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TECHNICAL NOTE

Evaluation of sample dissolution method for Sm-Nd isotopic analysis of scheelite

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Sm-Nd isotope systematics of scheelite is becoming a powerful geochronometer for dating the Au and W ore deposits. However, Sm-Nd isotopic analysis of scheelite is relatively difficult due to the formation of large amounts of tungstic acid (H_2WO_4) precipitates during the conventional acid decomposition of scheelite. In this study, both the low temperature attack and Teflon bomb acid dissolution methods for Sm-Nd isotope analysis of scheelite have been thoroughly investigated. It has been shown that, for both low temperature attack and Teflon bomb methods, although a large amount of tungstic acid precipitate remains during the 2.5 M HCl acidification process prior to cation exchange separation, only less than 10% of the Sm and Nd remains in the tungstic acid precipitate. On the other hand, it has been found that, for isotope dilution analysis, the spike-sample isotopic equilibration was only completely achieved for the Teflon bomb method and not completely achieved for the low temperature attack method, indicating that the low temperature attack method has possibly not liberated all the rare earth elements (REEs) from the scheelite crystal structure. Consequently, for high precision scheelite Sm-Nd dating purposes, the complex Teflon bomb rather than the simple low temperature attack method should be used in order to completely digest scheelite samples; alternatively, since it has been found that the tungstic acid precipitate formed during the acid dissolution process can be completely dissolved by self-purified low-blank 30% NaOH, a simple low temperature attack method combined with low-blank 30% NaOH dissolution of the remaining tungstic acid precipitate can also possibly be used to completely dissolve the scheelite sample for Sm-Nd isotopic analysis.

1. Introduction

The ability to accurately determine the timing of mineralization is crucial for understanding the genesis of hydrothermal ore deposits. However, it is very difficult to directly determine the age of the hydrothermal ore deposits, mainly due to the lack of minerals that can be dated by conventional radiometric methods.[1,2]

Scheelite, $CaWO_4$, is a common accessory mineral in hydrothermal Au-deposits and W-deposits.[3] The crystal structure of scheelite can accommodate high concentrations of rare earth elements (REEs); meanwhile, scheelite is one of the few minerals characterized by high Sm/Nd ratios.[3] As is well-known, Sm and Nd have similar chemical properties. Therefore, the daughter [143]Nd produced by α-decay from the parent [147]Sm can be easily preserved in the mineral lattice, *i.e.* the Sm-Nd isotope

systematics can be kept closed and are able to resist weathering and/or alteration to some degree.[4] Consequently, the Sm-Nd isotopes of scheelite can potentially be a powerful geochronometer for dating the Au and W ore deposits, even for relatively young ore deposits, provided there is a significant range of the Sm/Nd ratio. In recent years, the scheelite Sm-Nd system has been widely adopted for dating W or Au deposits.[1–3,5–11] In addition, REE elemental and Sr-Nd-Pb isotopic investigation of scheelite can provide important information on the origin and genesis of the ore deposits.[1–3,5–14]

However, although Sm-Nd dating of scheelite can provide important age constraints for Au or W ore deposits, Sm-Nd isotopic analysis of scheelite remains relatively difficult due to the formation of tungstic acid (H_2WO_4) precipitates during acid decomposition of the scheelite.[1,2,5] It has been reported that it is difficult to completely dissolve scheelite by acid decomposition using acids such as HF, HCl, HNO_3 and $HClO_4$ due to the protective coating of tungstic acid on the scheelite (*e.g.* ref. 7). In addition, the REE can possibly co-precipitate with the H_2WO_4 precipitates. Instead of acid decomposition, fusion (*e.g.*, Na_2CO_3) or sintering (*e.g.*, Na_2O_2) have also been adopted to attack and decompose the scheelite samples (*e.g.* ref. 11). However, due to the relatively high content of REE in Na_2CO_3

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or Na_2O_2 (e.g. ref. 15), these methods are not suitable for Sm-Nd isotopic analysis of scheelites, especially for scheelites that contain low amounts of Sm and Nd.

Currently, different acid decomposition methods such as low temperature acid attack (e.g. ref. 2, 3, 7) or Teflon bomb method (e.g. ref. 1, 2, 5) have mainly been adopted to dissolve the scheelites for Sm-Nd dating or REE elemental and Sr-Nd-Pb isotopic investigation of Au or W deposits. However, since there remains a large amount of tungstic acid precipitate after all dissolution stages during the acid decomposition of the scheelites,[2,3,5] the reliability of these acid decomposition methods still needs to be further investigated.

In this study, the scheelites have been decomposed by a mixed acid of $HF + HNO_3 + HClO_4$, both with simple low temperature attack and Teflon bomb methods, and the reliability and validity of these acid decomposition methods for Sm-Nd isotopic analysis have been fully investigated.

2. Experimental

2.1. Reagents and materials

Milli-Q H_2O: 18.2 MΩ at 25 °C.

HCl, HF, HNO_3, $HClO_4$: Purified by sub-boiling distillation using Teflon apparatus.

NaOH (30% m/v): NaOH (Acros Organics) was purified by addition of $FeCl_3$ to remove REEs.[16] 150 g NaOH was dissolved in 500 mL 0.05% m/v $FeCl_3$ (Analytical Reagent, AR) and the solution was then shaken thoroughly. After being cooled and allowed to stand for about 5 h, the solution was then centrifuged to separate $Fe(OH)_3$ precipitate, which collected most of the REEs originally in the solution.

$FeCl_3$: 20 mg mL^{-1}, 0.5 g high purity Fe_2O_3 (Shanghai Chemical Reagent Co., Ltd.) was dissolved in 5 mL 10 M HCl, and then diluted to 50 mL with Milli-Q H_2O.

Cation exchange column: 70 mm long × 6 mm i.d. with a 30 mL reservoir (made of quartz with a 30 μm polyethylene frit at the bottom), packed with 2 mL Bio-Rad AG50W × 12 resin (200–400 meshes).

HEHEHP chromatographic column: 160 mm long × 5 mm i.d. with a 40 mL reservoir (made of quartz with a 30 μm polyethylene frit at the bottom), packed with 3 mL HEHEHP resin; HEHEHP resin: particle size 120–200 meshes (75–125 μm), consisted of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP) coated Teflon powder, made by Beijing Research Institute of Chemical Engineering and Metallurgy.

2.2. Sample decomposition

The sample dissolution procedure is schematically illustrated in Fig. 1. The ^{149}Sm-^{150}Nd spikes were added at different stages for different analytical purposes.

2.2.1. Low temperature attack acid dissolution of scheelite (here defined as the "low temperature attack method"). About 30 mg (to precision 0.01 mg) of scheelite was dissolved in an acid mixture of 2 mL 22 M HF, 1 mL 15 M HNO_3 and 0.2 mL 70% (m/v) $HClO_4$ for one week in 7 mL Savillex® PFA vials on a hotplate at 120 °C. This amount of acid was in excess for digestion of about 30 mg of scheelite. Subsequently, the sample

was dried at 120 °C and then heated to 180 °C to completely remove HF. The residue was then treated overnight with 4 mL 6 M HCl at ca. 100 °C and then dried down again. Finally, the residue was leached with 1 mL 2.5 M HCl at 100 °C overnight. The sample solution together with the tungstic acid precipitates was then transferred to a 1.5 mL centrifuge tube and centrifuged at 4000 rpm for 10 min. The supernatant was pipetted out as completely as possible for chemical purification. The whole procedure is illustrated in Fig. 1a.

2.2.2. Teflon bomb acid decomposition of scheelite (here defined as the "Teflon bomb method"). About 30 mg (again to precision 0.01 mg) of scheelite was dissolved using a mixture of 2 mL 22 M HF, 1 mL 15 M HNO_3 and 0.2 mL $HClO_4$ in steel-jacketed Teflon digestion vessels and heated in an oven at 190 °C for five days. After drying down on a hot plate at 150 °C, 4 mL 6 M HCl was added and evaporated to dryness again. The sample residues were then leached using 1 mL 2.5 M HCl, again in steel-jacketed Teflon digestion vessels, at 150 °C for one day. Finally, the sample solution was centrifuged and the supernatant was pipetted out as completely as possible for column chemistry separation. The whole procedure is shown in Fig. 1b.

2.2.3. NaOH dissolution of tungstic acid precipitates. The tungstic acid precipitates remaining in the centrifuge tube from previous steps were dissolved using 1 mL 30% (m/v) self-purified NaOH solution. After the tungstic acid precipitates were completely dissolved, 0.2 mL 20 mg mL^{-1} $FeCl_3$ was added into the solution and thoroughly shaken to co-precipitate the REE. After the precipitate was settled for more than 5 h, the sample was centrifuged at 4000 rpm for 10 min. The supernatant (mainly Na_2WO_4 and NaOH) was pipetted out as completely as possible and discarded. The $Fe(OH)_3$ precipitate remaining in the centrifuge tube was then washed with 1 mL Milli-Q water and centrifuged again to further remove the WO_4^{2-}. Finally, the $Fe(OH)_3$ precipitate was dissolved in 1 mL 2.5 M HCl and centrifuged, and then the supernatant was ready for column chemistry. The entire procedure is illustrated in Fig. 1c.

2.3. Column chemistry

The supernatant obtained from the previous steps was loaded onto the pre-conditioned AG 50W × 12 columns for separation of REEs from the sample matrix. After rinsing with 0.5 mL 2.5 M HCl four times, the column was washed with 10 mL 5 M HCl to remove the matrix and other interfering elements. Subsequently, the REEs were stripped with 8 mL 6 M HCl. The Sm and Nd recovery yields were greater than 95% and some heavy REEs were separated from Sm and Nd during this step.[17,18]

The Ce, Pr, Nd, and Sm were separated using the HEHEHP chromatographic columns as described in detail by Chu et al.[17] The column was pre-cleaned with 20 mL 3 M HCl and 20 mL Milli-Q H_2O, and then conditioned with 3 mL 0.07 M HCl. The REE fraction obtained from the cation exchange column step was dried down and taken up with 0.2 mL 0.07 M HCl, and then loaded onto the HEHEHP columns. After rinsing with 0.2 mL 0.07 M HCl four times, the La, Ce and 80% of Pr were eluted with 35 mL 0.07 M HCl. Subsequently, the Nd was stripped with 12 mL 0.14 M HCl, and then the Sm was stripped with 8 mL
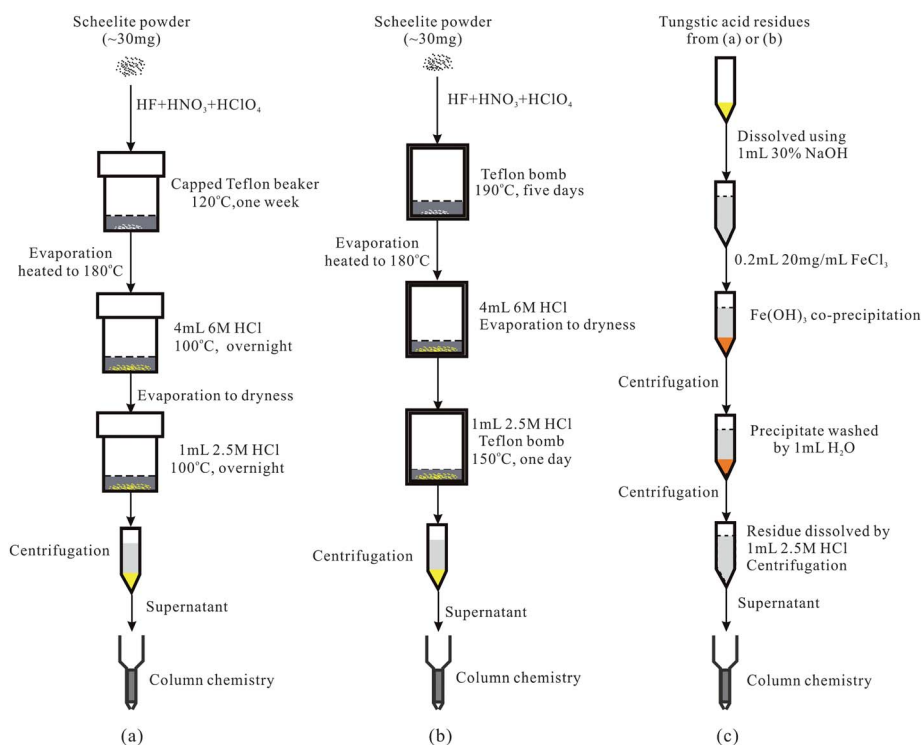
Fig. 1 General scheme of the chemical procedures for acid dissolution of scheelite. a): Low temperature attack method; b): Teflon bomb method; c): NaOH dissolution of tungstic acid precipitates.

0.4 M HCl. The fraction of Nd also contained *ca.* 20% of Pr, less than 1% of Ce and no detectable Sm. The recovery yields of Nd and Sm during this step were greater than 85% and 95%, respectively.

Minor amounts of Pr in Nd was found to have no significant influence on Nd isotopic measurements using the NdO^+ technique as described below. The reference material USGS BCR-2 was analyzed during the sample analytical session and the measured $^{143}Nd/^{144}Nd$ value was 0.512647 ± 6 (2SE), consistent with the reference value ($^{143}Nd/^{144}Nd = 0.512638$) (GeoREM, http://georem.mpch-mainz.gwdg.de), indicating that the column chemistry described here was reliable for Nd isotopic measurement using the NdO^+ method.

2.4. Mass spectrometry

Nd and Sm isotopes were analyzed on an IsoProbe-T thermal ionization mass spectrometer (TIMS) (isotopx company, formerly GV instruments, England), installed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG-CAS). The instrument is equipped with nine Faraday cups, seven Channeltron ion counters, one Daly detector and one ETP multiplier.

Neodymium isotopes were determined as NdO^+ using a single tungsten filament with TaF_5 as an ionization activator.[17] This method has very high sensitivity and can analyze Nd isotopes with high precision (2SE < 15ppm) on down to 0.5–1 ng Nd. Measured $^{143}Nd/^{144}Nd$ ratios were corrected for mass-fractionation using $^{146}Nd/^{144}Nd = 0.7219$. During the period of our data collection, the measured value for the JNdi-1 Nd standard was $^{143}Nd/^{144}Nd = 0.512117 \pm 10$ (2SD, $n = 8$). Sm isotopes were

analyzed as Sm^+, also using a single tungsten filament with TaF_5 as an ionization activator.[17] Measured $^{149}Sm/^{147}Sm$ ratios were corrected for mass-fractionation using $^{152}Sm/^{147}Sm = 0.56081$.[17]

3. Results and discussion

3.1. Amounts of Sm and Nd remaining in the tungstic acid precipitate

It was found that a large amount of tungstic acid precipitate finally remained during acid decomposition of scheelite, both for the low temperature attack and Teflon bomb methods. Normally, about 26 mg tungstic acid can potentially be produced upon acid digestion of 30 mg scheelite based on stoichiometry. It is possible that the Sm and Nd can co-precipitate with the tungstic acid precipitates. Therefore, the amounts of Sm and Nd remaining in the tungstic acid precipitate during acid dissolution of scheelite for both low temperature attack and Teflon bomb methods were investigated first.

The percentages of Sm and Nd remaining in the tungstic acid precipitates were evaluated in detail as follows: (1) the scheelite samples were first decomposed by either low temperature attack or Teflon bomb methods as shown in Fig. 1a and b; (2) the resulting 2.5 M HCl supernatants were then spiked with ^{149}Sm-^{150}Nd spike and allowed to equilibrate to measure the Sm and Nd amounts that had been taken up by the 1 mL 2.5 M HCl; (3) the remaining tungstic acid residues were also spiked with ^{149}Sm-^{150}Nd spike and then the entire procedure as outlined in Fig.1c was performed to measure the Sm and Nd amounts remaining in the tungstic acid precipitates. Since it was found that the tungstic acid precipitate could be completely dissolved

by the 30% NaOH, and more than 98% of the Sm and Nd was co-precipitated during the $Fe(OH)_3$ co-precipitation step, the amounts of Sm and Nd remaining in the tungstic acid precipitates could be accurately determined. By calculation from the results obtained from steps (2) and (3), the percentages of Sm and Nd remaining in the tungstic acid precipitate were consequently obtained. The analytical results are listed in Table 1. It was shown that, in general, more than 90% of Sm and Nd was taken up by the 1 mL 2.5 M HCl, while less than 10% of Sm and Nd remained in the tungstic acid residue, both for the low temperature attack and Teflon bomb acid dissolution methods.

In addition, as shown in Table 1, for the low temperature attack acid dissolution method, although 2.5 M HCl supernatant and tungstic acid precipitate dissolved in NaOH give identical $^{143}Nd/^{144}Nd$ values within analytical error, the Sm/Nd ratios obtained from the tungstic acid precipitate are obviously smaller than those obtained from the 2.5 M HCl supernatant, possibly an indication of Sm/Nd fractionation during the tungstic acid precipitation process or variable leaching of the REEs from the scheelite during the low temperature acid digestion process.

3.2. Sample-spike isotopic equilibration

During acid decomposition of scheelite by HF + HNO_3 + $HClO_4$, residues can be found during all the dissolution steps for both the low temperature attack and Teflon bomb methods. Therefore, it is very critical to ensure complete sample-spike isotopic equilibration during these acid decomposition procedures for scheelite Sm-Nd isotopic analysis.

In this study, the sample-spike equilibration between the 2.5 M HCl supernatant and the tungstic acid precipitate for Sm-Nd isotopes during the acid digestion process of scheelite was thoroughly evaluated as follows: (1) several scheelite samples were weighed and spiked with ^{149}Sm-^{150}Nd spike before sample decomposition; (2) the samples were thoroughly dissolved by either the low temperature attack or the Teflon bomb method as shown in Fig. 1a and b, and the remaining tungstic acid precipitates were subsequently dissolved using self-purified 30% NaOH

as outlined in Fig. 1c; (3) both the 2.5 M HCl supernatant and the tungstic acid precipitates dissolved in NaOH were measured for Sm, Nd concentrations and Nd isotopic compositions. The analytical results are listed in Tables 2 and 3. Since the tungstic acid precipitates can be completely dissolved by the 30% NaOH as mentioned above, this is a direct and complete method for the sample-spike isotopic equilibration evaluation compared to previously reported methods (e.g. ref. 2, 3, 5).

As shown in Table 2, for the low temperature attack method, although the 2.5 M HCl supernatant and the tungstic acid precipitates dissolved in NaOH give identical Nd isotopic composition values within analytical error, the Sm and Nd concentration and $^{147}Sm/^{144}Nd$ measured from the 2.5 M HCl supernatant and the tungstic acid precipitates dissolved in 30% NaOH show a slight difference (up to 3% for Nd concentration), indicating that the spike-sample equilibration for Sm-Nd isotopes between the 2.5 M HCl supernatant and the tungstic acid precipitate has not been completely achieved. Accordingly, it seems that the low temperature acid dissolution procedure has not liberated all the REEs from the scheelite crystal structure, possibly due to the protective coating of tungstic acid on the scheelite (e.g. ref. 3, 7). Nevertheless, as shown in Table 3, for the Teflon bomb method, in general, the 2.5 M HCl supernatant and the tungstic acid precipitates dissolved in NaOH not only give identical Nd isotopic compositions, but also give consistent Sm and Nd concentrations and $^{147}Sm/^{144}Nd$ ratios within analytical error for most samples, indicating that complete spike-sample equilibration has probably been achieved. Therefore, it is reasonable to conclude that the Teflon bomb acid dissolution procedure has possibly liberated all the REEs from the scheelite crystal structure.

3.3. Procedural blank levels

When the Teflon sub-boiling HF, HCl, HNO_3 and $HClO_4$ were used, and the 30% NaOH was purified as described in the Experimental section, the procedural blank including acid decomposition steps, NaOH dissolution of the tungstic acid

Table 1 Amounts of Sm and Nd taken up by 1 mL 2.5 M HCl and remaining in tungstic acid precipitate[a]

Sample No	Sample weight (g)	Digestion	Spike addition	Sm (µg g⁻¹)	Nd (µg g⁻¹)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$ (2SE)	Nd Percentage (%)
nr4103-118								
(1)	0.03193	LTA	2.5 M HCl supernatant	3.17	19.7	0.0973	0.512321 (7)	93
			tungstic acid precipitate	0.186	1.43	0.0789	0.512288 (8)	7
(2)	0.02958	LTA	2.5 M HCl supernatant	3.35	20.6	0.0986	0.512295 (8)	96
			tungstic acid precipitate	0.122	0.914	0.0808	0.512284 (6)	4
(3)	0.02984	Teflon bomb	2.5M HCl supernatant	3.34	21.0	0.0959	0.512312 (9)	96
			tungstic acid precipitate	0.134	0.837	0.0971	0.512320 (9)	4
(4)	0.033063	Teflon bomb	2.5M HCl supernatant	3.22	20.4	0.0955	0.512318 (6)	96
			tungstic acid precipitate	0.152	0.958	0.0958	0.512304 (11)	4
nr4103-120								
(1)	0.02954	LTA	2.5 M HCl supernatant	1.26	18.7	0.0408	0.512318 (7)	96
			tungstic acid precipitate	0.047	0.869	0.0324	0.512287 (6)	4
(2)	0.03466	LTA	2.5 M HCl supernatant	1.24	18.9	0.0397	0.512277 (7)	96
			tungstic acid precipitate	0.036	0.650	0.0330	0.512275 (5)	4
(3)	0.02984	Teflon bomb	2.5M HCl supernatant	1.30	18.70	0.0422	0.512292 (8)	96
			tungstic acid precipitate	0.0495	0.717	0.0417	0.512284 (8)	4

[a] Sm, Nd amounts taken up by the 2.5 M HCl and remaining in the tungstic precipitate are all depicted as concentrations relative to the whole sample; LTA: low temperature acid attack method; Teflon bomb: Teflon bomb method; 2SE means internal precision of individual analysis, reported as $\times 10^6$.

Table 2 The analytical results for isotopic equilibration tests for ID-TIMS analysis of scheelites: Low temperature acid attack method[a]

Sample	Phase	Sm ($\mu g\ g^{-1}$)	Nd ($\mu g\ g^{-1}$)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	2SE
nr4103-118	–HCl	3.49	21.65	0.0973	0.512325	0.000006
	–NaOH	3.42	21.12	0.0979	0.512350	0.000015
nr4103-118R	–HCl	3.39	21.18	0.0968	0.512325	0.000006
	–NaOH	3.34	20.73	0.0973	0.512328	0.000008
nr4103-120	–HCl	1.25	18.92	0.0400	0.512296	0.000008
	–NaOH	1.24	18.56	0.0403	0.512289	0.000006
nr4103-120R	–HCl	1.32	18.99	0.0420	0.512291	0.000008
	–NaOH	1.29	18.39	0.0425	0.512285	0.000010
03-8-2	–HCl	3.51	13.32	0.1593	0.511875	0.000016
	–NaOH	3.46	13.05	0.1605	0.511896	0.000012
03-1-2	–HCl	3.27	10.88	0.1817	0.511939	0.000012
	–NaOH	3.24	10.73	0.1826	0.511943	0.000010
03-8-1	–HCl	2.97	11.43	0.1569	0.511872	0.000010
	–NaOH	2.88	10.98	0.1587	0.511904	0.000008
03-2-2	–HCl	1.17	5.61	0.1258	0.511788	0.000009
	–NaOH	1.13	5.35	0.1275	0.511777	0.000023
01-4-1	–HCl	1.67	5.77	0.1752	0.511875	0.000010
	–NaOH	1.65	5.62	0.1773	0.511904	0.000008
03-1-1	–HCl	2.47	8.49	0.1758	0.511932	0.000009
	–NaOH	2.45	8.37	0.1768	0.511951	0.000013

[a] ID-TIMS: Isotope Dilution-Thermal Ionization Mass Spectrometry; –HCl: 2.5 M HCl supernatant; –NaOH: tungstic acid precipitate dissolved in NaOH; 2SE means internal precision for individual analysis.

precipitate, $Fe(OH)_3$ co-precipitation, column chemistry and mass spectrometry was found to be lower than 15 pg for Sm and 25 pg for Nd. The results confirm that the NaOH purified by $Fe(OH)_3$ co-precipitation method as described in the Experimental section contains very low amounts of Sm and Nd. The low total Sm and Nd procedural blanks ensure that the Sm-Nd analytical results in this study are reliable.

3.4. Evaluation of the sample digestion methods for scheelite

Based on the experimental results discussed above, it can be concluded that, for the Teflon bomb method, although a large amount of tungstic acid precipitate remains during 2.5 M HCl acidification of the sample prior to cation exchange separation, the isotopic equilibration between the 2.5 M HCl supernatant and the tungstic acid precipitate has been completely achieved. In contrast, for the low temperature acid dissolution method, although more than 90% of the Sm and Nd in the scheelite has also been incorporated into the acid dissolved phase, it is possible that the sample-spike isotopic equilibration has not been

completely achieved. As has been reported,[2,3,5] it is very important to ensure complete isotopic equilibration for scheelite Sm-Nd isotopic analysis to construct a more reliable scheelite Sm-Nd isochron. Therefore, for high precision Sm-Nd dating purposes, the Teflon bomb method rather than the low temperature attack acid method should be used to completely digest scheelite.

Since the Teflon bomb method is complex and difficult to operate as reported (e.g. ref. 2), we also suggest here an alternative method that combines low temperature acid dissolution of scheelite with low-blank 30% NaOH dissolution of the remaining tungstic acid precipitates as outlined in Fig. 2, to completely dissolve scheelite for high precision Sm-Nd isotopic analysis. Since the tungstic acid precipitates can be completely dissolved by the 30% NaOH, and the Sm and Nd can be co-precipitated efficiently by the $Fe(OH)_3$ as mentioned above, we believe that this method may be reliable.

Liu et al.[11] have reported a N_2O_2 fusion method to digest scheelite for REE elemental and Sm-Nd isotopic analysis. In brief, samples were dissolved in a graphite crucible with N_2O_2 in

Table 3 The analytical results for isotopic equilibration tests for ID-TIMS analysis of scheelites: Teflon bomb method[a]

Sample	Phase	Sm ($\mu g\ g^{-1}$)	Nd ($\mu g\ g^{-1}$)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	2SE
nr4103-118	–HCl	3.47	21.61	0.0972	0.512311	0.000013
	–NaOH	3.48	21.66	0.0971	0.512293	0.000009
nr4103-118R	–HCl	3.29	20.77	0.0957	0.512300	0.000006
	–NaOH	3.32	20.74	0.0967	0.512295	0.000009
nr4103-120	–HCl	1.28	19.16	0.0403	0.512285	0.000008
	–NaOH	1.30	19.26	0.0409	0.512281	0.000008
CL-176	–HCl	54.75	212.7	0.1556	0.512093	0.000013
	–NaOH	54.50	212.2	0.1553	0.512116	0.000011
CL-251	–HCl	70.61	279.1	0.1530	0.512120	0.000017
	–NaOH	70.55	278.4	0.1532	0.512096	0.000009

[a] Abbreviations as in Table 2; –HCl: 2.5 M HCl supernatant; –NaOH: tungstic acid precipitate dissolved in NaOH.
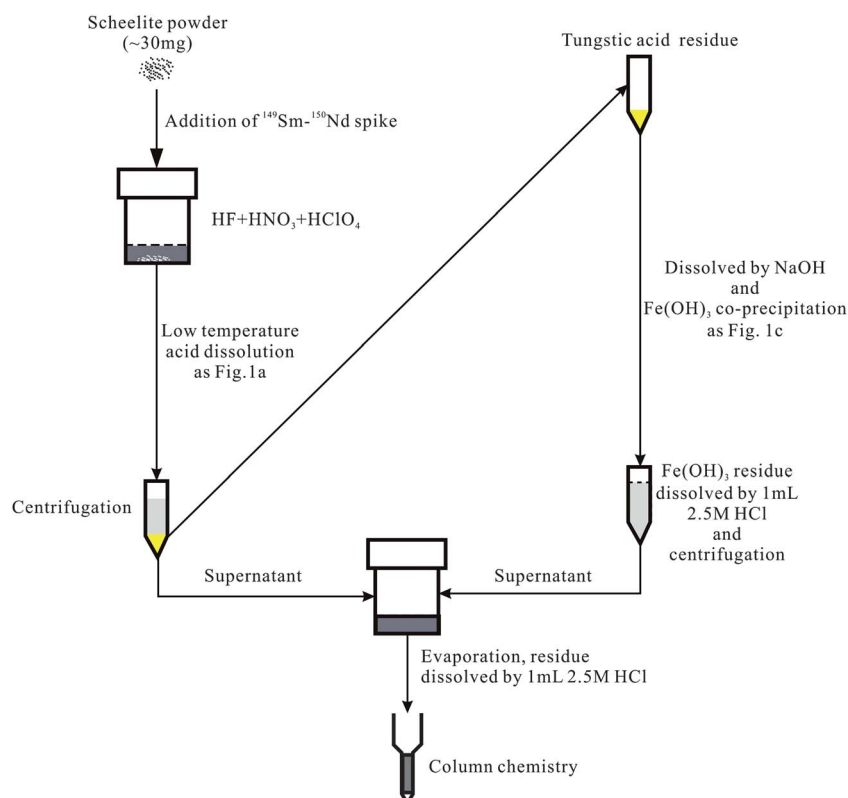
Fig. 2 Low temperature acid attack combined with NaOH dissolution of formed tungstic acid precipitate.

a muffle furnace at a temperature of 700 °C; after dissolving the fusion cake with Milli-Q H_2O, the analytes were precipitated in the strong alkaline solution, and sodium and WO_4^{2-} were separated by filtration; finally, the precipitates were dissolved by acid for subsequent analyses. This method is feasible and may ensure the complete digestion of scheelite. However, Na_2O_2 possibly has relatively high Sm and Nd blank levels.[15] For example, it was found in this study that the whole procedural Nd blank for the N_2O_2 fusion method could be as high as 20 ng. As is known, Na_2O_2 is difficult to further purify in the laboratory. In addition, the Na_2O_2 fusion method is relatively complex and time-consuming. Therefore, this method is not very suitable for Sm-Nd isotopic analysis of scheelite, compared with the low-blank acid dissolution method.

4. Conclusions

Acid dissolution of scheelite for Sm-Nd isotopic analysis by both Teflon bomb and low temperature attack methods was systematically investigated. It is concluded that: (1) for both simple low temperature attack and Teflon bomb acid dissolution methods, although a large amount of tungstic acid precipitates finally remains during the 2.5 M HCl acidification process prior to cation exchange separation, only less than 10% of the Sm and Nd remains in the tungstic acid precipitates; (2) for isotope dilution (ID) analysis, the isotopic equilibration for Sm-Nd isotopes has only been completely achieved for the Teflon bomb method but not completely achieved for the simple low temperature attack method, indicating that the Teflon bomb method has liberated the Sm and Nd from scheelite completely, while the low

temperature acid attack method has probably not liberated all the Sm and Nd from the scheelite; (3) the tungstic acid precipitates remaining during the acid dissolution process can be completely dissolved by self-purified 30% NaOH, thus it is possible that a low temperature attack method combined with 30% NaOH dissolution of formed tungstic acid precipitates can also be used to completely dissolve the scheelite sample.

Consequently, for the purpose of highly precise scheelite Sm-Nd dating, we suggest the Teflon bomb method or the low temperature acid attack method combined with low-blank 30% NaOH dissolution of remaining tungstic acid precipitates to completely dissolve the scheelite samples for Sm-Nd isotopic analysis.

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