

Article

# Distribution Characteristics and Influencing Factors of Uranium Isotopes in Saline Lake Waters in the Northeast of Qaidam Basin

Chen Zhao<sup>1</sup>, Pu Zhang <sup>1,2,\*</sup>, Xiangzhong Li <sup>3,4,\*</sup>, Youfeng Ning <sup>2</sup>, Liangcheng Tan <sup>4</sup>, R. Lawrence Edwards <sup>5,6</sup>, Xiunan Yao <sup>1</sup> and Hai Cheng <sup>2,5</sup>

- <sup>1</sup> College of Urban and Environmental Sciences, Northwest University, Xi'an 710127, China; 13186237444@163.com (C.Z.); nwuchyxn@163.com (X.Y.)
- <sup>2</sup> School of Human Settlements and Civil Engineering, Xi'an Jiao Tong University, Xi'an 710061, China; yfning@mail.xjtu.edu.cn (Y.N.); cheng021@xjtu.edu.cn (H.C.)
- <sup>3</sup> Research Center for Earth System Science, Yunnan University, Kunming 650500, China
- <sup>4</sup> State Key Lab of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China; tanlch@ieecas.cn
- <sup>5</sup> Department of Earth and Environmental Sciences, University of Minnesota, Minneapolis, MN 55455, USA; edwar001@umn.edu
- <sup>6</sup> School of Geography, Nanjing Normal University, Nanjing 210023, China
- \* Correspondence: zhangpu357@xjtu.edu.cn (P.Z.); xzhli04@163.com (X.L.)

Received: 28 November 2019; Accepted: 11 January 2020; Published: 17 January 2020



Abstract: Four saline lakes in the northeast of Qaidam Basin were selected to explore the distribution characteristics and influencing factors of uranium isotopes in lake waters with high evaporation background. The <sup>238</sup>U concentration and the activity ratios of <sup>234</sup>U/<sup>238</sup>U ([<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub>) showed that there was no significant change in the same lake, but there was a certain degree of difference in the distribution between different lakes. We found that aqueous <sup>238</sup>U concentration within a certain range increased with an increase in TDS (total dissolved solid) and salinity, as was also the case with pH. As in natural waters, the pH affects the speciation of <sup>238</sup>U, but TDS and salinity affect the adsorption process of aqueous <sup>238</sup>U. Further, the replenishment of water will also affect the uranium isotope concentration for lakes, but it is not the main influencing factor for saline lakes. Therefore, we suggest that pH is the dominant factor affecting changes in aqueous <sup>238</sup>U concentration of the sampled saline lakes. The [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub> in these saline lakes are closely related to the input water and the associated water-rock interactions involving sediments, atmosphere dust, and organic material, etc. during the evolution stage, metamorphous degree, and hydrochemistry of the saline lakes. Lake water samples collected in the maximum and minimum discharge water period, were used to evaluate the seasonal distribution characteristics of aqueous <sup>238</sup>U, and we found that <sup>238</sup>U concentration did not show an evident change with the seasons in these saline lakes. If the  ${}^{238}$ U concentration and  $[{}^{234}$ U/ ${}^{238}$ U]<sub>AR</sub> can remain consistent during a period of time, then the sediment ages and/or sedimentation rates could be determined by lake sediment and/or biogenic carbonate in future, thus allowing for the accurate reconstruction of the paleoclimate and paleoenvironment.

**Keywords:** uranium isotope; lake water; distribution characteristic; influencing factor; environmental impact; the northeast of Qaidam Basin

## 1. Introduction

In natural conditions, uranium (U) mainly exists as three isotopes: <sup>234</sup>U, <sup>235</sup>U, and <sup>238</sup>U. Among them, <sup>235</sup>U and <sup>238</sup>U have long half-lives with high abundance, and the content ratio of



 $^{238}$ U/ $^{235}$ U = 137.832 [1]. Further,  $^{234}$ U has the shortest half-life, and the atomic abundance of  $^{234}$ U is about five orders of magnitude lower than that of  $^{238}$ U [2]. Uranium isotopes are widely used as a typical tracer in the dating of various oceanographic processes and in the study of sources of dissolved solutes in river basins [3–8].

Studies of the distribution characteristic of uranium isotopes have mainly focused on glacial sedimentation at the two poles and oceanic circulation [9,10] and recent research has still mainly focused on the oceans. Existing research results show that the uranium concentration of seawater has a relatively consistent, linear relationship with salinity [11,12]. Some scholars have tried to convert oceanographic methods to inland areas, but inland research has focused on rivers and estuaries [13–15], river bends [16], and lakes [17], while very few studies have explored the uranium content and uranium isotopes in saline lakes.

Limited studies on hydrological systems in saline lakes have been conducted and research methods have been systematically developed. The research dates back to Osmond, et al. [18] who established a two-end mixing model based on the relationship between <sup>234</sup>U/<sup>238</sup>U, 1/U, and U/TDS (total dissolved solids) in the water of Sambhar lake. They found that one end of the lake had a low uranium content and low salinity, while the other end had the opposite. Yadav et al. [19]. explored the U/TDS relationship in different aqueous media (including river water, lake water, and inter-crystal brine) of the Sambhar saline lake during different periods of the year, finding that there was a strong linear relationship between aqueous U concentration and TDS, which was consistent with the two-end mixing model established by Osmond et al. [18]. Moreover, Yadav, et al. [19] mentioned that the seasonal distribution difference of uranium isotopes was mainly controlled by the process of water dilution and evaporation. Borole et al. [20] studied the two major water systems of Narbada and Tapti in the west coast of India and showed that the abundance ratio of the aqueous uranium content to the sum of the main cations was similar to that found in typical crustal rocks. Due to the process of evaporation and solute concentration in saline lakes, the aqueous uranium content is generally higher than that in freshwater lakes.

Reports of saline lakes in high uranium environments are limited. Since the 1950s, Zheng [21] has carried out extensive and in-depth research on saline lakes in the Qinghai-Tibet Plateau. Zhang [22] found that, in the mining of lithium, boron, potassium, and magnesium from the Qaidam Basin, both uranium and thorium could be enriched, meaning that uranium enrichment is one of the basic characteristics of the saline lakes of northwestern China. The concentration of uranium of soda lakes in Mongolia is 57~15,000 µg/L [23], 320 µg/L in Gasikule salt lake in Qaidam Basin [24], and 13.4 µg/L in Qinghai Lake [25]. The potential mechanism of high uranium content in a saline lake has also been explored. For example, Benjamin et al. [23] and Isupova et al. [26] found that there exist high concentrations of uranium(U) in soda lake basins with groundwater-fed hyperalkaline. Hence, uranium-rich groundwaters are concentrated by evaporation and the U(VI) is chelated by  $CO_3^{2-}$  to form the highly soluble  $UO_2(CO_3)_3^{4-}$  in water, which is the main cause of the enrichment of uranium content in lakes in northwestern Mongolia. Strakhovenko et al. [27] showed that biogeochemical processes have an impact on the mobility of uranium species. Andersson et al., [28] showed that the behavior of colloids suspended phase and colloids are beneficial for the removal of U at very low salinities. Koch-Steindl and Pröhl, [29] indicate that the mobility of U is influenced by sorption and complexation processes on inorganic soil constituents such as clay minerals, oxides, organic matter, and biological fixation and transformation. Fredrickson et al. [30] indicated that the Mn (III/IV) oxides in particular may significantly inhibit the microbial reduction of U(VI) and its subsequent precipitation as UO<sub>2</sub>(s). Belli et al. [31] thought that a certain number of OM and/or competing cations of iron (such as  $Ca^{2+}$  and  $Mg^{2+}$ ) may inhibit the adsorption effect of uranium complex on iron hydroxide.

In high-salinity environments, such high uranium features make it possible to extract uranium resources from saline lake brine. In addition, no matter when it is processed, boron lithium potassium salt products or waste liquid discharge will affect the product quality or pollute the environment.

Thus, it is necessary to determine the distribution characteristics of aqueous uranium isotopes in lakes with different salinity gradients in order to understand the influencing factors of uranium isotope distribution in lake waters. Previous research has shown that ion concentrations, TDS, salinity, pH, and biogeochemical process are factors that influence the aqueous uranium content distribution and the [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub>. For this study, we selected several lakes of different salinities with low human disturbance in the northeast of Qaidam Basin of the Qinghai-Tibet Plateau for water chemistry (anions, cation, TDS, salinity, and pH) and uranium isotope analysis to gain insight on the overall distribution pattern and possible seasonal variations in the distribution characteristics of uranium in the saline lakes of China. In particular, we wanted to gain insights into the controlling factors and underlying mechanism of aqueous uranium concentrations in the lakes and to explore the potential environmental applications of uranium isotopes with the goal of promoting the widespread use of radioactive isotopes as environmental indicators.

#### 2. Materials and Methods

## 2.1. Sampling Locations

There are many lakes in the Qaidam Basin and most of them are saline lakes. The water samples in this study were collected from four lakes of different salinities in the northeast of Qaidam Basin: Gahai lake (GH), Keluke lake (KLK), Tuosu lake (TS), and Xiligou lake (XLG). In order to further explore the influence of water sources on the uranium isotope of KLK lake, we obtained some water samples from the Bayin river (BY). These sampling locations are shown in Figure 1. Two sampling sites were established in XLG: one (XLG 1) in the center of the lake, and the other (XLG 2) in a shallow pool next to the lake, with the pool water mainly originating from natural precipitation with water quality indicators similar to those of KLK. The XLG 2 pool samples can therefore be regarded as freshwater lake samples. All five sampling sites could be roughly divided into two categories: freshwater lake and saline lakes, with the former consisting of KLK and XLG 2, and the latter GH, TS, and XLG 1. The study area belongs to the typical alpine continental climate, characterized by a large temperature difference between day and night, low precipitation, and high drought throughout the year. The main vegetation types are alpine meadows and alpine steppes. The overall elevation of the area is about 3000 m.



Figure 1. Map of sampling locations of these lakes.

According to data from the National Meteorological Station of Delhi city, Han [32] determined that the mean annual precipitation over the period of 1961–2017 was 185.1 mm, and the mean annual evaporation ranged between 2242.8–2439.4 mm. Precipitation is uneven during the year, showing a unimodal distribution. Maximum precipitation occurs in June–July, and the minimum precipitation occurs in December. The total area of GH is about 37 km<sup>2</sup> with a mean water depth of 8 m and a maximum water depth of 15 m. The lake basin has no perennial surface rivers, relying on atmospheric precipitation and subsurface runoff to supply water. TS has a total area of about 180 km<sup>2</sup> and a maximum water depth of 25.7 m, with the water mainly originating from the drainage of the TS waters, atmospheric precipitation, and groundwater [21,24].

The Bayin river originates from the northern foot of the ZongWu Long Mountain which has a total length of 188 km and a drainage area of 7281 km<sup>2</sup>. The main water supply source in the upper reaches of the Bayin river is natural precipitation, and in lower reaches is groundwater. After the Bayin river flows out of the ZongWu Long Mountain, a great deal of river water infiltrates into the ground water because the sediments on the riverbed in the Gobi Desert are mostly gravel. Then, the river passes through Delhi city. The infiltration process of river water was prevented by the hardening of the riverbed in Delhi city. After the river flows out of the city, the infiltration process of the river recommences. When the groundwater flows near a tree, a large amount of groundwater overflows into a pool of springs and becomes the main supply water source of the Bayin river, because of the lithological thinning and the blocking effect of the Denan hills. Then, the river water and the groundwater flow into the Keluke lake. Eventually, the Bayin river leaves Keluke lake and flows into Tuosu lake [33,34].

#### 2.2. Sampling Design and Methods

The samples were collected in three batches. The analysis of the first batch of samples showed no significant differences in the horizontal or vertical distribution of aqueous <sup>238</sup>U within the same lake, indicating a homogenous distribution of <sup>238</sup>U in the water column, such kind of phenomenon has also been showed in the published Qinghai Lake data [25]. Based on this feature, we suggest that one single sample was deemed representative of the whole water column. Therefore, we collected only limited samples in the second and third of batch samplings. The sampling information of each sample was presented in Table 1.

The sampling area is shown in Figure 1. We selected these sampling periods because water inputs northeast of the Qaidam Basin exists in greater variation, and during other seasons are almost covered with ice coverage. Thus, these sampled lake waters could show typical saline lake water uranium distribution characteristics.

The surface water dozens of meters off the shore was collected into HDPE (High Density Polyethylene) plastic bottles (Nalgene 2002-0032) from the depth of 10 cm below surface water by hand with Derma Free<sup>®</sup> Vinyl Gloves. We collected other samples from various depths using PMMA (Polymethyl Methacrylate) water collectors and placed into HDPE plastic bottles (Nalgene, 2002-0032). After collection, about 1000 mL of each water sample was filtered through a mixed cellulose filter membrane (0.8-µm pore size, Millipore AAWP04700) with a manual vacuum filter system (Nalgene, 300-4100; Nalgene, 6133-0010), and the filtrate was stored for later analysis.

Batch	Location	Sample No.	Depth (m)	Latitude (°N)	Longitude (°E)	Date	
		TS-1-1	0.5				
		TS-1-2	10	37°08′40″	96°57'24″		
		TS-1-3	21				
		TS-2	4	37°09'11″	96°57′49″		
	Tuosu lake	TS-3-1	0.02	27900/05//	0/950/10//	9 December 2017	
		TS-3-2	13	37*09*05*	96-58-18		
		TS-4-1	0.02	27900/11//			
		TS-4-2	14	37*09*11	96-58-58		
		TS-5	2	37°09'18″	96°59′31″		
1		GH-1-1	0.02	27000/00//	05001/04//		
		GH-1-2	8	37°08'28''	97°31′34″		
		GH-2-1	0.02	27000/01//	37°08′01″ 97°32′34″		
		GH-2-2	10	37 08 01			
	Cabai laka	GH-3-1	0.02	2700/27//	07°22/20″	10 December 2017	
	Ganai lake	GH-3-2	9.98	37*08*27*	37 08 27 97 32 29	10 December 2017	
		GH-4-1	0.02	27900/40//	07922/2//		
		GH-4-2	8.98	37 08 48	37°08′48″ 97°32′26″		
		GH-5-1	0.02	27000/10//	07022/01//		
		GH-5-2	7.48	37*09*19	97*32*21		
	Gahai lake	GH	0.2	37°07′51″	97°34′58″	15 June 2018	
		KLK 1-T	0.2				
		KLK 1-M	2.5	37°17′24″	96°53′34″		
	Keluke lake	KLK 1-B	4.5				
		KLK 2-T	0.2			16 June 2018	
		KLK 2-M	1.5	37°17′55″	96°53′42″	5	
		KLK 2-B	3.5				
•		KLK 3-T	0.2	37°18'27″	96°53′55″		
2		KLK 3-M	1	0, 10 2,	10 00 00		
		TS-1-T	0.2	37°10′21″	96°58′34″		
		TS-1-M	8	07 10 11	10 00 01		
	Tuosu lake	TS-2-T	0.2	37°10'27″	96°58′59″	16 June 2018	
		TS-2-M	4.5	0, 10 2,	10 00 01		
		TS-3-T	0.2	37°10′35″	96°58′57″		
		1S-3-M	3	<b>0</b> (0) (0) (0) (0)			
	Xiligou lake	XLG 1	0.2	36°49′10″	98°26′52″	17 June 2018	
	0	XLG 2	0.2	36°49′03″	98°26′41″	17 June 2018	
	Koluko laka	KLK-W	0.2	37°17′01″	96°51′35″	22 July 2010	
	Keluke lake	KLK-N	0.2	37°18′56″	96°54′07″	22 July 2019	
		Upper reaches	0.2	37°26′33″	97°44′19″		
3		Middle reaches	0.2	37°22'37″	97°26′44″		
	Bayin river	Delhi city	0.2	37°22′30″	97°21′43″	22 July 2019	
			Lower reaches	0.2	37°14′09″	97°1′22″	
		KLK-TS-River	0.2	37°13'11″	96°49′44″		

Table 1. The sampling information of each sample.

#### 2.3. Analytical Methods

Samples analysis for water chemistry parameters (anions, cations, salinity, TDS, and pH) were carried out at the Key Laboratory of Surface System and Environmental Carrying Capacity of Shaanxi Province, Northwest University. Anion and cation concentrations of the samples were determined using two Dionex AQUION ICs [35,36]. Conductivity (ms/cm), TDS (g/L), salinity (‰), and pH were determined using a Mettler-Toledo Five Easy Plus pH meter. Uranium isotopes in the samples were measured at the Xi'an Jiaotong University Isotope Laboratory. Methods of investigation of uranium isotopes mainly include chemical separation and instrument analysis. The chemical separation process mainly includes the digestion process, centrifugal coprecipitation, ion exchange resin separation,

uranium isotope collection, and purification. The steps involved are as follows. To analyze the U isotopic compositions of the water, the acidified aliquots of each sample were spiked with <sup>233</sup>U-<sup>236</sup>U-<sup>229</sup>Th, preconcentrated and digested with HNO<sub>3</sub> and HClO<sub>4</sub>, and then co-precipitated with Fe oxyhydroxide. The Fe precipitate was moved to a centrifuge tube for centrifugation and rinsed with deionized  $H_2O$  (>18 M $\Omega$ ) to eliminate the large seawater ions. The precipitate was then dissolved in 14N  $HNO_3$  (1N = 1M) and moved to a Teflon beaker, before being dried and dissolved in 7N  $HNO_3$ for an ion-exchange chromatography with AG1-X8, 100–200 mesh size resin and a polyethylene frit. Separation was perfromed on Teflon columns with a 0.5 mL column volume (CV). The first separation was performed on Teflon columns with 4CV 7N HNO<sub>3</sub>, 3 CV of 8N HCl (to get rid of Fe and Th fraction), and 3 CV of deionized  $H_2O$  (to gather the U fraction). The U fractions were then dried with 2 drops of HClO<sub>4</sub> and brought to volume with 7N HNO<sub>3</sub>. The final U fractions were then dried with 2 drops of HClO<sub>4</sub> and dissolved in weak nitric acid for analysis on the mass spectrometer. The concentrations of <sup>234</sup>U, <sup>235</sup>U, and <sup>238</sup>U were calculated by isotope dilution using the nuclide ratios determined on a Thermo-Finnigan Neptune mass spectrometer. All measurements were performed using a peak-jumping routine in ion counting mode on the discreet dynode multiplier behind the retarding potential quadrupole. Each sample measurement was bracketed by the measurement of an aliquot of the run solution, which was utilized to adjust for the instrument background count rates on the measured masses. For U, the measurement uncertainties involved propagated errors from ICP-MS isotope ratio measurements, spike concentrations, and blank corrections. The procedural blanks for chemical and mass spectrometric analyses at the Laboratory of Isotope Geochemistry in Xi'an Jiao Tong University are approximately 830 ag ( $2.2 \times 10^6$  atoms) for  $^{234}$ U, 29 fg ( $7.7 \times 10^7$  atoms) for  $^{235}$ U,  $2 \text{ pg} (5.2 \times 10^9 \text{ atoms})$  for <sup>238</sup>U. The methods used here have been fully described by Cheng et al. [1,37] and Shen et al. [38,39].

#### 3. Results

The water chemistry results of each sampled lake are presented in Table 2, including the aqueous uranium isotope concentration and the  $[^{234}U/^{238}U]_{AR}$ . Given that  $^{238}U$  is the dominant uranium isotope, accounting for 99.275% of the total U content, the uranium concentration in this paper refers to the  $^{238}U$  concentration, expressed as  $^{238}U$  hereafter. In general, freshwater lakes (KLK, XLH 2) are lower than saline lakes (GH, TS, XLG 1) for all measured parameters.

(a) Given that the salinity in the GH waters was above the detection limit of the instrument, we estimated these GH samples salinity by converting the measured conductivity as described below, resulting in an estimated salinity of 72.36‰ for the GH samples.

Conductivity can be converted to salinity between 0–40 °C using the following conversion formula:

$$y \text{NaCl} = 1.3888x - 0.02478xt - 6171.9 \tag{1}$$

where *y* NaCl is the salinity calculated as NaCl, *x* is the conductivity in  $\mu$ s/cm, and *t* is the water temperature in °C. Salinity calculated using the above formula is given in units of ppm, and must be subjected to a basic unit conversion for expression in ‰.

(b) These contents of  $HCO_3^-$  and  $CO_3^{2-}$  have been calculated by these two formulas [40].

$$lg[HCO_{3}^{-}] = -11.338 + pH$$
 (2)

$$lg[CO_3^{2-}] = -21.668 + 2pH$$
(3)

Sample	pН	Conductivity mS/cm	Cl− mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	HCO <sub>3 b</sub> mg/L	CO <sub>2-3b</sub> mg/L	NO mg/L	NO <sub>3</sub> mg/L	Na+ mg/L	K+ mg/L	Mg <sup>2+</sup> mg/L	Ca <sup>2+</sup> mg/L	TDS (g/L)	Salinity (‰)	<sup>238</sup> U (µg/L)	[ <sup>234</sup> U/ <sup>238</sup> U] <sub>AR</sub>
GH	7.84	78.62	31,865.59	9436.10	19.38	0.06	296.70	18.07	18,830.66	2102.96	2852.06	199.02	39.31	72.36 <sub>a</sub>	16.2	1.798
KLK 1-T	7.73	1.09	205.23	164.40	15.04	0.04	11.17	0.50	117.45	22.75	44.86	30.69	0.54	0.54	5.5	1.505
KLK 1-M	7.73	1.10	204.37	163.91	15.04	0.04	11.15	0.86	117.35	23.09	44.85	30.78	0.55	0.55	5.5	1.506
KLK 1-B	7.52	1.14	204.90	164.79	9.28	0.01	10.98	1.29	117.49	22.87	44.45	30.70	0.57	0.57	5.6	1.503
KLK 2-T	7.69	1.11	203.59	162.11	13.72	0.03	10.85	0.75	115.90	22.90	44.34	28.74	0.55	0.55	5.5	1.504
KLK 2-M	7.71	1.12	203.09	162.05	14.37	0.03	10.90	0.66	116.22	23.04	44.51	28.85	0.56	0.55	5.4	1.506
KLK 2-B	7.77	1.07	198.50	159.99	16.49	0.04	10.96	0.45	116.53	23.64	44.71	28.92	0.54	0.53	5.5	1.504
KLK 3-T	7.76	1.22	217.37	161.77	16.12	0.04	11.95	1.08	127.04	22.98	48.29	34.47	0.61	0.60	5.4	1.502
KLK 3-M	7.77	1.21	225.53	166.76	16.49	0.04	12.31	1.35	126.77	23.50	48.18	34.24	0.60	0.60	5.4	1.504
TS-1-T	8.83	33.51	13,212.45	7187.91	189.38	5.89	192.07	13.61	8294.33	848.16	2027.81	30.91	16.54	20.91	34.4	1.462
TS-1-M	8.87	33.20	10,942.59	5936.21	207.65	7.08	164.27	7.29	6809.05	801.47	1675.98	29.30	16.60	20.68	34.6	1.462
TS-2-T	8.87	33.08	10,802.30	5880.24	207.65	7.08	160.38	5.76	6758.64	776.27	1659.81	23.62	16.54	20.60	34.6	1.462
TS-2-M	8.88	33.10	11,206.53	6075.39	212.49	7.42	173.93	11.48	6944.53	855.72	1713.14	27.32	16.55	20.62	35.0	1.461
TS-3-T	8.88	33.29	14,840.03	8097.02	212.49	7.42	208.02	7.03	9666.54	894.58	2353.41	29.93	16.66	20.75	34.9	1.460
TS-3-M	8.88	33.99	11,192.01	6104.67	212.49	7.42	168.63	5.87	7037.38	801.03	1723.72	23.51	16.46	20.50	34.9	1.462
XLG 1	8.51	14.95	4030.92	1741.98	90.64	1.35	64.35	3.73	2129.13	361.96	385.49	62.99	7.20	8.67	19.8	1.565
XLG 2	7.53	1.25	242.26	163.88	9.49	0.01	12.94	3.37	196.65	23.60	24.53	32.25	0.63	0.63	12.6	1.673

Table 2. Water chemistry parameters and isotope measurement results for all lake samples.

# 3.1. Water Chemistry Characteristics in the Northeast of Qaidam Basin

As shown in a Piper diagram (Figure 2), the cations in these lake waters of the northeast of Qaidam Basin were mainly Na<sup>+</sup>, jointly accounting for 78.5%, 54.5%, 73.6%, 72.4%, and 71.0% of the total cations (TZ<sup>+</sup>) in GH, KLK, TS, XLG1, and XLG2 lakes, respectively. Na<sup>+</sup> and K<sup>+</sup> are followed by Mg<sup>2+</sup> with the second highest concentration, while Ca<sup>2+</sup> had the lowest cation concentrations measured. Of note, the XLG 2 waters had a slightly higher concentration of Ca<sup>2+</sup> than Mg<sup>2+</sup>. The anions were mainly Cl<sup>-</sup>, accounting for 76.5%, 52.2%, 63.4%, and 67.9% of all anions (TZ<sup>-</sup>) in GH, KLK, TS, XLG1, and XLG2 lakes, respectively. Cl<sup>-</sup> was followed by SO<sub>4</sub><sup>2-</sup> with the second highest concentration, while HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> jointly had the lowest anion concentrations measured. The concentration of an ion (or ion pair) remained essentially the same throughout the same water body.



Figure 2. Piper diagram of the water quality of all lake water samples.

# 3.2. Distribution Characteristics of Uranium Isotopes in These Lake Waters in the Northeast of Qaidam Basin

Multiple sampling sites were set at different depths in KLK and TS so that the horizontal and vertical distribution characteristics of  $^{238}$ U could be analyzed for these lakes. The horizontal distribution characteristics of the  $^{238}$ U concentration and the  $[^{234}$ U/ $^{238}$ U]<sub>AR</sub> in the KLK and TS waters are shown in Table 3.

Aqueous <sup>238</sup>U concentration of the freshwater lakes in the northeast of Qaidam Basin were generally low. In contrast, the concentration of <sup>238</sup>U in these saline lake waters were generally higher. There is no significant difference in the [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub> between freshwater lakes and saline lakes, with the values generally ranging from 1.460 to 1.798. A comparison of all five sampled lakes data revealed that <sup>238</sup>U (TS) was the highest of all, while [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub> (TS) was the lowest. There was no significant horizontal distribution difference among the three sampling sites for the <sup>238</sup>U concentration and the [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub>.

Sample		<sup>238</sup> U (µg/L)	Average Value	[ <sup>234</sup> U/ <sup>238</sup> U] <sub>AR</sub>	Average Value
	1	5.5		1.505	
KLK-T	2	5.5	5.4	1.504	1.504
	3	5.4		1.502	
	1	5.5		1.506	
KLK-M	2	5.4	5.5	1.506	1.505
	3	5.4		1.504	
VIVD	1	5.6	5 5	1.503	1 502
KLK-D	2	5.5	5.5	1.504	1.305
	1	34.4		1.462	
TS-T	2	34.6	34.6	1.462	1.461
	3	34.9		1.460	
	1	34.6		1.462	
TS-M	2	35.0	34.8	1.461	1.462
	3	34.9		1.462	

**Table 3.** Horizontal distribution characteristics of the  ${}^{238}$ U concentration and the  $[{}^{234}$ U/ ${}^{238}$ U]<sub>AR</sub> in the water of KLK and TS.

The vertical distribution characteristics of the  $^{238}$ U concentration and  $[^{234}U/^{238}U]_{AR}$  in the KLK and TS waters are shown in Table 4.

**Table 4.** Vertical distribution characteristics of the  ${}^{238}$ U concentration and the  $[{}^{234}$ U/ ${}^{238}$ U]<sub>AR</sub> in the water of KLK and TS.

Sample		Depth (m)	<sup>238</sup> U (µg/L)	Average Value	$[^{234}U/^{238}U]_{AR}$	Average Value	
	Т	0.2	5.5		1.505		
KLK-1	М	2.5	5.5	5.5	1.506	1.505	
	В	4.5	5.6		1.503		
	Т	0.2	5.5		1.504		
KLK-2	Μ	1.5	5.4	5.5	1.506	1.505	
	В	3.5	5.5		1.504		
KI K O	Т	0.2	5.4	5.4	1.502	1 502	
KLK-3	Μ	1	5.4	5.4	1.504	1.305	
TC 1	Т	0.2	34.4	24 5	1.462	1.4(2)	
15-1	М	8	34.6	34.5	1.462	1.462	
TC <b>2</b>	Т	0.2	34.6	24.9	1.462	1.4(2)	
15-2	М	4.5	35.0	34.8	1.461	1.462	
TS-3	Т	0.2	34.9	24.0	1.460	1 461	
	М	3	34.9	34.9	1.462	1.401	

Three sampling sites were set in KLK. At sampling sites 1 and 2, water samples were collected at three depths referred to as T (surface), M (middle), and B (bottom) from the surface water to the bottom water, while only two sampling depths (T and M) were collected at sampling site 3.

In summary, in natural lakes, in the absence of interference from other aqueous factors, the <sup>238</sup>U concentration increased with an increased water depth, while the  $[^{234}U/^{238}U]_{AR}$  showed an initial increase, then decreased gradually with depth. However, the ranges of these changes were very small, indicating that aqueous <sup>238</sup>U concentration and the  $[^{234}U/^{238}U]_{AR}$  were essentially evenly distributed vertically and horizontally within the same lake.

3.3. Influence of Water Sources Supply on the Uranium Isotopes of Lake

In order to further explore the influence of water sources supply on the uranium isotope of lake, we get some water samples from different sections of the Bayin river (BY) and KLK at the same single day, and the Bayin river is the only incharge river of KLK lake. Results of  $^{238}$ U concentration and  $[^{234}\text{U}/^{238}\text{U}]_{AR}$  in the BY river and KLK waters are shown in Table 5.

Table 5.  $^{238}$ U concentration and  $[^{234}U/^{238}U]_{AR}$  in different sections of BY river and KLK lake waters.

	Sample	<sup>238</sup> U (µg/L)	$[^{234}\text{U}/^{238}\text{U}]_{AR}$
	upper reaches	6.0	1.392
	middle reaches	5.9	1.402
<b>BY-River</b>	Delhi city	6.2	1.408
	lower reaches	2.8	1.464
	KLK-TS-River	5.6	1.482
	KLK-W	5.6	1.476
NLK	KLK-N	5.3	1.451

We found that the <sup>238</sup>U concentration and  $[^{234}U/^{238}U]_{AR}$  in different sections of BY river are not the same. The <sup>238</sup>U concentration is highest in the upper reaches (6.0 µg/L) and the lowest in the lower reaches (2.8 µg/L) of natural waters. However,  $[^{234}U/^{238}U]_{AR}$  shows the opposite of the distribution of <sup>238</sup>U concentration. The Bayin river passes through Delhi city. We collected the highest <sup>238</sup>U concentration samples (6.2 µg/L) from the watercourse of Delhi city.

The Bayin river flows into the KLK from the northeast and mixes with the original lake water. Two sampling results show that the average  $^{238}$ U concentration of KLK lake water is about 5.5 µg/L, which is slightly lower than the upper reaches of the Bayin River and is significantly higher than the lower reaches. The Bayin river flows out the KLK from the southwest. The  $^{238}$ U concentration of watercourse connecting KLK and TS is 5.6 µg/L. This is basically consistent with that of KLK lake water.

# 3.4. Seasonal Distribution Characteristics of Uranium Isotopes

We explored the seasonal distribution characteristics of U in these lake waters in the northeast of Qaidam Basin. The results from the first batch of samples (December 2017), with the minimum recharge water volume in winter, indicated that the aqueous  $^{238}$ U concentration of the same lake remained at a relatively stable level. However, it is unclear whether the contribution of exogenous inputs (e.g., atmospheric precipitation and river inputs) could affect the lake water  $^{238}$ U concentration and the [ $^{234}$ U/ $^{238}$ U]<sub>AR</sub> and the effects of exogenous inputs should be clarified before interpreting the environmental implications of the above indicators. Therefore, GH and TS were selected for a second round of sampling in summer with the maximum recharge water volume and measurement in order to conduct a seasonal comparison of the aqueous  $^{238}$ U concentration and the [ $^{234}$ U/ $^{238}$ U]<sub>AR</sub> and the results are shown in Table 6.

We found the <sup>238</sup>U concentration of GH and TS changed slightly with the season. In winter (December), <sup>238</sup>U concentration of GH is 18.4 µg/L, in summer (June), the result is 16.2 µg/L. We also see the same pattern in TS, where <sup>238</sup>U concentration of TS decreased from 35.5 µg/L to 34.7 µg/L in from winter to summer. Whether it is GH or TS, the [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub> in different seasons is approximative. From winter to summer, the maximum discharge water volume variation, the [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub> of GH vary from 1.792 to 1.798, and the result of TS vary from 1.463 to 1.462.

Season	Sample	Depth (m)	<sup>238</sup> U (µg/L)	Average Value	$[^{234}U/^{238}U]_{AR}$	Average Value
	011.4	0.02	18.5		1.791	
	GH-1	8.0	18.5	18.4	1.792	1.792
		0.02	18.3		1.792	
	GH-2	10.0	18.3		1.793	
December	CIL2	0.02	18.2		1.793	
(Winter)	GH-3	9.98	18.4		1.791	
		0.02	18.3		1.796	
	GH-4	8.98	18.4		1.794	
		0.02	18.3		1.793	
	GH-3	7.48	18.3		1.794	
June (Summer)	GH	0.2	16.2	16.2	1.798	1.798
		0.5	35.4		1.464	
	TS-1 10.0 35.8 21.0 35.6	10.0	35.8		1.462	
		35.6		1.462		
Docombor	TS-2	4.0	35.2	35.5	1.462	
(Winter)	TC 2	0.02	35.2		1.463	1.463
(Winter)	13-3	13.0	35.3		1.46	
	TC 1	0.02	35.5		1.464	
	15-4	14.0	35.7		1.460	
	TS-5	2.0	35.8		1.461	
	TC 1	0.2	34.4		1.462	
	15-1	8.0	34.6		1.462	
June	TC 2	0.2	34.6	34.7	1.462	1 460
(Summer)	15-2	4.5	35.0		1.461	1.402
	TC 2	0.2	34.9		1.460	
	15-3	3.0	34.9		1.462	

**Table 6.** Seasonal distribution characteristics of lake waters uranium isotopes using GH and TS as representative lakes.

# 4. Discussion

4.1. Factors Influencing the Concentration Distribution Characteristics of  $^{238}$ U in These Lake Waters in the Northeast of Qaidam Basin

Based on the existing literature, we hypothesized that TDS, salinity, and pH may account for the differences in the spatial distribution of aqueous <sup>238</sup>U concentration. The factors that are likely to affect the distribution of <sup>238</sup>U concentration in these lake waters in the northeast of Qaidam Basin are addressed in more detail as follows. For the convenience of discussion, we will use the parameters measured in KLK and TS as representative of the freshwater and saline lakes of the region, respectively.

4.1.1. Response Relationship of  $^{238}\rm{U}$  Concentration to TDS and Salinity in These Lake Waters in the Northeast of Qaidam Basin

Water Chemistry parameters of these lake waters show that the major cation is mainly Na<sup>+</sup> and the major anion is mainly Cl<sup>-</sup>. This means that TDS and salinity may be similar in the saline lake from the northeast of Qaidam Basin. As shown in Figure 3, the relationship between TDS and salinity of these lake waters clarifies this perspective.



Figure 3. Relationship between TDS and salinity of sampled lake water samples.

Therefore, we selected TDS as the research object to investigate the response relationship of <sup>238</sup>U concentration in these lake waters to TDS. The relationship of <sup>238</sup>U concentration to TDS in these lake waters in the northeast of Qaidam Basin is shown in Figure 4.



Figure 4. Relationship between <sup>238</sup>U concentration and TDS of all lake water samples.

Where TDS increases as TDS (KLK): 0.56 g/L < TDS (XLG 2): 0.63 g/L < TDS (XLG 1): 7.2 g/L < TDS (TS): 16.56 g/L. For the <sup>238</sup>U concentration, we found TDS increased as <sup>238</sup>U (KLK): 5.5  $\mu$ g/L < <sup>238</sup>U (XLG 2): 12.6  $\mu$ g/L < <sup>238</sup>U (XLG 1): 19.8  $\mu$ g/L < <sup>238</sup>U (TS): 34.7  $\mu$ g/L. When it comes to the relationship of <sup>238</sup>U concentration to TDS in these lake waters in the northeast of Qaidam Basin, in the absence of interference from exogenous factors, we found a higher lake water TDS in a certain range would lead to a higher concentration of <sup>238</sup>U. This indicates that the enrichment process of uranium involves a series of evaporation and concentration steps. We could speculate that the migration and the ability of uranium to transform in water increases with an increase of the TDS. Shi [41] suggested the main reason for this phenomenon is that <sup>238</sup>U is difficult to be adsorbed in an environment with high TDS. The mobility of U is largely controlled by their ability to form complexes both with inorganic (F<sup>-</sup>, Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>) and organic ligands. This has been described in detail for U [42,43]. Studies in the ocean [44] and the Jiu long River Estuary [45] also showed that the aqueous <sup>238</sup>U concentration increase in TDS.

The results of the KLK and TS samples are compared in Figure 5.

5.6

5.5

5.4

35.6

35.2 34.8 34.4 34.0

0.52

 $^{238}$ U ( $\mu g/L$ ) 5.3



. 16.45 16.50 16.55 16.60 16.65 16.70 TDS (g/L)

Figure 5. Relationship between <sup>238</sup>U concentration and TDS of the KLK and TS water samples

The TDS varied over a small range within same lake. TDS (KLK) from 0.54 g/L to 0.61 g/L, TDS (TS) from 16.46 g/L to 16.66 g/L. The results showing the <sup>238</sup>U concentration was basically at the same level within same lake. The change range of <sup>238</sup>U concentration is 3.64% in KLK and 1.73% for TS.

In addition, the TDS of GH samples far exceeded the TS samples (TDS (TS): 16.56 g/L < TDS (GH): 39.31 g/L; However, mean aqueous <sup>238</sup>U concentrations were less for the GH samples than for the TS samples ( $^{238}U_{(GH)}$ : 16.2 µg/L <  $^{238}U_{(TS)}$ : 34.7 µg/L). These results indicate that TDS are not the only factors affecting <sup>238</sup>U concentration in the waters of terrestrial lakes. The other possibility is there is a certain threshold. When above a TDS range, the <sup>238</sup>U concentration will decrease with the increase of TDS [22]. This should be the reason for GH with high TDS but low <sup>238</sup>U concentration. In summary, the positive relationship of aqueous <sup>238</sup>U concentrations to the factors of TDS may exist only when TDS are lower than certain thresholds, and if the impacts of other factors are deemed negligible. In other words, we speculate that, within a certain range of TDS, the aqueous <sup>238</sup>U concentration increases with the increase of TDS, but this will decrease rather than increase once beyond the range. More research is required to determine the veracity of this speculation, and to understand the underlying mechanism of thresholds for TDS that affect aqueous <sup>238</sup>U concentrations.

4.1.2. Response Relationship of <sup>238</sup>U Concentration to pH in These Lake Waters in the Northeast of Qaidam Basin

Most of these lakes in the northeast of Qaidam Basin are saline lakes with a pH generally above 7.0 (i.e., basic). As shown in Figure 6, the  $^{238}$ U concentration in these lake waters in the northeast of Qaidam Basin increased with pH.

Since KLK is an open lake, it was excluded from the following discussion of close lakes. For the close saline lakes, the pH results of these sampled lake waters show that pH  $_{(XLG 2)}$ : 7.53 < pH  $_{(GH)}$ : 7.84  $< pH_{(XLG 1)}$ : 8.51 $< pH_{(TS)}$ : 8.87. The <sup>238</sup>U concentration of different waters samples were <sup>238</sup>U <sub>(XLG 2)</sub>: 12.6 µg/L  $< ^{238}U_{(GH)}$ : 16.2 µg/L $< ^{238}U_{(XLG 1)}$ : 19.8 µg/L  $< ^{238}U_{(TS)}$ : 34.7 µg/L. We can see the aqueous concentration of <sup>238</sup>U of these lake waters increased with pH, which is attributed to the fact that weakly basic conditions would enhance the leaching of uranium in rocks and thereby increase the migration of uranium into water [41]). The pH value of lake waters depends mainly on the contents of HCO<sub>3</sub><sup>-</sup> and  $CO_3^{2-}$  [40]. The results show that the pH value of these lakes increases with an increase in the contents of HCO<sub>3</sub> and CO<sub>3</sub><sup>2-</sup>. Under basic conditions, uranium is mainly present in the form of UO<sub>2</sub>(CO<sub>3</sub>) $^{4-}_{3-}$ . As the decrease of pH,  $UO_2(CO_3)_3^{4-}$  decompose into  $UO_2(CO_3)_2^{2-}$  slowly in water. Two highly mobile forms will eventually become one of the stable forms  $(UO_2CO_3, UO_2(OH)_3^-, and UO_2(OH)^+)$  when the pH is low enough. A study by Mochizuki [46] on Lake Biwa in Japan showed that the change of

lake waters pH affected the leaching process of uranium at the sediment/water interface, which would directly affect the aqueous <sup>238</sup>U concentration.



Figure 6. Relationship between <sup>238</sup>U concentration and pH of all lake water samples.

Under natural conditions, aqueous <sup>238</sup>U concentrations are affected by TDS, and pH, which jointly make different lakes in the same region have different aqueous <sup>238</sup>U concentrations. In order to identify the major controlling factors of aqueous <sup>238</sup>U concentration of saline lake, we performed a correlation analysis of aqueous <sup>238</sup>U concentration with TDS and pH. The results showed that the <sup>238</sup>U concentration was affected by pH to a far greater extent than by TDS. The <sup>238</sup>U concentration in these sampled lakes vary with the range from 12.6  $\mu$ g/L to 34.7  $\mu$ g/L. The pH only changes from 7.53 to 7.88, but TDS changes from 0.63 g/L to 39.31 g/L. Namely, the slightly pH variation can result in the bigger variation of <sup>238</sup>U concentration in the sampled saline lake waters than that of TDS.

4.1.3. Response Relationship of  $^{238}\mathrm{U}$  Concentration to Organic Matter in These Lake Waters in the Northeast of Qaidam Basin

Studies have also confirmed the <sup>238</sup>U concentration could be related with biogeochemical process (i.e., the presence of organic matter (OM) and its interaction with iron and manganese oxides/hydroxides) [28–30]. The sorption of uranium complexes on iron hydroxides is significantly reduced in the presence of organic matter and/or competing cations, such as  $Ca^{2+}$  and  $Mg^{2+}$  [31]. Other studies have shown that the concentration of U(VI) in the aqueous phase drastically decreases during bacterial processes because of the formation of insoluble U(IV) compounds [47,48]. In addition, humic substances (HS), including fulvic acid and humic acid, have a strong complexing ability for <sup>238</sup>U of all types of organic matter. If the bottom sediment of a lake is covered with a large amount of organic matter, <sup>238</sup>U could precipitate after forming organic complexes with HS, thereby reducing the concentration of <sup>238</sup>U in the lake waters [49,50]. Some researches mentioned that Qinghai is one of the few provinces in China where natural Artemia is distributed and GH is the largest saline lake producing Artemia in Qaidam Basin of Qinghai Province [51–53]. There could exist a layer of organic matter attached to the bottom of GH. If we speculate that there exists an evident biogeochemical process in GH, then the decomposition of organic matter and release of  $CO_2$  is possible, which will result in the carbon isotope variation of DIC (Dissolved Inorganic Carbon) and/or biological shell in lake. The carbon and oxygen isotope research of DIC and shell in GH, showed that there is a limited effect on lake water chemistry from biogeochemical process with shallow lake water environment [54,55]. Because the limited data about organic matter effect and the Fe/Mn element result of the sampled lakes, here, we will not present much more discussion.

Based on the above discussion about the relationship between <sup>238</sup>U concentration, TDS, pH, and organic matter, we infer that the dominant factor leading to the low <sup>238</sup>U concentration in GH waters was also pH, although other factors such as TDS and organic matter could have non-negligible effects. There exists a negative correlation between pH value and TDS when TDS is between 50 and 310 g/L for salt lakes [22]. Under natural conditions, when TDS reaches a certain level, pH value will gradually decrease with increasing TDS, and the concentration of aqueous <sup>238</sup>U will be lowered too. Therefore, we conclude that pH is the dominant factor affecting the changes in aqueous <sup>238</sup>U concentration in the sampled saline lakes. The pH values of these saline lakes are not only controlled by the input water, but associated with water–rock interaction during the lake evolution stage, metamorphous degree, and hydrochemistry type [22,56].

# 4.1.4. Response Relationship of <sup>238</sup>U Concentration to Water Sources Supply in Open Lake Waters

Taking "KLK-Bayin river" as an example to discuss the response relationship of <sup>238</sup>U concentration to water supply sources in an open lake, one of the most important sources of uranium isotopes in water bodies, we note that a large amount of debris is produced by physical erosion and chemical weathering of mountain masses on both sides of rivers.

The upper reaches of the Bayin river are characterized by rolling mountains and abundant rainfall. The leaching effect of the river makes the uranium isotope content of water in the upper reaches generally higher than others. The physical erosion and chemical weathering of mountain masses on both sides of rivers from upper reaches to lower reaches gradually weakened due to the smooth terrain. Because of the large amount of gravel in the riverbed of the Gobi Desert, a large amount of river water supplies groundwater. This makes the uranium content of water in the middle reaches slightly lower than that in the upper reaches

The watercourse hardening of the Bayin river in Delhi city prevents the infiltration process of the river. There are many materials used for watercourse hardening, such as concrete, marble, and so on. This may be one of the main reasons why the uranium isotope content in of Bayin river in Delhi city is higher than others. A large amount of spilt groundwater has become the main source of water for the Bayin river, due to the change of lithology of the watercourse and the obstruction of Denan hills. The dilution of groundwater may result in a significant reduction in uranium isotope content of lower reaches for Bayin river [33,34].

Research [21,24] shows that the evaporation of KLK is greater than precipitation every year under such a high evaporation environment. This means that there is a large amount of replenishing water into KLK every year under such high evaporation environment. The results of samples show that the <sup>238</sup>U concentration of Bayin river near the estuary (2.8  $\mu$ g/L) is lower than that for KLK (5.5  $\mu$ g/L). However, the result of the watercourse near the exit of KLK is 5.6  $\mu$ g/L, which indicates certain effect on aqueous <sup>238</sup>U concentration for KLK.

# 4.2. Distribution Characteristics and Influencing Factors of the $[^{234}Ul^{238}U]_{AR}$

There is a certain degree of difference between waters and sediment in the radioactivity of  $^{234}$ U and  $^{238}$ U under natural conditions. At present, the activity of the number of atoms of a nuclide is the number of decay events per unit of time, referred to as the [ $^{234}$ U/ $^{238}$ U]<sub>AR</sub> In theory, the rate at which  $^{238}$ U decays into  $^{234}$ U is the same as the decay rate of  $^{234}$ U. When the so-called radioactive equilibrium is reached, the [ $^{234}$ U/ $^{238}$ U]<sub>AR</sub> is equal to 1 [57]. However, the actual [ $^{234}$ U/ $^{238}$ U]<sub>AR</sub> in natural waters is usually greater than 1. Scott [58] made a statistical compilation of the data published before 1982 about  $^{238}$ U concentrations and the [ $^{234}$ U/ $^{238}$ U]<sub>AR</sub> in the water of main rivers on five continents and found that the radioactivity ratio of  $^{234}$ U to  $^{238}$ U was basically 1.2–1.3, which was indicative of radioactive disequilibrium between uranium isotopes attributed to the properties of the rock formations and soils in the rivers. Chabaux et al. [59] calculated the mean [ $^{234}$ U/ $^{238}$ U]<sub>AR</sub> of the world's major rivers to be 1.17, confirming the above conclusion.

Under natural conditions, the enrichment of  $^{234}$  U in water is related to the  $\alpha$ -decay of  $^{238}$ U nuclides and there are two main ways. When  $^{238}$ U in a mineral undergoes  $\alpha$ -decay at the interface between a uranium-bearing mineral and waters, the daughter <sup>234</sup>Th will be ejected out of the crystal lattice due to the recoil effect. <sup>234</sup>Th has a short half-life (24 day) and decays into <sup>234</sup>U, which readily forms complex ions and thereby enters the waters, resulting in an increase in aqueous <sup>234</sup>U concentration. This process is called the " $\alpha$ -recoil process". When the <sup>238</sup>U radioactive decay occurs, the daughter <sup>234</sup>U will be placed into the crystal lattice destroyed by the <sup>238</sup>U radioactive decay.

The increase in <sup>234</sup>U concentration due to the preferentially dissolution of destroyed crystal lattice. Given the above processes, the  $[^{234}U/^{238}U]_{AR}$  in natural waters is ultimately greater than 1 [14,18,60–64].





**Figure 7.** Distribution characteristics of  $[^{234}U/^{238}U]_{AR}$  of all lake water samples.

The results are as follows:  $[^{234}U/^{238}U]_{AR (GH)}$ : 1.798,  $[^{234}U/^{238}U]_{AR (KLK)}$ : 1.504,  $[^{234}U/^{238}U]_{AR (TS)}$ : 1.462,  $[^{234}U/^{238}U]_{AR (XLG 1)}$ : 1.565, and  $[^{234}U/^{238}U]_{AR (XLG 2)}$ : 1.673. The  $[^{234}U/^{238}U]_{AR}$  of each sampled lake clearly deviated from the equilibrium value (i.e., value of  $[^{234}U/^{238}U]_{AR} \neq 1$ ), which is due to frequent water-rock interaction (i.e., sediments, atmosphere dust and organic material etc.) that promotes the production and release of  $^{234}$ U into the waters due to the  $\alpha$ -recoil process. This increases the aqueous  $^{234}$ U concentration and thereby causes the  $[^{234}U/^{238}U]_{AR}$  to significantly deviate from the equilibrium.

Based on the current data, we only could show that there are big differences of  $[^{234}U/^{238}U]_{AR}$  in the sampled different lakes located in the same regional background, but show consistent  $[^{234}U/^{238}U]_{AR}$  in vary sites and depths in any one lake. Further, the  $[^{234}U/^{238}U]_{AR}$  in all sampled saline lakes is above 1.5 which is higher than the reported average value (1.17) of river from the world [58], lower than the reported value (~2.5) of lakes in Namshi-Nur and Tsagan-Tyrm [64] and that of rivers in same region [25]. These results mean that the  $[^{234}U/^{238}U]_{AR}$  of these saline lakes may be related to the input water and the water-rock interaction during the evolution stage, metamorphous degree, and hydrochemistry type. The input water of saline lakes in the northeast of Qaidam Basin is mainly based on natural precipitation, river water, and groundwater [56,65]. The factors affecting the [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub> in water-rock interaction during the evolution stage, metamorphous degree, and hydrochemistry type could be related with the redox conditions, pH of water, and biogeochemical process (i.e., the presence of organic matter (OM) and its interaction with iron and manganese oxides/hydroxides and/or competing cations, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>) during evolution stage, metamorphous degree, and hydrochemistry of the saline lakes. This will be resolved. By analyzing the major and trace element geochemistry distribution and the  $[^{234}U/^{238}U]_{AR}$  of the suspended particles filtered from the water of these sampled lakes in future.

# 4.3. Seasonal Effects on $^{238}$ U Concentration and the [ $^{234}$ U/ $^{238}$ U]<sub>AR</sub> in Lakes and Their Potential Environmental Impact

The concentration of <sup>238</sup>U in natural lake waters and the [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub> are the best tracers for determining changes in the water environment. The main source of <sup>238</sup>U in lake waters are water–rock interaction and rock weathering, in addition to other sources such as exogenous inputs from rivers, atmospheric precipitation, and groundwater recharge. The radioactive disequilibrium of <sup>234</sup>U/<sup>238</sup>U is the best evidence of the water-rock interaction of <sup>238</sup>U. The <sup>238</sup>U concentration and the [<sup>234</sup>U/<sup>238</sup>U]<sub>AR</sub> of various sites in a lake remain almost consistent. However, this will be affected by seasonal variation due to an input of precipitation mainly occurring in the rainy season. The annual precipitation in GH and TS is subject to significant variation, with precipitation mainly concentrated in May–September every year [21,32], which is likely to induce the seasonal variation of aqueous <sup>238</sup>U concentration. However, compared with the total water volume in GH and TS, the effect of seasonal precipitation variation on aqueous <sup>238</sup>U concentration was insignificant. Based on the seasonal effect on the result of <sup>238</sup>U concentration in GH is 11.96%, and the result is 2.25% for TS. Therefore, we conclude that the subtle seasonal difference of <sup>238</sup>U concentration in the lake waters are due to the dilution effect of precipitation and/or groundwater.

In summary, the concentration of  $^{238}$ U in natural lake waters and the  $[^{234}U/^{238}U]_{AR}$  remain almost consistent for a certain period of time. Studies of U-series disequilibria in lakes mainly include the determination of sediment ages and/or of sedimentation rates [66]. Stable U- and Th-series nuclides in lakes is the basis of the determination of sediment ages. The ability of obtaining precise sediment ages is critical to the accuracy of the reconstruction of paleoclimate and paleoenvironment.

U- and Th-series nuclides in lakes are closely related. U- and Th-series nuclides of lake waters may give us some information about geochemical behavior and mixing characteristics of lakes [6]. There are many environmental changes recorded by lake sediments. We can chronologically decipher such records by measuring the U–Th nuclides of these sediments.

## 5. Conclusions

Four lakes in the northeast of Qaidam Basin were selected to represent a sequence of waters salinity in order to test the effect of lake salinity on aqueous uranium isotopes. A total of 43 water samples were taken during three different sampling campaigns and analyzed for water chemistry and uranium isotope concentrations. The aqueous <sup>238</sup>U concentration of the freshwater lakes was generally low, while it was generally high in these saline lakes, which is a response to the combined effects of TDS and pH.

Furthermore, pH is the dominant factor affecting changes in aqueous <sup>238</sup>U concentration of the sampled saline close lakes, as the lake waters pH could directly affected the speciation of <sup>238</sup>U, with lower water pH leading to more fractions of <sup>238</sup>U into stable forms, and thereby smaller aqueous <sup>238</sup>U concentration. With the exception of pH value, the replenishment of water likely exerts a certain effect on the uranium isotope concentration for open KLK fresh lake located in the northeast of Qaidam Basin in the same high evaporation environment background as close saline lakes.

The  $[^{234}U/^{238}U]_{AR}$  of each lake was greater than one, ranging roughly from 1.460 to 1.798, which was likely due to the  $\alpha$ -recoil of  $^{238}U$  at the water-rock interface and the leaching-precipitation process. The degree of consistency in the  $^{238}U$  and  $[^{234}U/^{238}U]_{AR}$  values across various sites in a lake indicated that aqueous  $^{238}U$  and  $[^{234}U/^{238}U]_{AR}$  were evenly distributed in the same lakes.

The  $[^{234}\text{U}/^{238}\text{U}]_{AR}$  in these saline lakes are closely related to the input water and the associated water–rock interactions involving sediments, atmosphere dust, and organic material etc. during the evolution stage, metamorphous degree, and hydrochemistry of these saline lakes. If the concentration of  $^{238}\text{U}$  in natural lake waters and the  $[^{234}\text{U}/^{238}\text{U}]_{AR}$  remain almost consistent for a certain period of

time. The potential environmental impact is that which is the base of the determination of sediments ages in lake and/or of sedimentation rates could be determined by lake sediment and/or biogenic carbonate in future. Further, we can chronologically decipher the environmental change records in them by measuring the U–Th nuclides of these sediments.

**Author Contributions:** The research was supervised by P.Z. and X.L. with guidance provided by H.C. and R.L.E. Samples were collected by C.Z., P.Z. and X.L. Experiment method was instructed by P.Z., Y.N. and X.Y. The paper written by C.Z. and P.Z. with revised provided by L.T., R.L.E. and H.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This study was supported by the National Natural Science Foundation of China (No. 41873013; No.41888101), the National Natural Science Foundation of USA (No. 1702816) and the 111 program of China (No. D19002).

**Acknowledgments:** The samples collection was supported by Weiguo Liu and Hu Liu of Institute of Earth Environment, Chinese Academy of Science. And we are grateful to two reviewer and editor's constructive comments for improve manuscript quality and Haiwei Zhang's help for improving framework of manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

# References

- Cheng, H.; Edwards, R.L.; Shen, C.C.; Polyak, V.J.; Asmerom, Y.; Woodhead, J.; Hellstrom, J.; Wang, Y.; Kong, X.; Spötl, C.; et al. Improvements in <sup>230</sup>Th dating, <sup>230</sup>Th and <sup>234</sup>U half-life values, and U–Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. *Earth Planet. Sci. Lett.* 2013, 371, 82–91. [CrossRef]
- Wang, L.; Ma, Z.; Sun, Z.; Wang, Y.; Wang, X.; Cheng, H.; Xiao, J. U concentration and <sup>234</sup>U/<sup>238</sup>U of seawater from the Okinawa Trough and Indian Ocean using MC-ICP-MS with SEM protocols. *Mar. Chem.* 2017, 196, 71–80. [CrossRef]
- 3. Broecker, W.S.; Peng, T.H. Reactive metals and the great particulate sweep. In *Tracers in the Sea*; Broecker, W.S., Peng, T.H., Eds.; Lamont-Doherty Geol Obs: Palisades, NY, USA, 1982; pp. 166–235.
- Andersen, M.B.; Stirling, C.H.; Porcelli, D.; Halliday, A.N.; Andersson, P.S.; Baskaran, M. The tracing of riverine U in Arctic seawater with very precise <sup>234</sup>U/<sup>238</sup>U measurements. *Earth Planet. Sci. Lett.* 2007, 259, 171–185. [CrossRef]
- Schmidt, S.; Saari, H. Residence time of suspended particles in the Garonne River (SW France): Indications derived from Th-234, Be-7 and Pb-210. In Proceedings of the EGU General Assembly Conference Abstracts, Vienna, Austria, 7–12 April 2013.
- Chabaux, F.; Bourdon, B.; Riotte, J. U-series geochemistry in weathering profiles, river waters and lakes. In *U/Th Series Radionuclides in Aquatic Systems*; Krishnaswami, S., Cochran, J.K., Eds.; Elsevier: Edinburgh, UK, 2008; Volume 13, pp. 49–104.
- 7. Aciego, S.M.; Aarons, S.M.; Sims, K.W. The uranium-isotopic composition of Saharan dust collected over the central Atlantic Ocean. *Aeolian Res.* **2015**, *17*, 61–66. [CrossRef]
- Chutcharavan, P.M.; Dutton, A.; Ellwood, M.J. Seawater <sup>234</sup>U/<sup>238</sup>U recorded by modern and fossil corals. *Geochim. Cosmochim. Acta* 2018, 224, 1–17. [CrossRef]
- 9. Aciego, S.M.; Aarons, S.M.; Sims, K.W. Behaviour of uranium during mixing in the delaware and chesapeake estuaries. *Estuar. Coast. Shelf Sci.* **1994**, *39*, 619–631.
- 10. Moran, S.B.; Ellis, K.M.; Smith, J.N. <sup>234</sup>Th/<sup>238</sup>U disequilibrium in the central Arctic Ocean: Implications for particulate organic carbon export. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **1997**, *44*, 1593–1606. [CrossRef]
- 11. Rengarajan, R.; Sarin, M.M.; Krishnaswami, S. Uranium in the Arabian Sea: Role of denitrification in controlling its distribution. *Oceanol. Acta* 2003, *26*, 687–693. [CrossRef]
- 12. Schmidt, S. Impact of the Mediterranean Outflow Water on particle dynamics in intermediate waters of the Northeast Atlantic, as revealed by <sup>234</sup>Th and <sup>228</sup>Th. *Mar. Chem.* **2006**, *100*, 289–298. [CrossRef]
- 13. Li, P.; Zhu, P.; Wang, X.; Yu, Y. Distribution of uranium in seawater on the continental shelf of the East China sea. *Oceanol. Limnol. Sin.* **1982**, *13*, 514–552. (In Chinese)
- 14. Li, G.; Li, L.; Li, L.; Li, T. Controling mechanism of riverine uranium isotope and its implication for weathering limitation theory. *Bull. Mineral. Petrol. Geochem.* **2019**, *38*, 11–17. (In Chinese)

- 15. Xu, Y.; Zhang, F.; Jin, Z. Uranium isotopic compositions of fine detrital particles in a glacial catchment of the Pamir Plateau and its implication for sediment transfer. *J. Earth Environ.* **2019**, *10*, 116–127. (In Chinese)
- 16. Peng, A.; Huang, Y.; Chen, M.; Yang, W.; Qu, Y. Depth distribution of uranium isotopes of different grades in Xiamen Bay seawater. *J. Appl. Oceanogr.* **2012**, *31*, 3–11. (In Chinese)
- 17. Francois, C.; Matheiu, G.; Philippe, L.; Jean, R.; Eugeni, V.; Olga, S.; Ludmilla, A. Geochemical and isotopic (Sr, U) variations of lake waters in the Ol'khon Region, Siberia, Russia: Origin and paleoenvironmental implications. *Comptes Rendus Geosci.* **2011**, *343*, 462–470.
- 18. Osmond, J.K.; Kaufman, M.I.; Cowart, J.B. Mixing volume calculations, sources and aging trends of Floridan aquifer water by uranium isotopic methods. *Geochim. Cosmochim. Acta* **1974**, *38*, 1083–1100. [CrossRef]
- 19. Yadav, D.N.; Sarin, M.M. Geo-chemical behavior of uranium in the Sambhar Salt Lake, Rajasthan (India): Implications to "Source" of salt and uranium "Sink". *Aquat. Geochem.* **2009**, *15*, 529–545. [CrossRef]
- Borole, D.V.; Krishnaswami, S.; Somayajljlu, B.L.K. Uranium isotopes in rivers, estuaries and adjacent coastal sediments of western India: Their weathering, transport and oceanic budget. *Geochim. Cosmochim. Acta* 1982, 46, 125–137. [CrossRef]
- 21. Zheng, X. China Salt Lake; Science Press: Beijing, China, 2002. (In Chinese)
- 22. Zhang, P. Qaidam Basin Salt Lake; Science Press: Beijing, China, 1987. (In Chinese)
- 23. Benjamin, L.; Philip, C.B.; Tamir, P.; Gerel, O. Geochemical evolution of uraniferous soda lakes in Eastern Mongolia. *Environ. Earth Sci.* **2011**, *62*, 171–183.
- 24. Lin, H.; Fengqing, H. Salt Lake Evolution and Paleoclimate Fluctuations in Qaidam Basin; Science Press: Beijing, China, 2007. (In Chinese)
- Zhang, P.; Cheng, H.; Liu, W.; Mo, L.; Li, X.; Ning, Y.; Ji, M.; Zong, B.; Zhao, C. Geochemical and isotopic (U, Th) variations in lake waters in the Qinghai Lake Basin, Northeast Qinghai-Tibet Plateau, China: Origin and paleoenvironmental implications. *Arab. J. Geosci.* 2019, *12*, 92. [CrossRef]
- Isupov, V.P.; Vladimirov, A.G.; Lyakhov, N.Z.; Shvartsev, S.L.; Ariunbileg, S.; Kolpakova, M.N.; Shatskaya, S.S.; Chupakhina, L.E.; Kuibida, L.V.; Moroz, E.N. Uranium in saline lakes of Northwestern Mongolia. *Dokl. Earth Sci.* 2011, 437, 352–356. [CrossRef]
- 27. Strakhovenko, V.D.; Gas'kovaet, O.L. Thermodynamic model of formation of carbonates and uranium mineral phases in lakes Namshi-Nur and Tsagan-Tyrm (*Cisbaikalia*). *Russ. Geol. Geophys.* **2018**, *59*, 374–385. [CrossRef]
- 28. Andersson, P.S.; Porcelli, D.; Gustafsson, Ö.; Ingri, J.; Wasserburg, G.J. The importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary. *Geochim. Cosmochim. Acta* 2001, 65, 13–25. [CrossRef]
- 29. Koch-Steindl, H.; Pröhl, G. Considerations on the behaviour of long-lived radionuclides in the soil. *Radiat. Environ. Biophys.* **2001**, *40*, 93–104. [CrossRef] [PubMed]
- Fredrickson, J.K.; Zachara, J.M.; Kennedy, D.W.; Liu, C.; Duff, M.C.; Hunter, D.B.; Dohnalkova, A. Influence of Mn oxides on the reduction of uranium (VI) by the metal-reducing bacterium *Shewanella Putrefaciens*. *Geochim. Cosmochim. Acta* 2002, *66*, 3247–3262. [CrossRef]
- 31. Belli, K.M.; DiChristina, T.J.; Van Cappellen, P.; Taillefert, M. Effects of aqueous uranyl speciation on the kinetics of microbial uranium reduction. *Geochim. Cosmochim. Acta* **2015**, *157*, 109–124. [CrossRef]
- 32. Han, T.; QI, D.; Chen, H.; Xiang, S.; Shi, S.; Liu, C.; Li, N.; Wu, S. Spatial and Temporal Distribution of Precipitation in Qaidam Basin. *Desert Oasis Meteorol.* **2019**, *29*, 18–24. (In Chinese)
- 33. Li, J.; Li, M.H.; Fang, X.M.; Wu, F.L.; Meng, Q.Q.; Zhang, Z.G.; Liu, X.M. Hydrochemical characteristics of the Hurleg Lake. *Arid Land Geogr.* 2015, *38*, 43–51. (In Chinese)
- 34. Chen, B.; Wang, W.; Duan, L.; Gu, X.; Liu, C.; Song, R. Spatial variability of hydraulic conductivity of riverbed sediment in the lower reaches of Bayin River. *Water Resour. Hydropower Eng.* **2019**, *50*, 52–57. (In Chinese)
- 35. Chen, Z.L.; Megharaj, M.; Naidu, R. Determination of Bromate and Bromide in Seawater by Ion Chromatography, with an Ammonium Salt Solution as Mobile Phase, and Inductively Coupled Plasma Mass Spectrometry. *Chromatographia* **2006**, *65*, 115–118. [CrossRef]
- 36. Thermo Scientific. *Dionex Aquion Ion Chromatography System Installation Instructions*; Thermo Scientific Press: Waltham, MA, USA, 2016.
- 37. Cheng, H.; Edwards, R.L.; Hoff, J.; Gallup, C.D.; Richards, D.A.; Asmerom, Y. The half-lives of uranium-234 and thorium-230. *Chem. Geol.* **2000**, *169*, 17–33. [CrossRef]

- Shen, C.C.; Edwards, R.L.; Cheng, H.; Dorale, J.A.; Thomas, R.B.; Moran, S.B.; Weinstein, S.; Edmonds, H.N. Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. *Chem. Geol.* 2002, *185*, 165–178. [CrossRef]
- 39. Shen, C.C.; Wu, C.C.; Cheng, H.; Edwards, R.L.; Hsieh, Y.T.; Gallet, S.; Chang, C.C.; Li, T.Y.; Lam, D.D.; Kano, A.; et al. High precision and high-resolution carbonate Th-230 dating by MCICP-MS with SEM protocols. *Geochim. Acta* **2012**, *99*, 71–86. [CrossRef]
- 40. Shugui, D. Environmental Chemistry; Higher Education Press: Beijing, China, 2006. (In Chinese)
- 41. Shi, W. The Principle of Water Geochemistry of Uranium Atomic; Energy Press: Beijing, China, 1990. (In Chinese)
- 42. Langmuir, D. Uranium-solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* **1978**, *42*, 547–569. [CrossRef]
- 43. Langmuir, D.; Herman, J.S. The mobility of thorium in natural waters at low temperatures. *Geochim. Cosmochim. Acta* **1980**, 44, 1753–1766. [CrossRef]
- 44. Owens, S.A.; Buesseler, K.O.; Sims, K.W.W. Re-evaluating the <sup>238</sup>U salinity relationship in seawater: Implications for the<sup>238</sup>U-<sup>234</sup>Th disequilibrium method. *Mar. Chem.* **2011**, *127*, 31–39. [CrossRef]
- 45. Lü, E.; Lei, Z.; Min, C.; Yusheng, Q.; Na, X.; Weifeng, Y.; Yanping, L.; Yipu, H. Size-fractionated uranium isotopes in surface waters in the Jiu-long River Estuary in China. *Acta Oceanol. Sin.* **2007**, *29*, 59–68. (In Chinese)
- 46. Mochizuki, A.; Hosoda, K.; Sugiyama, M. Characteristic seasonal variation in dissolved uranium concentration induced by the change of lake water pH in Lake Biwa, Japan. *Limnology* **2016**, *17*, 127–142. [CrossRef]
- 47. Newsome, L.; Morris, K.; Lloyd, J.R. The biogeochemistry and bioremediation of uranium and other priority radionuclides. *Chem. Geol.* **2014**, *363*, 164–184. [CrossRef]
- 48. Newsome, L.; Morris, K.; Shaw, S.; Trivedi, D.; Lloyd, J.R. The stability of microbially reduced U (IV); impact of residual electron donor and sediment ageing. *Chem. Geol.* **2015**, *409*, 125–135. [CrossRef]
- Burgos, W.D.; Senko, J.M.; Dempsey, B.A.; Roden, E.E.; Stone, J.J.; Kemner, K.M.; Kelly, S.D. Soil humic acid decreases biological uranium(VI) reduction by *Shewanella putrefaciens* CN32. *Environ. Eng. Sci.* 2007, 24, 755–761. [CrossRef]
- 50. Bogdanov, R.V.; Timofeev, S.A.; Selivanov, S.S. Radiogenic <sup>234</sup>U and <sup>210</sup>Po in humus acids of dyctionemic shale. *Radiochemistry* **2006**, *48*, 409–418. [CrossRef]
- 51. Xu, M.; Cao, H.; Jia, Q.; Gao, Y.; Chen, S. Preliminary study of plankton community diversity of the Gahai Salt Lake in the Qaidam Basin of the Qaidam Basin of the Qinghai-Tibet Plateau. *Biodivers. Sci.* 2002, *10*, 38–43. (In Chinese)
- 52. Shu, L. Protection and Development of the artemia in the salt lakes of Qinghai Province—A case of Ga Hai lake. *Resour. Dev. Mark* **2003**, *19*, 311–313. (In Chinese)
- 53. Zhao, S.; Chen, L. Institutional selection and analysis on the development of halogen resources in Gahai lake. *Chin. Fish.* **2007**, *9*, 71–72. (In Chinese)
- Li, X.; Liu, W.; Xu, L. Stable oxygen isotope of ostracods in recent sediments of Lake Gahai in the Qaidam Basin, northwest China: The implications for paleoclimatic reconstruction. *Glob. Planet. Chang.* 2012, 94–95, 13–19. [CrossRef]
- 55. Jin, Y.; Qiang, M.; Liu, Y.; Li, Y.; Li, H.; Li, F. Variations in carbon and oxygen isotopes of carbonate and water environments: Genggahai Lake, northeastern Qinghai-Tibetan Plateau. *Chin. Sci. Bull.* **2015**, *60*, 847–856. (In Chinese)
- 56. Liu, W.G.; Xiao, Y.K.; Wang, Q.Z.; Qi, H.P.; Wang, Y.H.; Zhou, Y.M.; Shirodkar, P.V. Chlorine isotopic geochemistry of salt lakes in the Qaidam Basin, China. *Chem. Geol.* **1997**, *136*, 271–279. [CrossRef]
- 57. Bourdon B, Turner S, Henderson G M, Introduction to U-series Geochemistry. *Rev. Mineral. Geochem.* 2003, 52, 1–21. [CrossRef]
- Scott, M.R. The chemistry of U and Th series nuclides in rivers. In *Uranium Series Disequilibrium: Applications to Environmental Problems*; Ivanovich, M., Harmon, R.S., Eds.; Oxford Clarendon Press: Oxford, UK, 1982; pp. 181–201.
- 59. Chabaux, F.; Riotte, J.; Clauer, N.; FranceLanord, G. Isotopic tracing of the dissolved U fluxes of Himalayan rivers: Implications for present and past U budgets of the Ganges-Brahmaputra system. *Geochim. Cosmochim. Acta* 2001, 65, 3201–3217. [CrossRef]
- 60. Osmond, J.K.; Rydell, H.S.; Kaufman, M.I. Uranium disequilibrium in groundwater: An isotope dilution approach in hydrologic investigations. *Science* **1968**, *162*, 997–999. [CrossRef]

- 61. Kigoshi, K. Alpha-recoil thorium-234: Dissolution into water and the Uranium-234/Uranium-238 disequilibrium in nature. *Science* **1971**, *173*, 47–48. [CrossRef] [PubMed]
- 62. Fleischer, R.L. Isotopic disequilibrium of uranium: Alpha-recoil damage and preferential solution effects. *Science* **1980**, 207, 979–981. [CrossRef] [PubMed]
- 63. Chabaux, F.; Riotte, J.; Dequincey, O. U-Th-Ra fractionation during weathering and river transport. *Rev. Mineral. Geochem.* **2003**, *52*, 533–576. [CrossRef]
- 64. Bourdon, B.; Bureau, S.; Andersen, M.B.; Pili, E.; Hubert, A. Weathering rates from top to bottom in a carbonate environment. *Chem. Geol.* **2009**, *258*, 275–287. [CrossRef]
- Vengosh, A.C.; Chivas, A.R.; Starinsky, A.; Kolodny, Y.; Baozhen, Z.; Pengxi, Z. Chemical and boron isotopic composition of non-marine brines from the Qaidam Basin, Qinghai, China. *Chem. Geol.* 1995, 120, 136–155. [CrossRef]
- 66. Ivanovich, M.; Harmon, R.S. *Uranium-Series Disequilibrium: Application to Earth, Marine, and Environmental Sciences*; Oxford Clarendon Press: Oxford, UK, 1992.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).