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A simple way to extract baddeleyite (ZrO_2)

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[1] Baddeleyite is a reliable geochronometer for dating the crystallization of mafic and other silica-undersaturated intrusive rocks. Its high U and negligible initial Pb content enable precise age determinations with statistical errors of a few million years or less. The widespread use of baddeleyite for dating has, however, been limited by the low content of baddeleyite in many samples and by difficulties in isolating baddeleyite. We have developed a new separation technique that utilizes differences in transport velocity among grains of varying size as they move across the deck of a water-shaking table. A small sample portion is loaded instantly on the table, and only the finest and densest material remaining after ~120 s is collected. Repeated recovery of sample portions yields a concentrate strongly enriched in baddeleyite and opaque minerals; the latter is easily removed by a hand magnet. The "water-based" separation technique will improve yields of baddeleyite from samples processed on a water-shaking table and is capable of recovering very fine grains. As the entire separation is made in water, problems arising from adhesive forces between minerals are minimized, as is the risk of cross contamination. No heavy liquids are necessary, making separation quick, uncomplicated and inexpensive.

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1. Introduction

[2] Baddeleyite (ZrO_2) is a common accessory mineral in many silica-undersaturated plutonic rocks and dykes. U contents of 200–1000 ppm and negligible amounts of initial Pb allow for precise, typically concordant, U-Pb ages. Baddeleyite transforms into polycrystalline zircon during metamorphism, and xenocrystic baddeleyite is rare [*Heaman and LeCheminant*, 1993; *Schärer et al.*, 1997]. This is why many scientists prefer U-Pb baddeleyite dating over U-Pb zircon dating when

trying to identify key palaeomagnetic poles [e.g., *Buchan et al.*, 2000].

[3] In spite of the potential of this geochronometer for dating mafic magmatism and, together with palaeomagnetic measurements, for reconstructing palaeopositions of lithospheric plates, the number of U-Pb baddeleyite ages in the literature is relatively few. The small grain size, often $\leq$30 μm in width, and nonspherical crystal shape yield high surface/volume ratios; hence special precautions are needed for isolating baddeleyite from the finest particles in a sample. A new, efficient separation technique is presented which largely circumvents these problems. From the results of a test study we try to illustrate the relative ease with which the new method can be performed and identify steps in the conventional separation where losses of baddeleyite may be significant.

2. Background

[4] The general principle during mineral separation is to avoid contamination and to make the separation efficient. Because simplicity reduces the risk of contamination, the goal is to attain an acceptable enrichment of the mineral of interest with a minimum of separation steps. So far, extraction of high-density minerals generally involves a mixture of magnetic and heavy liquid separation steps performed in the following sequence: (1) crushing and grinding, (2) water shaking table (Wilfley table), (3) sieving, (4) "free-fall" magnetic separation (removal of magnetite), (5) removal of magnetic minerals using a Franz Isodynamic Separator, and (6) heavy liquid.

[5] These steps are also commonly employed for the separation of baddeleyite. However, owing to the small size of baddeleyite grains and their fragile nature, two steps in the procedure are particularly important. The first is careful crushing of the sample to liberate as many grains as possible yet avoid destroying the baddeleyite grains. The second concerns removal of the finest material without loosing the baddeleyite grains. Unless the finest particles are removed, the sample will cluster into aggregates upon drying and obstruct a proper response of individual grains to differences in magnetic susceptibility and density, step 4–6 above. Removal of the finest fraction is generally accomplished either by careful and repeated washing of a crushed sample portion or by employing a water-shaking table. On the latter, baddeleyite behaves as a less dense mineral phase despite its 5.7 g/cm^3 density. This is a consequence of baddeleyite's high surface/volume ratio which in turn results from its small size and needle- to wafer-shaped crystal morphology. Minimizing loss of baddeleyite on the water-shaking table requires special operating condition, including a flat forward table tilt, gentle water flow, and slow sample feeding speed (~5 kg/h according to *Heaman and LeCheminant* [1993]).

[6] Regardless which technique is employed for removing the superfine particles in a sample, the concentration of baddeleyite in the remaining fraction is generally far below 0.1%. Thus further separation involving magnetic and heavy-liquid steps is necessary. Although these steps are relatively uncomplicated, they are time consuming and require costly (and toxic) heavy liquids. Finally, as shown by the results of a test study (below), it is during these separation steps in particular, we notice significant losses of baddeleyite.

3. The "Water-Based" Separation Technique

[7] The efficiency of the "water-based" technique for extracting baddeleyite lies in the use of the water-shaking table. The new technique is based on the observation that the velocity at which large grains move across the table deck is much faster than for small grains. For instance, if a portion of a crushed sample of pyrite is loaded at once, both the fine and the coarser grains will move toward the lower left, "high-density" tailing edge of the deck, while any superfine (clay-size) material will be washed out shortly after sample loading (see Figure 1). However, large pyrite grains will be discharged before the smallest grains owing to (1) the higher momentum transferred to the coarser grains as the table deck shakes and (2) a stronger tendency for small, i.e., the lighter, grains to slip against the deck as it shakes. This is why smaller

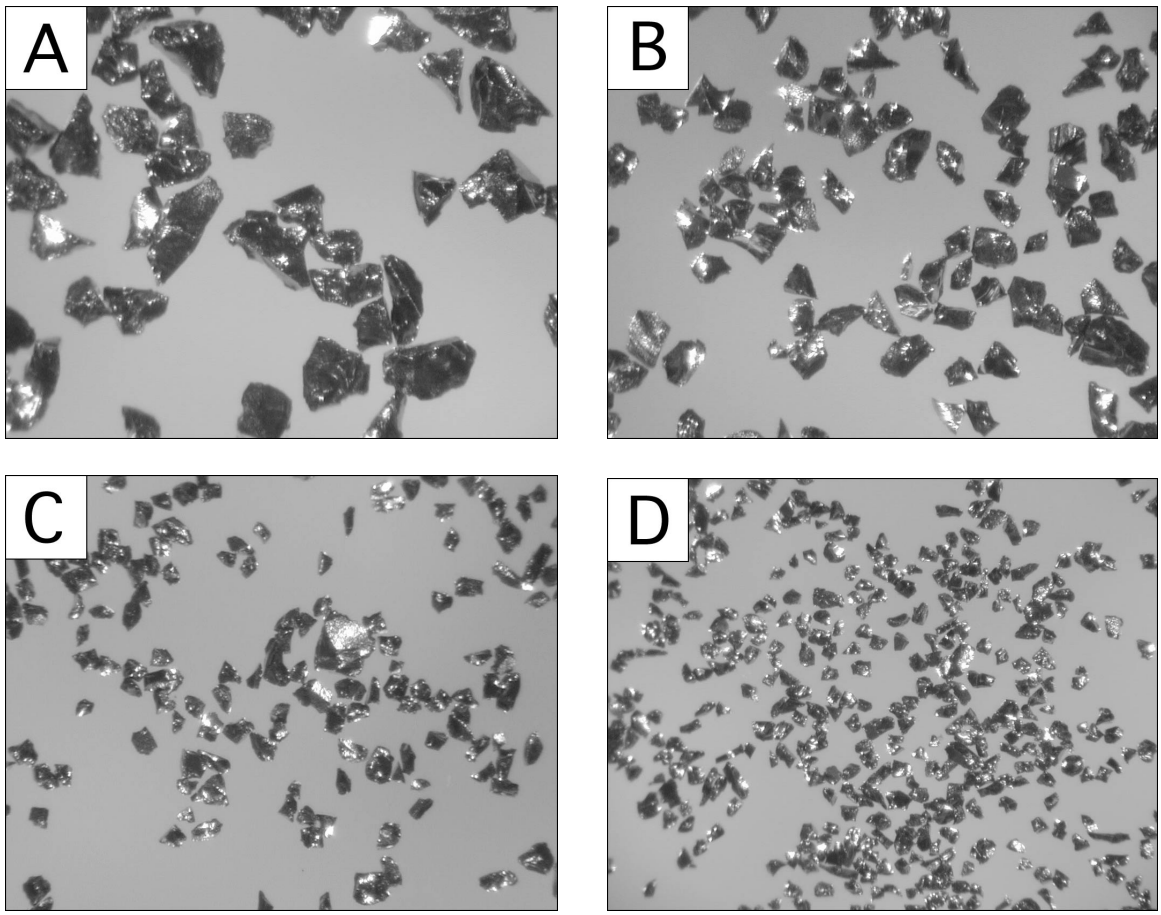

Figure 1. Photographs taken with the same magnification of mineral fractions collected in the time intervals (a) 25–30 s, (b) 55–75 s, (c) 95–110 s, and (d) 160–220 s from the instant a sample of pure pyrite, ranging between 20 and 250 μm, was loaded on a Wilfley table. All fractions were collected at the lower-left "high-density" corner. This sequence of pictures demonstrates the distinctly higher transport velocity for larger grains relative to smaller ones.

grains of a specific mineral move much slower across the deck than coarser, heavier grains.

[8] Details of the application of the water-based technique described below and in Figure 2 differ from one table to another depending on design and size of the deck (a larger deck is probably preferable). Successful separation can be achieved only with training and experience. Here a Wilfley shaking table supplied with a fibreglass sand deck (1270 × 610 mm) is employed. The original wash water pipe was replaced with a hand-made plastic pipe with small and tightly spaced drainage openings to allow for an even flow across the deck. Tilt angles are set to 7° (forward, i.e., wash water flow direction) and 2° (slope), and stroke length and frequency to 11 mm and ~550 strokes/min. A higher efficiency may be achieved with minor modifications of the sample amount in each portion, the angles of tilt, the shaking frequency and the stroke length. The technique is as follows:

1. The sample is cut into ~1 cm thick slices using a slab saw and crushed down to gravel size using a sledge hammer. An appropriate amount of sample to start with should be 0.5–1 kg. Put the gravel in a 2–5 mm disposable sieve, wash several times with water, and dry. This precaution limits the risk of contaminating the sample with baddeleyite from earlier processed samples.

2. The relatively coarse-grained sample is gently crushed, employing a small mill tray (used here) or a disc mill (pulverizer). Careful crushing is essential to avoid fracturing the fragile baddeleyite grains; still, the sample must be thoroughly crushed to liberate as many baddeleyite grains as possible, prerequisites probably

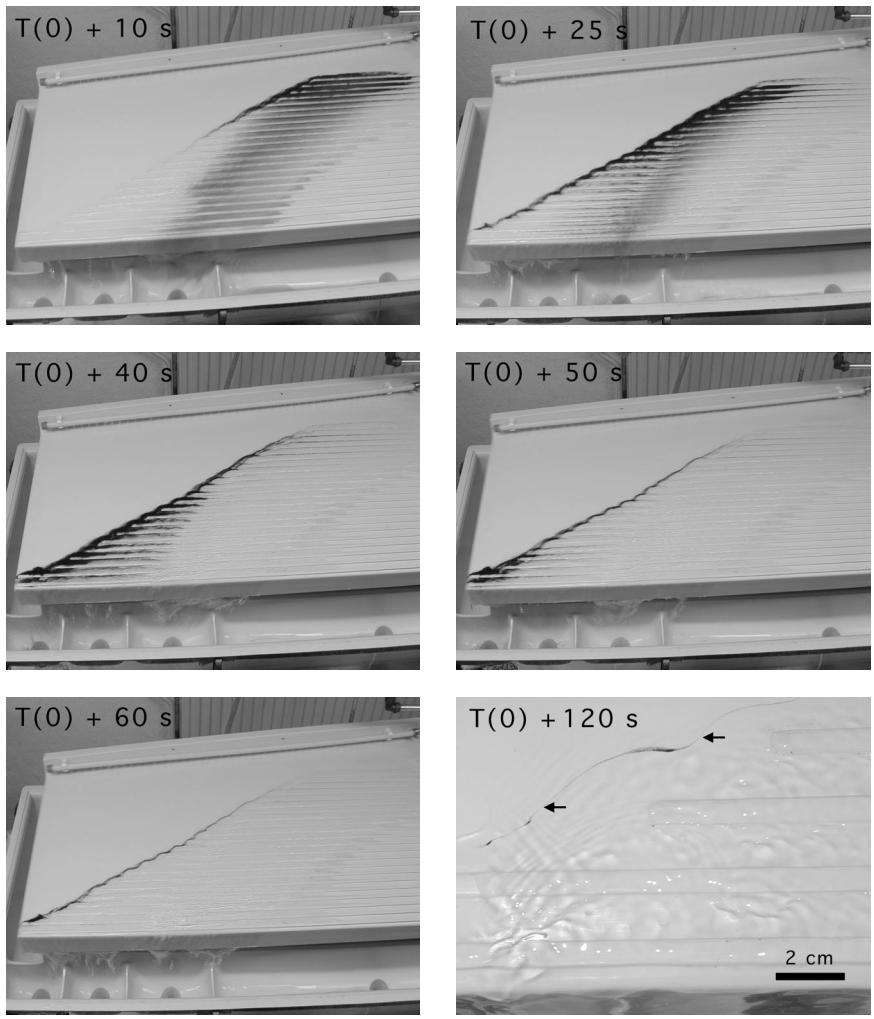

Figure 2. Use of the water shaking table in the "water-based" technique. Photographs show the distribution of a sample on the table deck at different times after sample loading at $T(0)$. $T(0) + 10$ s, and $T(0) + 25$ s show that much of the very finest material is washed off shortly after the sample was loaded. At $T(0) + 40$ s, all of the very finest material has been washed off. At $T(0) + 50$ s and $T(0) + 60$ s, there is a distinct fining of material toward the upper right corner of the deck as the result of a much faster transport of coarser relative finer material. At $T(0) + 120$ s, more than 99% of the total sample has been discharged, and only the smallest and densest grains remain as a thin dark trace (arrows) hugging the ends of the riffles; this is the approximate time to begin collect the sample. The photograph taken at 120 s after sample loading is a close-up of the bottom left-most area of the table deck.

best fulfilled by the disc mill. The sample is repeatedly suspended in water together with a detergent agent interrupted by short immersions in an ultrasonic bath. These procedures enhance complete moistening of the sample and reduce adhesive forces between particles.

3. Slowly increase the quantity of wash water across the water shaking table until an even film of water covers most of the deck. The "correct" quantity of water can only be achieved by "trial-and-error" but should be significantly less than what is ample for zircon separation.

4. Sample loading on the water-shaking table must be made instantaneously, i.e., do not use the "sample-water mixer" if such a device is available. In this study, a suspension that contains ~50 g sample is loaded each time. Significant amounts of baddeleyite may get wasted together with the finest material if larger portions are taken. If there is reason to suspect that the baddeleyites are exceptionally small (e.g., when processing volcanic rocks or thin dykes), smaller

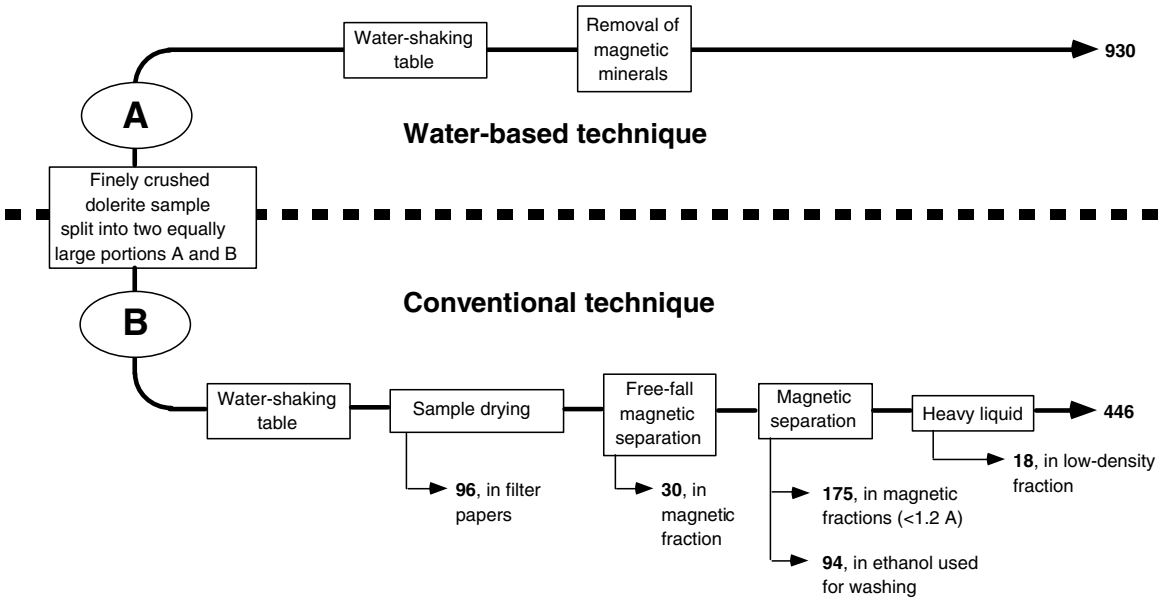

Figure 3. A schematic flow chart showing the results after mineral separation using the "water-based" (portion A) and the conventional (portion B) techniques. Portion A and B weighted 530 and 567 g, respectively, before crushing. See text for further description.

portions and even less wash water is recommended.

5. Allow almost the whole sample portion to be discharged from the table before starting to collect; only a millimeter-thick, dark trace made up of the smallest and densest grains should be visible on a diagonal domain hugging the ends of the riffles (Figure 2). Delaying recovery generally yields a higher concentration of baddeleyite, but larger grains may get lost if one waits too long. For our samples, collection has started between 2 and 3 min after sample loading. Put the sample bucket and the adjustable splitter pieces into position. The sample bucket must be relatively large to minimize turbulent flow and loss of baddeleyite (secure release of the material at the bottom of the bucket by using a plastic pipe). Use a water bottle and carefully rinse the mineral concentrate from the deck into the collector. Make sure nothing is left on the table before removing the sample bucket. Add the next sample portion to the table, i.e., go back to 4, and repeat until the whole sample is processed.

6. Transfer the sample to a flat-bottom glass container large enough so that each grain can be in direct contact with the bottom. Ideally, the recovered mineral concentrate should now consist entirely of opaque phases (often > 90%), baddeleyite, and possibly some apatite (Figure 3a). All grains should range between 5 and <50 μm in the shortest dimension. The total weight of the recovered sample after this step is generally far less than 0.1 g.

7. Use a strong hand-magnet (a pencil magnet works fine), wrapped in a plastic, to remove the magnetic minerals. The hand-magnet is brought close to the sample beneath the water surface and carefully moved above the container bottom. Magnetic minerals attached to the magnet must repeatedly be removed; nonmagnetic minerals, for example, baddeleyite, may otherwise stick to the magnetic minerals.

8. If separation has been successful, the concentration of baddeleyite grains is sufficiently high for hand picking under the optical microscope.

[9] At times, there may be a portion of superfine ($\ll$10 μm) transparent particles left in the recovered concentrate. It is therefore recommended to check the mineral concentrate under the microscope immediately after using the water-shaking table.

The superfine material can be removed by running the concentrate another time on the water-shaking table. Larger grains making up a significant amount of the sample are easiest removed using a disposable nylon sieve. Transfer the sample to the sieve and gently rinse by water repeatedly. Do not dry down the sample after using the water-shaking table and before removing the magnetic minerals. Upon drying grains will adhere to the glass container and attractional forces seem to remain even when water is later added (e.g., they obstruct the removal of magnetic grains).

4. A Comparison Between the Water-Based and the Conventional Separation Techniques

[10] A sample of the Karlshamn dolerite dyke in Blekinge, Southern Sweden, was crushed and split into two portions weighting 530 (A) and 567 g (B), respectively. Portion A was processed using the "water-based" technique, whereas B was processed employing the conventional separation technique (steps 1–6 above). Both portions were run on the water-shaking table at identical conditions without changing the water flow or tilt angles. The "free-fall" magnetic separation of portion B was made on a vertical-positioned Franz magnetic separator at 1.0 A. Continuing magnetic separation was made on a Franz (model LB-1) with tilt angles set to 10° (forward slop) and 15° (side slope). Magnetic fractions were withdrawn at currents 0.15, 0.3, 0.6, and 1.2 A. The nonmagnetic fraction at 1.2 A was put into methylene iodide for heavy liquid separation (density $\sim$3.3 g/cm^3).

[11] The results obtained during this comparing study are illustrated in Figure 3. From portion A, 930 baddeleyite grains were isolated employing the water-based technique. From portion B, approximately half the amount (446) was found after completed separation. To examine the loss of baddeleyite during processing portion B, recovered filter papers were investigated for trapped baddeleyites. The filter papers were inverted, held in a container filled with ethanol, and run for a few seconds in an ultrasonic bath. Ethanol used for cleaning material that had been in contact with the sample was examined under the microscope. The magnetic fractions recovered during magnetic separation and the low-density mineral fraction following heavy liquid separation were reprocessed by the "water-based" technique.

[12] As shown in Figure 3, a significant amount of baddeleyite from portion B was recovered in the magnetic fractions run at currents <1.2 A, 175 baddeleyite grains totally were counted. Ninety-four grains were found in ethanol used for cleaning the Franz after separation, and an equal amount was found trapped in filter papers after sample drying. Eighteen baddeleyite grains were recovered from the light-density mineral fraction following heavy liquid separation. Adding the baddeleyite grains recovered from different sources to those in the high-density fraction yield approximately the same amount of grains (859) as recovered from portion A (930 grains).

5. Discussion and Summary

[13] The large number of grains present in low-magnetic fractions and in ethanol used for cleaning (see Figure 3) suggests that these losses result from the tendency of baddeleyite to adhere to other grains as well as surrounding materials in a dry condition; that is, these adhesive forces superseded differences in magnetic susceptibility and density utilized in the conventional separation technique. Furthermore, baddeleyite grains are easily trapped in filter papers and may remain among the floating minerals during heavy liquid separation. Here the number of grains found in the low-density mineral fraction after heavy liquid separation was surprisingly high (175 grains) relative to the amount found in the high-density fraction. It is, however, difficult to evaluate whether sinking of baddeleyite grains, in general, is hindered by adhesive forces between minerals in the heavy liquid or obstructed physically by the surrounding low-density mineral grains. The importance of multiple agitation periods while performing heavy-liquid separation was highlighted by *Heaman and LeCheminant* [1993].

[14] In this study, the average size of baddeleyite grains in the processed samples of the Karlshamn dolerite ranged between 20 and 40 μm in width and some are up to $\sim$100 μm in the longest dimension,

comparable to what has been reported from other dolerite dykes [e.g., *Heaman and LeCheminant*, 1993; *Wingate and Compston*, 2000]. Nevertheless, a significant amount of the baddeleyites clearly represents fragments of larger crystals. It must be noted that the number of grains given in the text and in Figure 3 also includes fragments. Many grains were presumably broken into pieces as the sample was pulverized in the mill tray. Thus the importance of careful crushing is once more emphasised. It is possible that the water-based technique is particularly efficient for samples containing small baddeleyite grains, for example, volcanic rocks and thin mafic dykes.

[15] The "water-based" technique may also prove capable for extracting tiny ($\leq$20 μm) metamorphic zircons in meta-basic rocks, for example, amphibolites, granulites, and eclogites. However, so far it has not been possible to achieve a similar high concentration of zircon in the same manner. A common problem is that much of the remaining phases, for example, garnet and titanite, are not sufficiently magnetic for removal with a hand-magnet.

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