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An Acid-Based Method for Highly Effective Baddeleyite Separation from Gram-Sized Mafic Rocks

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ABSTRACT: Dating mafic igneous rocks (silica-undersaturated) is difficult for the lack of suitable minerals such as zircons ($ZrSiO_4$) commonly found in the sialic rocks such as granites. In this regard, baddeleyite (ZrO_2) has been long recognized as the most important mineral to serve as a geochronometer for dating silica-undersaturated igneous rocks. However, separating baddeleyite is difficult due to its small grain size, typical tabular morphology, and low abundance in samples. The standard water-based separation technique requires kilogram-sized samples and usually has a very low recovery rate. In this study, a new separation method based on the different solubilities of the minerals within HF + HCl + HNO_3 reagents was developed to achieve a high recovery of baddeleyite. With ∼19 g of diabase powder, the new method recovers 150−160 baddeleyite grains of 10−100 μm length and 4−50 μm width, an order of magnitude improvement over the water-based separation method, which typically recovers 11−12 similarly sized baddeleyite grains out of the ∼19 g sample. Subsequent secondary ion mass spectrometry U−Pb analyses demonstrate that the baddeleyite grains recovered by the new separation method keep the U−Pb system closed, indicating no Pb loss during acid treatment. Thus, this new method enables the most efficient baddeleyite recovery from gram-sized rocks and is anticipated to greatly contribute to the geochronological study of silica-unsaturated mafic rocks.
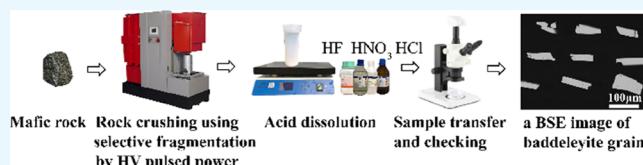
1. INTRODUCTION

Baddeleyite (ZrO_2) is a common accessory mineral that forms under silica-undersaturated, or marginally saturated, conditions in a variety of rock types such as kimberlites, carbonatites, syenites, mafic−ultramafic intrusions, dolerite dykes, and anorthosites. In these rocks, baddeleyite has long been considered as an ideal mineral to serve as a geochronometer for U−Pb isotopic dating because (1) it contains high U concentrations and negligible initial common Pb, (2) it rarely occurs as xenocrysts, and (3) it appears to be much less susceptible to Pb loss than zircon.[1−4] However, it is difficult to separate baddeleyite by the conventional water-based mineral separation method due to its low abundance, small grain size (often <10 μm in width), and typical tabular morphology yielding high surface/volume ratios. Söderlund and Johansson[5] improved the conventional water-based separation technique using a shaking table to separate baddeleyite. This method can increase the recovery but requires a lot of training and experience to achieve a successful separation.[6] Still, it requires kilogram-sized samples and usually has a low success rate for small-volume samples.[7]

An alternative approach of isolating individual minerals is the chemical acid separation method, which uses various acids to dissolve nontarget minerals based on their different solubilities.[8] For example, Neuerburg[9] applied the HF dissolution separation method at room temperature to separate sulfide from quartz monzonite and granodiorite, and the results showed that the sulfide amount separated by the HF

dissolution method was two to three times greater than that by the heavy liquid method. However, the author did not evaluate the degree of acid treatment on subsequent chemical changes or isotope shifts. Lawley and Selby[10] used the HF dissolution separation method at room temperature to separate fine-grained molybdenite from quartz sandstone and carried out a comparative experiment to show that the Re and Os isotope composition of molybdenite was not affected by exposure to HF at room temperature.

In this study, an acid-based method for effective baddeleyite separation with a low sample volume was developed. Subsequent secondary ion mass spectrometry (SIMS) U−Pb dating was conducted to demonstrate that there is no detrimental effect on the U−Pb system of the separated baddeleyite grains.
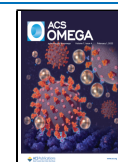
2. MATERIALS AND METHODS

2.1. Reagents. Commercially available nitric acid (HNO_3, 16 M, AR grade), hydrofluoric acid (HF, 22 M, AR grade), hydrochloric acid (HCl, 12 M, AR grade), boric acid (H_3BO_3,

AR grade), and distilled water were used for the experiments reported in this study.

2.2. Rock Sample. A diabase sample was collected from Yangjiaogou Village, Huai'an County, Hebei Province (GPS: N 40°44′, E 114°07′). It was mainly composed of pyroxene, olivine, plagioclase, and amphibole with some accessory minerals like pyrite, magnetite, apatite, and baddeleyite. According to the previous study,[11] the SiO_2 and Zr contents of the whole rock were 47.79% and 75.7 ppm, respectively. The baddeleyite grains separated by the water-based separation method were brownish, yellowish, lamellar, and about 50−150 μm in their longest dimension. The weighted mean $^{207}Pb/^{206}Pb$ age of baddeleyite analyzed by ID-TIMS was 921.8 ± 2.6 Ma (2σ, n = 4, MSWD = 0.42).[11]

2.3. Instruments and Vessels. SelFrag high-voltage pulse fragmentation equipment (SELFRAG AG Company, Switzerland),[12−14] an automatic sample divider, a hot plate, a microscope, and 300 mL PFA Teflon vessels with screw-top lids were employed.

2.4. Separation Procedures. In this study, SelFrag high-voltage pulse fragmentation equipment was applied to crush the sample with the following conditions: a voltage of 120 kV, 130 pulses, a frequency of 3, and an electrode gap of 20 mm. A 200 μm screen mesh was used to control the particle size. The powder weight was 113 g after a piece of 118 g whole rock was ground and dried. This sample powder was divided into 6 portions by an automatic sample divider, which ensured the homogeneity and was representative of each portion. Each portion weighted about 19 ± 1 g.

Two protocols were designed for the acid-based separation method. One was HF dissolution at room temperature; the other was HF dissolution in heating conditions. The acid-based separation processes were described in the following sections. All operations were performed in a fume hood.

2.4.1. HF Dissolution at Room Temperature (Cold HF Dissolution). The use of HF could affect the U−Pb system of baddeleyite, so we first adopted the most conservative HF dissolution at room temperature like what previous studies used for sulfide separation (e.g., refs 9, 10).

(1) For silicate dissolution, a fraction of the rock powder (∼19 g, <200 μm) and 150 mL of 22 M HF were placed into a PFA Teflon vessel with a screw-top lid for 36 h at room temperature. This step mainly aims to dissolve the silicate minerals, including pyroxene, olivine, plagioclase, and amphibole. Shaking the mixture several times every few hours helped the sample to fully react with HF. Then, the supernatant was decanted into the waste liquid tank, and white precipitates were left, which were water-insoluble fluorides formed after HF reacted with minerals.

(2) For fluoride removal, the fluoride was dissolved with 200 mL of 3% (W/V) H_3BO_3 in 2.5 M HCl heated at 100 °C on a hot plate for 4 h.[15] The supernatant was decanted into the waste liquid tank. Then, only a small amount of minerals remained, mainly sulfide, magnetite, and baddeleyite.

(3) For nonsilicate dissolution, 45 mL of 12 M HCl and 15 mL of 8 M HNO_3 were added to the vessel and heated at 120 °C on a hot plate for 24 h with a closed cap. This step mainly dissolves pyrite and magnetite. The supernatant in the vessel was decanted into the waste liquid tank after cooling to room temperature.

(4) For sample transfer, the final remaining minerals in the vessel were rinsed 4 times with distilled water. The cleaned residual minerals were transferred to a watch glass and checked under a microscope. Finally, the concentrated baddeleyite grains were transferred into a sample bag through a very thin plastic dropper.

2.4.2. HF Dissolution in Heating Conditions (Hot HF Dissolution). Though it may be safe for baddeleyite in cold HF, the efficiency is one of the general principles. Therefore, we tried the hot HF dissolution method to shorten the dissolution time. A simpler way is to dissolve the nonsilicate and silicate minerals simultaneously. The sample powder (∼19 g, <200 μm) was dissolved by a 120 mL 22 M HF and 60 mL 8 M HNO_3 mixture and heated at 120 °C on a hot plate for 5 h. After cooling, the supernatant in the vessel was decanted into the waste liquid tank, and white precipitates were left. Subsequent steps of fluoride removal and sample transfer were the same with the cold HF dissolution method.

Caution! (1) When the sample mass of the rock powder is greater than 1 g, the reaction is violent when HF is added; thus, the acid should be added slowly with great care. (2) For safety, the operator must wear a gas mask, a special laboratory suit, and gloves to prevent HF and HF gases from contacting the skin.

2.4.3. Water-Based Separation Method. To evaluate the recovery efficiency of baddeleyite by the acid-based separation method, the water-based separation method was applied for comparison. The methodology follows those described by Söderlund and Johansson.[5] First, water and the sample powder (∼19 g, <200 μm) were mixed to make the pulp with a 30% concentration. Tilt angles of the shaking table were set to 7.6 (side slope) and 2.1° (forward slope). The water amount was 7 L/min. The pulp was loaded on the water-shaking table instantaneously. When only a millimeter thick, a dark trace made up of the smallest and densest grains was visible on a diagonal domain hugging the ends of the riffles; the minerals were collected with a glass bottle and transferred to a watch glass. Then, the magnetic minerals were removed using a strong hand-magnet wrapped in plastic. Finally, baddeleyite grains were picked under a microscope.

2.5. SIMS U−Pb Baddeleyite Dating. The acid-based separation method has a risk of disturbing the baddeleyite U−Pb system, so it is necessary to evaluate the effect of acid treatment on the baddeleyite U−Pb isotopic system. Considering that hot HF is more reactive, we conducted SIMS U−Pb dating on baddeleyite separated by the hot HF acid-based separation method to compare with the previously published ID-TIMS dating results[11] on baddeleyite separated by the water-based separation method.

Measurements of U and Pb isotopes were conducted using a CAMECA IMS-1280HR SIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS) in Beijing. The detailed analytical method of baddeleyite was described by Li et al.[3] The beam spot was set to be ∼8 × 10 μm. Data reduction was carried out using the Isoplot program.[16]

3. RESULTS AND DISCUSSION

3.1. Comparison between the Acid-Based and Water-Based Separation Methods. Almost the same amount of the rock powder (∼19 g, <200 μm) was applied to carry out experiments by the acid-based separation method and the water-based separation method. To ensure the accuracy of

results, two parallel experiments were carried out for each method. Through observation under a microscope, it is found that the baddeleyite concentration reaches >80% by the acid-based separation method before hand picking, whereas the baddeleyite concentration achieved by the water-based separation method is <20%. Consequently, our new method has a higher concentration, which greatly reduces the final manual concentration (hand picking) work under a microscope.

The number and size of recovered baddeleyite grains are given in Table 1. Only the grains with a length of >10 μm and

Table 1. The Number and Size of Baddeleyite Grains Recovered by the Acid-Based and Water-Based Separation Methods from the Same Amount of the Rock Powder

method		number of grains		size of grains (μm)	
		first	second	length	width
acid-based separation method	cold HF dissolution	154	160	10−150	4−50
	hot HF dissolution	158	153	10−150	4−50
water-based separation method		12	11	30−150	10−50

a width of >4 μm were recovered and picked. The baddeleyite grains separated by the acid-based separation method are 10−150 μm in length and 4−50 μm in width (Table 1 and Figures 1a−d and 2a,b), while the grains separated by the water-based separation method are 30−150 μm in length and 10−50 μm in width (Table 1 and Figures 1e,f and 2c). As for cold HF dissolution, 154 and 160 grains are recovered respectively from

the two parallel experiments; for hot HF dissolution, 158 and 153 baddeleyite grains are recovered. In other words, more than 8 baddeleyite grains can be recovered on average from 1 g of the rock powder, while 12 and 11 baddeleyite grains are recovered from two parallel experiments by the water-based separation method out of ∼19 g of rock powder. It is worth noting that only 12 baddeleyite grains are recovered from 1 kg of the same rock sample by a commercial mineral-separation company. The number of baddeleyite grains recovered by the acid-based separation method is more than 10 times greater than that by the water-based separation method. On the other hand, compared with the water-based separation method, the acid-based separation method does not require the operator to have a lot of experience and just needs to be able to use various chemical reagents, following our described protocol and safety measures, to achieve a successful separation. In addition, no intervention and attention are required during sample digestion. This differs from the water-based separation method, where constant attention is required for the shaking table through the mineral separation process.

We therefore conclude that the acid-based separation method is more conducive to the separation of baddeleyite with a smaller size and can significantly improve the recovery rate. The reasons for such improvement are twofold: (1) the acid-based separation method could well expose the baddeleyite grains, which exist in the form of inclusions, whereas the water-based separation method always renders them unexposed and unpicked; (2) the water-based separation method is prone to lose the grains with high surface/volume ratios because their small grain size and typical tabular morphology would cause them to float on the pulp and to be washed away before reaching the end of the shaking table. In addition, the mineral size and the operating conditions of the shaking table, such as the water velocity, vibration frequency, vibration amplitude, and dip angle, also affect the outcomes of separation.[17−20] The acid-based separation method only depends on the solubility of the minerals, so it is more both robust and accurate.

Some other minerals, such as zircon, cassiterite, and rutile, are not soluble in HF + HNO_3 + HCl without a higher pressure and temperature, indicating that the same separation method may also be applied to recover these minerals but needs further geochemical validity check.

3.2. U−Pb Ages. A total of 17 SIMS analyses for baddeleyite separated by the hot HF dissolution separation method were conducted. The weighted mean ^{207}Pb−^{206}Pb age is 919.5 ± 4.4 Ma. A U−Pb concordant age is calculated at 920.1 ± 6 Ma (Figure 3a and Supporting Information Table S1). They are in good agreement within errors with the ID-TIMS U−Pb upper intercept age of 920 ± 12 Ma and the weighted mean ^{207}Pb−^{206}Pb age of 921.8 ± 2.6 Ma[11] for baddeleyite separated by the water-based separation method (Figure 3b). It demonstrates that the baddeleyite grains recovered by the hot HF separation method are not subjected to Pb loss during acid treatment. Therefore, the acid-based method for baddeleyite separation is practical and reliable. Taking into account that the hot HF dissolution separation method can greatly shorten the acid dissolution time, we recommend it.

4. CONCLUSIONS

We describe an acid-based separation method for baddeleyite from a gram-sized mafic rock, mainly using HF + HNO_3 + HCl
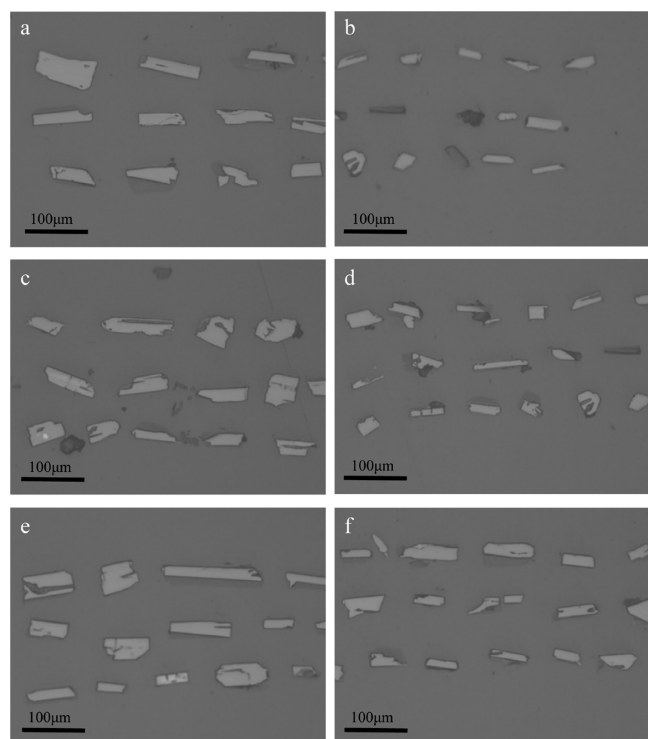

Figure 1. Reflected light images of baddeleyite grains separated by the different methods. (a,b) Cold HF dissolution separation method. (c,d) Hot HF dissolution separation method. (e,f) Water-based separation method.
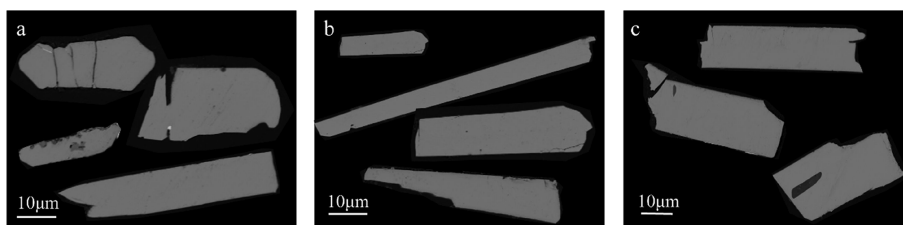
Figure 2. Representative back-scattered electron (BSE) images of small baddeleyite grains separated by the different methods. (a) Cold HF dissolution separation method. (b) Hot HF dissolution separation method. (c) Water-based separation method.
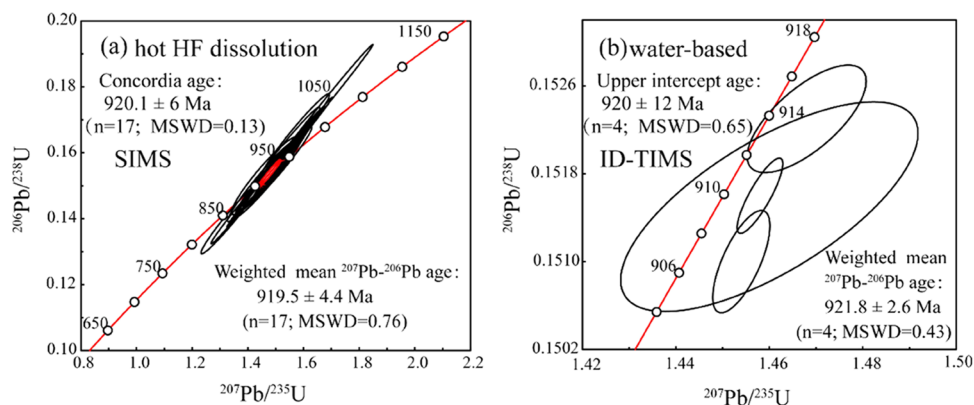

Figure 3. Comparison of U−Pb analyses for baddeleyite. (a) U−Pb concordia diagram showing SIMS analytical data for baddeleyite separated by the hot HF dissolution separation method. (b) U−Pb concordia diagram showing ID-TIMS analytical data for baddeleyite separated by the water-based separation method. Modified with permission from Peng et al. (2011). Copyright 2011 Elsevier. Data point error ellipses/bars are 2σ.

to dissolve the gangue minerals. The number of baddeleyite grains recovered by the acid-based separation method is more than 10 times greater than that by the water-based separation method with the same amount of the whole rock. SIMS U−Pb analyses demonstrate that the U−Pb system of baddeleyite remains closed, unaffected by the hot HF acid-based separation treatment. This new method enables the most efficient baddeleyite recovery from gram-sized rocks and will greatly contribute to the geochronological study of silicate-unsaturated rocks.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06264.

SIMS U−Pb data for baddeleyite separated by the hot HF dissolution separation method (PDF)

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Notes

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