

## Article

# Rapid Extraction Chemistry Using a Single Column for $^{230}\text{Th}/\text{U}$ Dating of Quaternary Hydrothermal Sulfides

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**Abstract:**  $^{230}\text{Th}/\text{U}$  dating can provide high-precision age constraints on Quaternary hydrothermal sulfides. However, low content of U and Th often involves extraction chemistry for the separation and enrichment of U and Th, but these chemical processes are very complex. We developed a simplified procedure consisting of total sample dissolution and single-column extraction chemistry, which can reduce the time and improve the accuracy of the dating. Concentrated HCl-HF followed by  $\text{HNO}_3$  was added to ensure complete dissolution. A single column filled with 0.4 mL of AG 1-X8 anion resin was used, then 8 M  $\text{HNO}_3$ , 8 M HCl and 0.1 M  $\text{HNO}_3$  were used to elute most of the matrix metals, Th and U. This process provided more than 95% recoveries for U and Th, and negligible blanks. Meanwhile, Pb and Bi interferences were tested and showed no effect on the U and Th isotope ratio. The  $^{230}\text{Th}/^{238}\text{U}$  activity of the Geological Survey of Japan geochemical reference material JZn-1 in secular equilibrium was determined and showed a radioactive equilibrium ( $1.00 \pm 0.01$ ,  $n = 5$ , all errors  $2\sigma$ ) and an in-house standard QS-1 was consistent to  $0.0078 \pm 0.0001$  ( $n = 8$ ,  $\pm 2\sigma$ ) with an average age of  $705 \pm 10$  yrs BP ( $n = 8$ ,  $\pm 2\sigma$ ). The technique greatly shortens the sample preparation time and allows more concise and effective analysis of U-Th isotopes. It is ideally suited for the high-precision  $^{230}\text{Th}/\text{U}$  dating of Quaternary submarine hydrothermal sulfides and sulfides from other settings.

**Keywords:**  $^{230}\text{Th}/\text{U}$  dating; quaternary hydrothermal sulfides; MC-ICPMS; extraction



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## 1. Introduction

$^{230}\text{Th}/\text{U}$  dating, also called U-Th dating or  $^{230}\text{Th}$ - $^{234}\text{U}$ - $^{238}\text{U}$  dating, is a conventional high-precision tool for dating Quaternary carbonate [1–4] and sulfides [4–9]. This process can act as an accurate chronological control for submarine hydrothermal systems and provides important time constraints for the formation mechanism, the history of transformation and the growth rate of large sulfide deposits [10–15]. The ages obtained may be continuous or scattered and can provide information regarding hydrothermal metallogenic evolution when combined with complimentary geochemical studies [5,11,15].

The  $^{230}\text{Th}/\text{U}$  dating method is based on measuring the degree of secular equilibrium between  $^{238}\text{U}$  and its daughters,  $^{234}\text{U}$  and  $^{230}\text{Th}$ . As the abundances of  $^{234}\text{U}$  and  $^{230}\text{Th}$  are low, the precision of  $^{230}\text{Th}/\text{U}$  dating is limited by counting statistics. Therefore, before analysis, it is necessary to enrich and purify the U and Th in the samples. In recent years, with the development and application of high-precision mass spectrometry (multicollector inductively coupled plasma mass spectrometry; MC-ICPMS), per mil and even epsilon-level

(1 part in 10,000) precision of  $^{234}\text{U}$  and  $^{230}\text{Th}$  analysis have been widely achieved [1,16–22]. The dating range has also been extended from the modern age to 640,000 yrs BP [1,3]. At present,  $^{230}\text{Th}/\text{U}$  dating is mainly applied to carbonate materials, whereas its use for sulfides is still limited.

As with authigenic carbonate, submarine Quaternary sulfides are known to meet the two preconditions for  $^{230}\text{Th}/\text{U}$  dating, namely: (1) a large amount of highly soluble U and almost no Th are taken up during mineral deposition; (2) after deposition, the system remains closed to U and Th. According to the literature, the  $^{238}\text{U}$  content of most submarine hydrothermal sulfide minerals ranges from several ppb to tens of ppm, whereas the  $^{232}\text{Th}$  content is generally less than a few ppb [7–9,13,23,24].

U and Th separation and enrichment methods for sulfides have mostly been established by modifying the chemical processes used for carbonate dating. For Quaternary carbonate dating, these methods generally involve sample digestion, double spike addition, coprecipitation and U-Th separation by ion-exchange chromatography. Compared with carbonates, submarine hydrothermal sulfides have much more complex compositions. Sulfides usually contain many metals (Fe, Zn, Cu, Pb, etc.) and sulfur, but lower uranium contents; therefore, a larger sampling size is needed than for carbonates, which leads to difficulties in sample complete dissolution or re-precipitation with the same chemical conditions. Th tends to adsorb on the insoluble resistate minerals [25], resulting in a lower Th content or poor data repeatability for incompletely dissolved samples.

In typical literature procedures, several grams of sulfide are dissolved in concentrated nitric acid at 85 °C for several days, during which any insoluble minerals are discarded [7,9]. Then,  $\text{Fe}^{3+}$  and  $\text{OH}^-$  are added to the solution in sequence to form  $\text{Fe}(\text{OH})_3$  precipitate. U and Th are coprecipitated with  $\text{Fe}(\text{OH})_3$  [6] and loaded directly into double columns packed with AG 1-X8 and U/TEVA resins to separate the U and Th [7,9] using HCl and  $\text{HNO}_3$ . The separated U and Th fractions are analyzed using MC-ICPMS or thermal ionization mass spectrometry (TIMS) [6,10,12,26–28]. However, our preliminary experiments showed that such procedures do not completely dissolve sulfide samples and are subject to significant matrix effects, resulting in poor precision. Therefore, the accuracy of dating could not be guaranteed. For example, we obtained  $249,630 \pm 6025$  yrs and  $551 \pm 65$  yrs (unpublished data) for the same sulfide sample.

For these reasons, it was necessary to develop one more simple, accurate and reproducible method to reduce the sample mass, labor and time costs. To solve these problems, a rapid extraction procedure using a single column for U and Th in sulfides was designed using the AG 1-X8 resin. In our work, the dissolving efficiency performed better than others [6,7,9]; the separation of U and Th could be completed within one day and the accuracy and precision for the U and Th isotope ratios and the  $^{230}\text{Th}$  age were improved. Using this method, repeated analyses of the Geological Survey of Japan geochemical reference material JZn-1 (about 65 Ma) and an in-house hydrothermal sulfide standard QS-1 gave very consistent results, which suggest that QS-1 is potentially a very good Quaternary U-Th age reference material.

## 2. Materials and Methods

### 2.1. Reagents and Standards

Nitric acid ( $\text{HNO}_3$ ,  $\approx 14$  M) and hydrochloric acid (HCl,  $\approx 12$  M) (CMOS grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were purified three times using a Savillex DST-1000 sub-boiling system (Savillex, Eden Prairie, MN, USA) at 30 °C. All reagents and standards were diluted with the purified acids and ultrapure water (18.2 M $\Omega$ -cm; Milli-Q system, EMD Millipore, Billerica, MA, USA). The ultrapure hydrofluoric acid (HF, 46.0%–51.0%) and perchloric acid ( $\text{HClO}_4$ ) are from Kanto Chemical Co., Inc. (Tokyo, Japan).

U and Th were separated from the sample matrix through an AG1-X8 column (200–400 mesh, chloride form, Bio-Rad [29], Hercules, CA, USA) with a 0.4 mL resin volume. S can form volatile  $\text{H}_2\text{S}$  after dissolution, whereas most matrix and interfering

elements exist as cations. So, a standard sulfide simulation solution (SS-1) without S was prepared by mixing various standard solutions, including 100 ppm Cu, Fe, Zn and Pb (plasma level, Alfa Aesar, Tewksbury, MA, USA); 1 ppm Na, K Ca and Mg; 140 ppb U; 100 ppb Th and a 10 ppb multi-element standard solution (Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Ga, Li, Mg, Mn, Ni, Sb, Sn, Sr, Ti, Tl and V, NCS, Beijing, China).

The accuracy of  $^{235}\text{U}/^{233}\text{U}$ ,  $\delta^{234}\text{U}$  (equal to  $(^{234}\text{U}/^{238}\text{U})_{\text{activity}} - 1) \times 1000$ ) and  $^{230}\text{Th}/^{232}\text{Th}$  were determined by one work standard U (IU-1, prepared with NBS SRM 950a and  $^{233}\text{U}$ - $^{236}\text{U}$  double spike,  $^{235}\text{U}/^{233}\text{U} = 13.01 \pm 0.50$  and  $\delta^{234}\text{U} = (-18.35 \pm 2.00)\%$ ) and one Th isotopic standard (ITh-1). ITh-1 was prepared from the carbonate standard GBW04412 and NCS  $^{232}\text{Th}$ , and the long-term mean value of  $^{230}\text{Th}/^{232}\text{Th}$  for ITh-1 was  $0.0085 \pm 0.0001$ , which was calibrated by a gravimetric working standard Th-1 ( $^{230}\text{Th}/^{232}\text{Th} = (51.68 \pm 0.26) \times 10^{-6}$ ) and Th-2 ( $^{230}\text{Th}/^{232}\text{Th} = (5.083 \pm 0.008) \times 10^{-6}$ ) [28].

A geochemical reference material, zinc ore JZn-1, was obtained from the Geological Survey of Japan at about 65 Ma (in secular equilibrium) [29]. JZn-1 is a crude ore from the Kamioka Pb-Zn mine in Gifu Prefecture, Japan, consisting of hedenbergite, quartz, calcite, sphalerite and epidote [29]. A marine hydrothermal sulfide sample QS-1 collected from the Wocan Hydrothermal Field on the slow-spreading Carlsberg Ridge in the Indian Ocean [30] was analyzed to verify the accuracy and precision of the method for  $^{230}\text{Th}/\text{U}$  dating.

## 2.2. Sample Digestion and U/Th Purification

After removing the surface dirt by a physical method, the fresh parts were selected to be peeled off, pulverized using a tungsten steel crusher to 200-mesh powder and subjected to U and Th elemental analysis.

All chemical procedures were performed in a class-100 clean hood at the Uranium Series Chronology Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing, China.

For ample digestion, 20–50 mg of powder was placed in a pre-cleaned 7 mL PFA beaker (Saville, Eden Prairie, MN, USA). A total of 2 mL of mixed acid (12 M HCl/46% HF = 3:1) was added into the beaker, seated for 1 h and then sealed tightly. Subsequently, the beaker was heated on a hot plate at 120 °C for 12 h. After cooling, 0.5 mL of 14 M HNO<sub>3</sub> was added into the sample and the resealed beaker was heated at 120 °C for 6 h. After cooling, 0.1 mL of HClO<sub>4</sub> and a 0.1–0.5 mL U-Th spike with a known concentration ( $^{233}\text{U}/^{236}\text{U} = 1.006747$  and  $^{229}\text{Th}$ ) were added (to ensure identical mass bias, the optimum  $^{235}\text{U}/^{233}\text{U}$  ratio in the samples was 10–30 [31]). After drying on a hot plate at 180 °C, the sample was dissolved in several drops of 14M HNO<sub>3</sub> and then dried again. Finally, the sample was dissolved in 0.2 mL of 8 M HNO<sub>3</sub> and loaded on the ion-exchange chromatography resin.

For the purification and separation of U and Th, a PFA column was filled with approximately 0.4 mL of AG 1-X8 resin (Table 1, column volume = 0.5 mL, liquid volume = 1.5 mL, with a polyethylene frit at the bottom; see Wang et al. for details [6]) and pre-cleaned using acid (Table 1). Then, 0.2 mL of digested sample in 8 M HNO<sub>3</sub> was loaded on the resin. The sample matrix elements were eluted using 1.0 and 0.5 mL of 8 M HNO<sub>3</sub>. Then, a > 95% Th fraction was eluted using 1.0 and 0.5 mL of 8 M HCl and a > 95% U fraction was eluted using 1.0 and 1.0 mL of 0.1 M HNO<sub>3</sub>.

Subsequently, 1 drop of HClO<sub>4</sub> was added to both of the Th and U fractions to remove the trace organic matter. They were then dried on a hotplate at 180 °C, dissolved in 2 drops of 14 M HNO<sub>3</sub>, dried and dissolved in 0.4 M HNO<sub>3</sub> and 0.01 M HF for MC-ICPMS measurements.

Two parallel chemical blanks for the entire process were  $8.2 \pm 0.4$  pg for  $^{238}\text{U}$ ,  $0.3 \pm 0.7$  fg for  $^{230}\text{Th}$  and  $2.5 \pm 0.1$  fg for  $^{232}\text{Th}$ , which were negligible for the measured samples. The monitored recoveries (the ratio of the recovered to the total amount of known) of U and Th were better than 95%.

**Table 1.** U and Th separation using an AG 1-X8 resin column.

Step	Acid Condition	Volume (mL)	Elements Eluted	Fractions
Clean	8 M HNO <sub>3</sub>	1.0		
		0.5		
	8 M HCl	1.0		
		0.5		
		1.0		
	H <sub>2</sub> O (18.2 MΩ·cm)	1.0		
		1.0		
1.0				
Condition	8 M HNO <sub>3</sub>	1.0		
		1.0		
Load Sample	8 M HNO <sub>3</sub>	0.2		a
Wash	8 M HNO <sub>3</sub>	1.0	matrix elements	b
		0.5	matrix elements	c
Elute Th	8 M HCl	1.0	Th	d
		0.5	Th	e
Elute U	0.1 M HNO <sub>3</sub>	1.0	U	f
		1.0	U	g

### 2.3. Instrumental Analysis

The U and Th isotope analyses were performed using MC-ICPMS (Neptune, Thermo Fisher, Waltham, MA, USA). The sample solution was introduced using a PFA 50 µL/min Nebulizer on an Aridus II desolvating nebulizer system. The U and Th isotopes were analyzed in a peak-jumping mode, using one retarding potential quadrupole lens (RPQ) system with a secondary electron multiplier (SEM) to improve the abundance sensitivity in the following order: <sup>233</sup>U-<sup>234</sup>U-<sup>235</sup>U-<sup>236</sup>U (<sup>238</sup>U was calculated from the measured <sup>235</sup>U amount using a constant 137.818 [32]) and <sup>229</sup>Th-<sup>230</sup>Th and <sup>232</sup>Th (<sup>232</sup>Th was determined using a Faraday cup and calibrated by <sup>238</sup>U(Faraday)/<sup>236</sup>U(SEM) and <sup>238</sup>U(Faraday)/<sup>235</sup>U(SEM)) [1,27]. We estimated the tailing effect of <sup>238</sup>U by measuring the ion counts at m/z positions 232.5-233.5-234.5-235.5-236.5 and <sup>232</sup>Th at 228.5-229.5-230.5. The detailed information was described by Cheng et al. [1] and Wang et al. [27]. The SEM/Faraday intensity conversion factor was monitored by a <sup>235</sup>U amount of 5–7 mv every other two or three samples and the drift was less than 0.5‰ per hour with no effect on age accuracy.

We obtained transmission efficiencies of 1%–2% for the U and Th in routine measurements by a peak-jumping mode with an SEM [1,27]. All tests were conducted in a block of 500 cycles, with each cycle having an integration time of 3 s. The typical internal precision for one <sup>234</sup>U/<sup>235</sup>U block was better than  $5 \times 10^{-5}$ . Instrumental mass bias and shift were corrected using a <sup>233</sup>U/<sup>236</sup>U double spike and the standard deviation of the mass bias factor for routine tests between adjacent ratios was less than 1%.

During daily analysis, the signal stability was monitored using standard NBS-CRM 112A, which spiked with <sup>229</sup>Th-<sup>233</sup>U-<sup>236</sup>U with a known isotope ratio. The long-term test results gave a mean value of  $(52.84 \pm 0.03) \times 10^{-6}$  ( $n = 12, \pm 2\sigma$ ) for <sup>234</sup>U/<sup>238</sup>U and  $(-38.5 \pm 0.03) \%$  ( $n = 12, \pm 2\sigma$ ) for  $\delta^{234}\text{U}$ , which agreed with the reference values  $(52.841 \pm 0.082$  and  $-38.7 \pm 1.5$  ( $n = 82$ ) for <sup>234</sup>U/<sup>238</sup>U and <sup>234</sup>U) within  $2\sigma$  error [28].

The U and Th isotope ratios were collected by MC-ICPMS, then isotope fraction corrected, quality controlled (closely related to the precision and accuracy) and age calculated via the equation shown in Formulas (1) and (2) using Excel. The specific instrument parameters and the cup configurations for data acquisition are shown in Tables 2 and 3.

**Table 2.** Instrument parameters.

Instrument	Parameter	Setting
MC-ICPMS	RF power	1250 W
	Cooling gas	16 L/min
	Auxiliary gas	1.8 L/min
	Sample gas	1 L/min
	Extraction voltage	−2000 V
	Low resolution	300
CETAC Aridus II	Sample injection rate	50 µL/min
	Ar sweep gas	2 L/min
	Nitrogen gas	3 mL/min
	Spray chamber temperature	110 °C
	Membrane oven temperature	160 °C

**Table 3.** Faraday cup configurations for measurement of U and Th by MC-ICPMS.

Element	L1	C(SEM)	H1	H2	H3
U		<sup>233</sup> U			
		<sup>234</sup> U			
		<sup>235</sup> U			<sup>238</sup> U
		<sup>236</sup> U		<sup>238</sup> U	
Th		<sup>229</sup> Th			
		<sup>230</sup> Th		<sup>232</sup> Th	

Equations (1) and (2) were used to calculate age  $t$ :

$$\left[ \frac{^{230}\text{Th}}{^{238}\text{U}} \right]_{\text{activity}} = 1 - e^{-\lambda_{230}t} + \left( \frac{\delta^{234}\text{U}_t}{1000} \right) \left( \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) \left( 1 - e^{(\lambda_{234} - \lambda_{230})t} \right) \quad (1)$$

$$\delta^{234}\text{U}_t = \left[ \frac{\left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)}{\left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)_{eq}} - 1 \right] \times 10^3 \quad (2)$$

where  $\lambda$  is the decay constant,  $t$  is the age, and  $eq$  is secular equilibrium.  $\lambda_{230} = 9.17052 \times 10^{-6} \text{ a}^{-1}$  [1],  $\lambda_{234} = 2.82206 \times 10^{-6} \text{ a}^{-1}$  [1],  $\lambda_{238} = 1.55125 \times 10^{-10} \text{ a}^{-1}$  [33].

Mineralogical analysis of sample QS-1 was measured using X-ray diffraction (XRD) by a D/max 2400 system with a Cu target tube and an X'Celerator detector (Rigaku Corporation, Japan) under the conditions of a tube voltage of 40 kV and a tube flow of 40 mA. The major elements were quantitatively determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher, USA) and uncertainty was within  $\pm 5\%$ .

### 3. Results and Discussion

#### 3.1. Impact of Dissolution Protocols on U and Isotopes

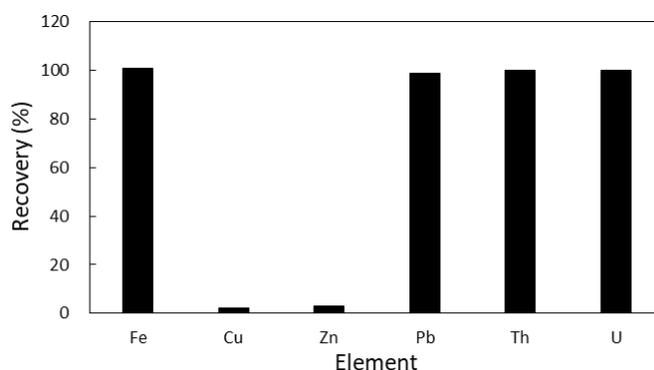
Various dissolution methods for submarine hydrothermal sulfides were evaluated. Aqua regia [4–6,26], HNO<sub>3</sub> [7,9] or HNO<sub>3</sub> + HF were usually used in various references, but insoluble residues, mainly including undissolved silicates, sulfur, the precipitation and residual BaSO<sub>4</sub>, were rarely reported. Sulfur could be effectively oxidized by HNO<sub>3</sub> + HBr generating more toxic Br<sub>2</sub> [34]. The modified dissolution method for the whole rock of the hydrothermal sulfide deposit gave much better dissolving efficiency and took less time. Using the HCl + HF and HNO<sub>3</sub> protocol in this study (in Section 2.2), a less than 100 mg sample can be completely dissolved with a total U  $\geq$  5 ng in one working day (see Table 4).

**Table 4.** Dissolution conditions and resin types in sulfide dating.

No.	Mass (g)	Dissolution Acid	Resin	Dissolution Time (Day)	Instrument	Reference
1	2.0–4.0	aqua regia	AG 1 × 8 or AV-17	>2	α-counting and MC-ICP-MS	Lalou et al., 1985, 1986 [4,5]; Kuznetsov et al., 2006 [26]; Wang et al., 2019 [6]
2	1.0–2.0	HNO <sub>3</sub> + H <sub>2</sub> O	AG1-X8 and U/TEVA	2–7	ICPMS and MC-ICP-MS	Takamasa et al., 2013 [9]; Ishibashi et al., 2015 [12]; Nakai et al., 2018 [7]
3	<0.1	HCl + HF followed by HNO <sub>3</sub>	AG 1-X8	<1	MC-ICP-MS	This study

### 3.2. Yields of Th and U, and Leaching

The most abundant elements after digestion in sulfides were Fe, Cu, Zn and Pb, which account for up to 95% of the total. Therefore, the elution efficiencies of Fe, Cu, Zn and Pb were mainly to be considered during leaching. Usually, Fe(OH)<sub>3</sub> precipitation was used to adsorb most of the U and Th from carbonates or sulfides for removing most of the Ca, Mg and other major elements [1,6]. We compared the element-selective adsorption efficiencies of six elements (Fe, Cu, Zn, Pb, Th and U) during Fe(OH)<sub>3</sub> precipitation to the standard solution SS-1. It showed that the precipitation operation could not efficiently remove Cu and Zn. The recovery rates of Pb, Th and U were similar to those of Fe (Figure 1) and incomplete Fe precipitation could lead to low U and Th recoveries. Thus, Fe(OH)<sub>3</sub> precipitation should be considered abandoned for Quaternary hydrothermal sulfides.

**Figure 1.** Recovery efficiencies of six elements for SS-1 using Fe(OH)<sub>3</sub> precipitation.

AG1-X8 is a common anion exchange resin used in the analysis of geological samples. As shown in Figure 2, the separation of Th and U was investigated using 0.4 mL of AG1-X8 resin for the standard solution SS-1 (see Section 2.1). Fe, Cu, Zn and Pb were completely eluted by less than 3.0 mL of 8 M HNO<sub>3</sub>. Recoveries of Th and U (measured vs. loaded) were greater than 95%. Therefore, we considered another separation step in the reports [7,9,12] to separate omittable Pb.

### 3.3. Impact of Pb and Bi on U-Th Isotopes

As many studies have found, Pb and Bi can produce peaks at the masses ranging from U to Th [7,9], but the studies have been not very clear about the interfering species. So, we performed Pb and Bi interference tests. Eleven standards were prepared with compositions similar to the separated U fractions of the sample, but with different amounts of Pb and Bi (no addition, 50 ppb and 100 ppb). The measured <sup>235</sup>U/<sup>233</sup>U atom ratios and δ<sup>234</sup>U of the standards are shown in Figure 3. <sup>235</sup>U/<sup>233</sup>U isotopic ratios and δ<sup>234</sup>U were all within 2σ error, indicating that there was little interference from Pb and Bi. The <sup>230</sup>Th/<sup>232</sup>Th isotopic ratios in the twelve standards are shown in Figure 4 and are also close to the standard value (within ±2σ error).

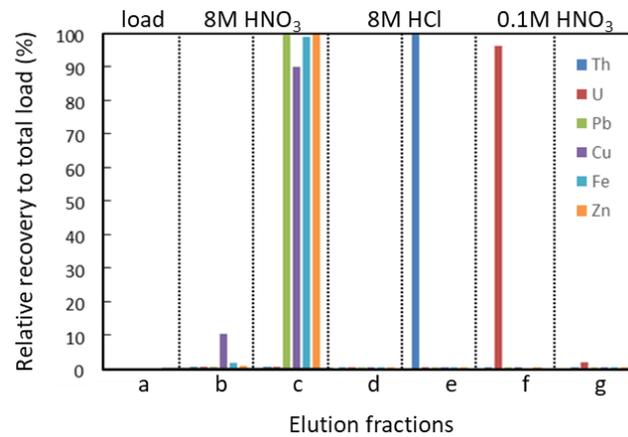


Figure 2. Relative recovery (measured vs. loaded) and elution fractions for the standard SS-1.

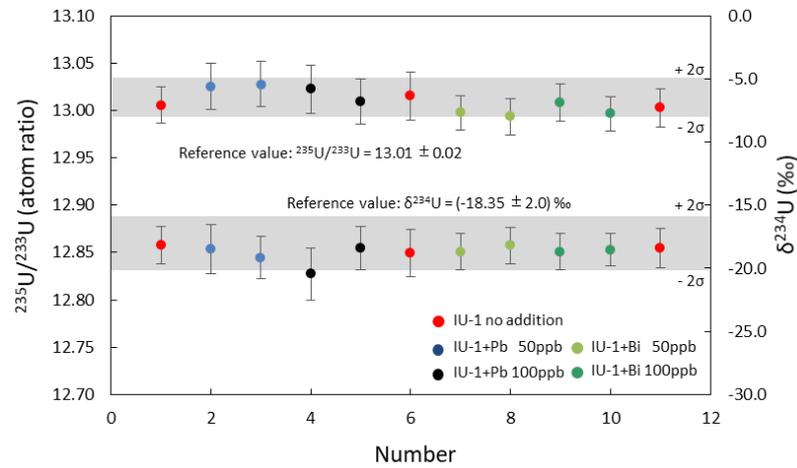


Figure 3. Effects of Pb and Bi on  $^{235}\text{U}/^{233}\text{U}$  and  $\delta^{234}\text{U}$  of IU-1.

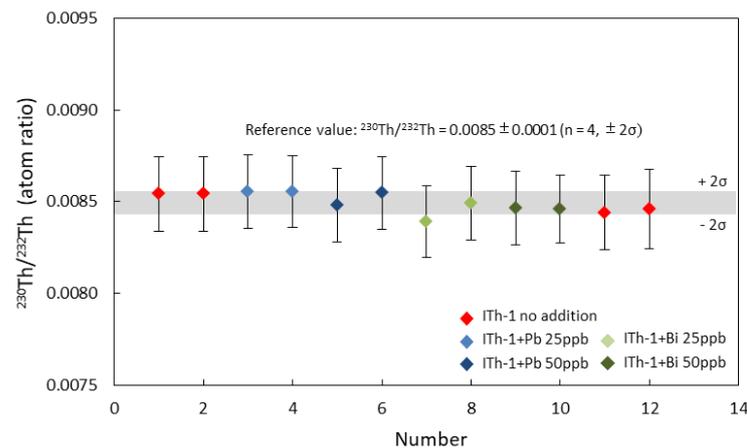


Figure 4. Effects of Pb and Bi on  $^{230}\text{Th}/^{232}\text{Th}$  isotopic ratio of ITh-1.

### 3.4. High-Precision $^{230}\text{Th}/\text{U}$ Dating of Sulfide Standard and Geological Sample

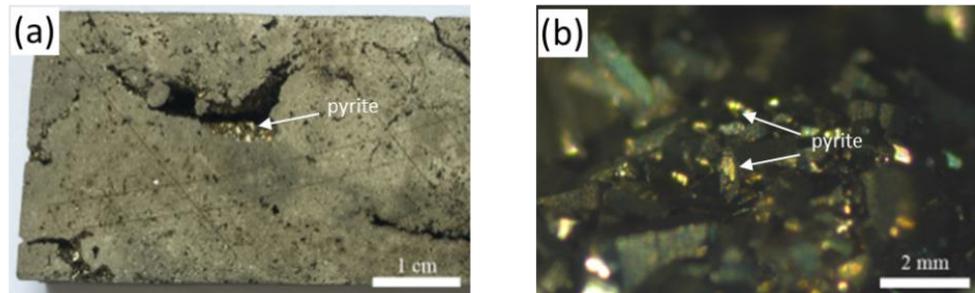
Until now, there has been no international sulfide standard for  $^{230}\text{Th}/\text{U}$  dating. Therefore, we chose the Geological Survey of Japan geochemical reference material JZn-1 (a sulfide ore powder) to determine the technical reliability. As shown in Table 5, the five independent measurements were consistent within  $\pm 2\sigma$  error. The  $^{238}\text{U}$  content varied from 2033 to 2042 ppb; the  $^{232}\text{Th}$  from 9178 to 9218 ppb and the  $\delta^{234}\text{U}$  from 17 to 20‰. The  $^{230}\text{Th}/^{238}\text{U}$  activity ratio was the same value,  $1.00 \pm 0.01$  ( $n = 5, \pm 2\sigma$ ) within  $\pm 2\sigma$  error.

**Table 5.** U-Th contents and isotopic ratios for sulfide standard JZn-1 ( $\pm 2\sigma$ , absolute value).

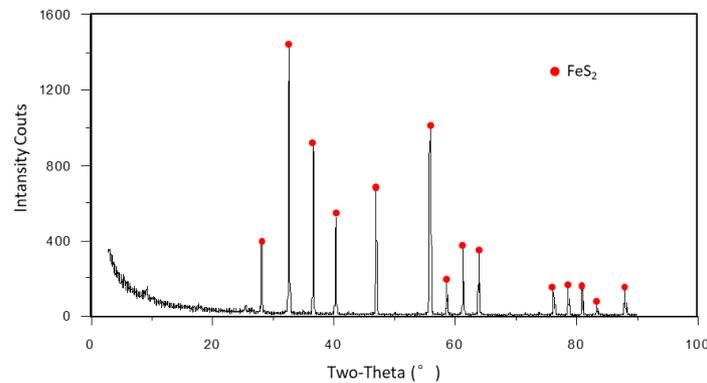
Standard	Mass (mg)	$^{238}\text{U}$ (ppb)	$^{232}\text{Th}$ (ppb)	$^{230}\text{Th}/^{232}\text{Th}$ ( $\text{AT} \times 10^{-6}$ )	$\delta^{234}\text{U}$ * (Measured)	$^{230}\text{Th}/^{238}\text{U}$ (Activity Ratio)
JZn-1	53	2033 $\pm 2$	9218 $\pm 47$	3.64 $\pm 0.03$	19 $\pm 1$	1.00 $\pm 0.01$
	50	2038 $\pm 2$	9178 $\pm 47$	3.65 $\pm 0.03$	20 $\pm 1$	1.00 $\pm 0.01$
	52	2037 $\pm 2$	9185 $\pm 47$	3.64 $\pm 0.03$	17 $\pm 1$	1.00 $\pm 0.01$
	53	2042 $\pm 2$	9189 $\pm 47$	3.64 $\pm 0.03$	20 $\pm 1$	1.00 $\pm 0.01$
	57	2034 $\pm 2$	9207 $\pm 47$	3.64 $\pm 0.03$	19 $\pm 1$	1.00 $\pm 0.01$
Mean	2037 $\pm 7$	9195 $\pm 33$	3.64 $\pm 0.01$	19 $\pm 2$	1.00 $\pm 0.01$	

$\lambda_{230} = 9.17052 \times 10^{-6} \text{ a}^{-1}$  [1],  $\lambda_{234} = 2.82206 \times 10^{-6} \text{ a}^{-1}$  [1],  $\lambda_{238} = 1.55125 \times 10^{-10} \text{ a}^{-1}$  [33]. \*  $\delta^{234}\text{U} = ([^{234}\text{U}/^{238}\text{U}]_{\text{activity}} - 1) \times 1000$ .

We also selected a large iron sulfide mineral, QS-1, collected in the Indian Ocean with an intact crystal form as a work standard. QS-1 was observed for pyrite under a microscope (Figure 5). The XRD pattern indicated that the main component of sulfide QS-1 was 99% pyrite ( $\text{FeS}_2$ , Figure 6). Elemental analysis showed that the Fe content was approximately 33% (Table 6).



**Figure 5.** Pictures of sulfide QS-1. (a) Profile of the sample. (b) Micrographs of the pyrite.



**Figure 6.** X-ray diffraction pattern of sulfide QS-1.

**Table 6.** Element contents of sulfide QS-1.

Element	Wt. %	100 Elt./Fe
Fe	33.0	100.0
Na	1.8	5.5
Mg	0.4	1.2
Si	0.4	1.2
Al	0.2	0.6
Ca	0.2	0.6
Cu	0.1	0.3
Zn	0.1	0.3

Using the developed method, the U and Th contents and isotopic ratios of QS-1 were measured eight times (Table 7). The age of this sample was determined to be from 701 to 715 yrs BP. All results were consistent with each other with an average value of  $705 \pm 10$  yrs BP ( $n = 8, \pm 2\sigma$ ).

**Table 7.** U-Th contents and isotopic ratios for sulfide QS-1 ( $\pm 2\sigma$ , absolute value).

Sample Number	$^{238}\text{U}$ (ppb)		$^{232}\text{Th}$ (ppt)		$^{230}\text{Th} / ^{232}\text{Th}$ ( $AT \times 10^{-6}$ ) <sup>a</sup>		$\delta^{234}\text{U}$ (Measured) <sup>b</sup>		$^{230}\text{Th}/^{238}\text{U}$ (Activity)		$^{230}\text{Th}$ Age (yr, UC) <sup>c</sup>		$^{230}\text{Th}$ Age (yr, C) <sup>d</sup>		$\delta^{234}\text{U}_{\text{Initial}}$ (C) <sup>e</sup>		$^{230}\text{Th}$ Age (yr BP, C) <sup>e</sup>	
1	4872	$\pm 14$	2780	$\pm 56$	223.4	$\pm 4.7$	146	$\pm 2$	0.0077	$\pm 0.0001$	738	$\pm 5$	723	$\pm 11$	147	$\pm 2$	703	$\pm 11$
2	4997	$\pm 14$	2621	$\pm 50$	246.0	$\pm 4.9$	144	$\pm 2$	0.0078	$\pm 0.0001$	749	$\pm 5$	735	$\pm 11$	144	$\pm 2$	715	$\pm 11$
3	4853	$\pm 13$	2770	$\pm 56$	225.5	$\pm 4.7$	147	$\pm 2$	0.0078	$\pm 0.0001$	745	$\pm 5$	730	$\pm 11$	147	$\pm 2$	710	$\pm 11$
4	5010	$\pm 14$	2739	$\pm 55$	231.6	$\pm 4.8$	144	$\pm 2$	0.0077	$\pm 0.0001$	735	$\pm 5$	721	$\pm 11$	144	$\pm 2$	701	$\pm 11$
5	4921	$\pm 14$	3090	$\pm 62$	203.7	$\pm 4.3$	145	$\pm 2$	0.0078	$\pm 0.0001$	741	$\pm 5$	725	$\pm 12$	145	$\pm 2$	705	$\pm 12$
6	5083	$\pm 10$	2895	$\pm 79$	225.2	$\pm 4.4$	147	$\pm 2$	0.0078	$\pm 0.0001$	742	$\pm 6$	728	$\pm 12$	147	$\pm 2$	702	$\pm 15$
7	4980	$\pm 12$	3039	$\pm 61$	208.6	$\pm 4.4$	146	$\pm 2$	0.0077	$\pm 0.0001$	737	$\pm 5$	721	$\pm 12$	147	$\pm 2$	701	$\pm 12$
8	4933	$\pm 11$	2634	$\pm 73$	238.8	$\pm 6.9$	147	$\pm 2$	0.0077	$\pm 0.0001$	737	$\pm 6$	724	$\pm 11$	148	$\pm 2$	704	$\pm 11$
Mean	4956	$\pm 153$	2821	$\pm 347$	225.4	$\pm 28.3$	146	$\pm 3$	0.0078	$\pm 0.0001$	740	$\pm 9$	726	$\pm 10$	146	$\pm 3$	705	$\pm 10$

$\lambda_{230} = 9.17052 \times 10^{-6} \text{ a}^{-1}$  [1],  $\lambda_{234} = 2.82206 \times 10^{-6} \text{ a}^{-1}$  [1],  $\lambda_{238} = 1.55125 \times 10^{-10} \text{ a}^{-1}$  [33]. <sup>a</sup>  $AT$  = atomic. <sup>b</sup>  $\delta^{234}\text{U} = ((^{234}\text{U}/^{238}\text{U})_{\text{activity}} - 1) \times 1000$ . <sup>c</sup> UC = uncorrected. The age is before present or chemical date. The corrected  $^{230}\text{Th}$  ages assume an initial  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratio of  $(4.4 \pm 2.2) \times 10^{-6}$ , which is the value for a material at secular equilibrium, with a bulk earth  $^{232}\text{Th}/^{238}\text{U}$  value of 3.8. The errors are arbitrarily assumed to be 50%. <sup>d</sup> C = corrected.  $\delta^{234}\text{U}_{\text{initial}}$  was calculated based on  $^{230}\text{Th}$  age (T), i.e.,  $\delta^{234}\text{U}_{\text{initial}} = \delta^{234}\text{U}_{\text{measured}} \times e^{\lambda_{234} \times T}$ . <sup>e</sup> C = corrected. BP denotes “before present”, where “present” is defined as the year 2000 A.D.

The  $\delta^{234}\text{U}$  and  $\delta^{234}\text{U}_{\text{initial}}$  values of sulfide QS-1 ( $(146 \pm 3)\text{‰}$  and  $(146 \pm 3)\text{‰}$ ) were similar to the  $\delta^{234}\text{U}$  of open ocean seawater ( $(144.9 \pm 0.1)\text{‰}$  [35]). The average U content was 4.956 ppm, slightly higher than seawater ( $\sim 3$  ppm). These results illustrated that the dating was reasonable. In addition, the  $^{230}\text{Th}$  age of QS-1 was  $705 \pm 10$  yrs BP with a precision of 1.4%. Overall, these results indicated that the developed method could determine U-Th ages of sulfides in the seabed accurately. This method can be applied to dating samples younger than 600,000 years with a precision of better than 1% in theory.

#### 4. Conclusions

$^{230}\text{Th}/\text{U}$  dating of hydrothermal sulfides provides an age estimate based on the measurement of uranium ( $^{238}\text{U}$  and  $^{235}\text{U}$ ), thorium ( $^{232}\text{Th}$ ) and certain intermediate daughter nuclides in the three naturally occurring radioactive decay series. The sulfide digestion and U-Th chromatographic separation protocols developed in this study are simple methods for the  $^{230}\text{Th}/\text{U}$  dating of sulfides with high precision. These methods are successfully applied to the reference material JZn-1 and a marine hydrothermal sulfide sample QS-1. The age of QS-1 is consistent at  $705 \pm 10$  yrs BP ( $n = 8, \pm 2\sigma$ ), suggesting that it could potentially be a very good reference material. This method can be applied to dating samples younger than 600,000 years with a precision of better than 1% in theory. In addition, the developed method can be also applied to dating carbonates or phosphates in environmental tracer studies, assisting in building an ageing framework for the formation of minerals.

**Author Contributions:** L.-S.W. wrote the manuscript. L.-S.W., Z.-B.M. and J.-L.X. conceived the idea. L.-S.W. and X.-F.W. carried out the chemical and MC-ICPMS experiments. Z.-B.M., Y.-J.W. and J.Y. contributed to the collection of the standard materials and best samples for analysis. L.-S.W., Y.-J.W. and J.Y. arranged this research and provided the project support. Y.-J.W., J.Y. and J.-L.X. provided the methodology-improving suggestions in editing. All authors have read and agreed to the published version of the manuscript.

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