enter sediments through traditional ways such as adsorption of clay minerals and Fe-Mn oxides in runoff area, the influence of salt minerals on the occurrence state of Li and B could not be ignored, and different salt minerals have different effects on the occurrence state of Li and B.

### 5.3. The influence for migration process of key elements

In this study, the extraction of residual fraction was not executed, which means that the elements originally existing in the original mineral lattice were not released, thus the extracted elements were more from the exchange between sediments and the external environment (Tessier et al., 1979; Rauret et al., 2000). In the study area, the contact between water and sediment is the closest (Xu, 2015; Li, 2020). Meanwhile, the samples collected in this study basically cover different parts of Nalengele River Basin. Therefore, different occurrence states of elements could reflect the geochemical behavior of typical elements in the process of mutual contact between water and sediment, further reflecting the influence of sediment on the migration process of typical elements in water. The content of Ca and Mg in the study
area is very high (Fig. 4), and the strong evaporation makes the whole Nalengele River basin appear the characteristic of supersaturated carbonate precipitation (Xu, 2015; Li, 2020), which finally causes the extremely high content of acid-soluble Ca and Mg. In addition, although the main occurrence phases of B and Sr are different, it could be seen from the above discussion that the influence of carbonate minerals on the geochemical behavior of these in sediments could not be ignored and is an important factor determining the distribution of boron and strontium in sediments. K content is lower than Ca and Mg in each phase, and only slightly increased in salt lake regions, indicating that adsorption of clay minerals and precipitation of carbonate minerals in runoff area did not make a large amount of K enter sediments from water. In salt lake regions, it content entering sediments increased due to the influence of salt mineral precipitation and clay mineral adsorption, but overall, it migration process was less affected by sediments than Ca and Mg.

Because the terminal salt lake is an important Li resource enrichment area, it is important to understand the influence of sediments on Li behavior during migration. According to the previous discussion, Li mainly enters the Fe-Mn oxides fraction by chemical adsorption or co-precipitation in the runoff region (Chan and Hein, 2007; Wimpenny et al., 2010; Wimpenny et al., 2015). Chemisorption involves the formation and breaking of chemical bonds, and in this process, the two isotopes of lithium will choose different chemical bond types due to their own energy differences (Schauble, 2004; Liu et al., 2021), which may lead to isotopic fractionation. The specific performance in Fe-Mn oxidation state is that $^6$Li is more easily adsorbed (Chan and Hein, 2007; Wimpenny et al., 2010; Wimpenny et al., 2015), resulting in the increase of $\delta^7$Li value in water. In salt lake regions, Li mainly enters the halite and the crystal water of sulfate minerals, in which chemical bond formation is not involved in the process of entering sulfate mineral crystal water, thus it is speculated that Li isotope fractionation would not occur, and during the crystallization process of halite, if Li is located in the crystal lattice vacancy (Garcia et al., 2020), the formation of chemical bonds could cause Li isotope fractionation. Therefore, there are factors that lead to Li isotope fractionation in the process of it entering sediments from water. Although the specific contribution of the above processes to the Li isotope fractionation could not be determined, this trend is well verified by the previous measurements of $\delta^7$Li values in the water of the Nalengele River Basin (Fig. 8; Miao et al., 2022).

In conclusion, the typical elements in the Nalengele River Basin are affected by different factors in the migration process, in which Ca, Mg and Sr enter the sediment from the water mainly through the precipitation of carbonate minerals, and the phase states of the sediment have little effect on K. B is mainly absorbed into sediments by carbonate minerals, Li is influenced by Fe-Mn oxides in runoff area, and is significantly influenced by salt minerals precipitation in salt lake regions, especially halite and soluble sulfate minerals. Therefore, the precipitation of salt minerals is an important way for typical elements to enter sediments, followed by the adsorption of clay minerals and Fe-Mn oxides.

6. Conclusions
In order to fully understand the effects of different components in sediments on the migration and enrichment of typical elements in salt lakes. We systematically collected surface sediment samples from Nalengele River Basin, Gansen and Dazaohuo River. Through sequential extraction experiments, the occurrence states of different phase elements and their influence on migration and enrichment process were analyzed and discussed in detail. The experimental results show that the contents of various phase elements in sediments of salt lake region are generally higher than runoff area. Besides, the phase distribution patterns of typical elements in sediments are different, because of the different chemical properties of different elements. Ca, Mg and Sr mainly exist in acid-soluble fraction in sediments, which is controlled by carbonate mineral precipitation, K mainly exists in water-soluble fraction, which is controlled by clay mineral adsorption and salt mineral precipitation, B mainly exists in water-soluble fraction, which is controlled by salt mineral adsorption, and Li mainly exists in water soluble fraction and Fe-Mn oxides fraction, which is controlled by Fe-Mn oxide adsorption in runoff area and clay mineral adsorption, halite and sulfate mineral precipitation in salt lake region. The above processes could make δ^7Li values in the water increase to some extent, which is consistent with the previous measurement results of δ^7Li values of water in the Nalengele River Basin. Generally speaking, in the whole study area, the precipitation of salt minerals is the key factor affecting the migration of typical elements from water to sediments, and then there is adsorption of clay minerals and Fe-Mn oxides. Therefore, from mountain area to salt lake regions, the precipitation of salt minerals is of great significance to the loss of element resources in sediments. Future research is needed to further quantify the amount of resources lost during salt precipitation in order to improve the utilization of salt lake resources and increase economic benefits.

**Declarations**

**Author Contribution**

H.Z and L.M. wrote the main manuscript text and prepared all figures. All authors reviewed the manuscript.

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**References**


**Figures**

![Figure 1](image-url)
Regional geological, hydrological settings and sampling stations of Nalenggele River Basin, Ganseng and Dazaohuo (modified after Miao et al., 2022).

**Figure 2**

The results of the preliminary experiment (XTX30-40 comes from the pit profile in West Taijinaier Lake)
Figure 3

Different fraction proportions of elements and the total amount of experimental extraction. TEC=Total extraction content

![Graph showing different fraction proportions of elements](image)

- Water-soluble fraction
- Acid-soluble fraction
- Fe-Mn oxides fraction
- Organic fraction

Figure 4

K, Ca, Mg, Li, Sr, B content in different types of water of Nalenggele River Basin, Ganseng and Dazaohuo. These data are from Miao et al., 2022

![Graph showing K, Ca, Mg, Li, Sr, B content](image)
Figure 5

Point plot of content of different fraction elements.
Figure 6

The structure of Lithiophorite. Layer of MnO$_6$ (blue) and (Al, Li)(OH)$_6$ (red) are stacked on top of each other (modified after Post., 1999).

Figure 7

The schematic diagrams of positions of the Li$^+$ in clay minerals. The interlayer of smectite is the main part of adsorbing Li (modified after Vigier et al., 2008).

Figure 8
Lithium isotope composition of water from Kunlun Mountain to Salt Lake. These data are from He et al. (2020) and Miao et al. (2022)