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Removal of barite from zircon using an aqueous solution of diethylenetriaminepentaacetic acid and potassium carbonate

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KEYWORDS

DTPA; chelant; sandstone; mineral separation; bias; provenance; maximum deposition age

ABSTRACT

In most geologic applications, if barite is present, it must be separated from zircon to enable analysis of the zircon. Current methods of barite removal include mechanical comminution in a ball mill or conversion to barium carbonate by boiling in an aqueous solution of sodium carbonate. Both procedures have potentially serious drawbacks. We optimized an alternative technique for barite removal to avoid these shortcomings. In repeated experiments, boiling in an aqueous solution of 0.1 M diethylenetriaminepentaacetic acid (DTPA) and 6 weight percent potassium carbonate for one hour dissolved about 90% of sand-size barite grains. Examination of barite after boiling in DTPA solution revealed evidence for attacks on crystal surfaces in the form of microscopic scallops and pits. In contrast, zircon crystal surfaces were not detectably altered at the microscopic scale by a boiling solution of DTPA and potassium carbonate. The DTPA and potassium carbonate solution procedure may be superior to the other two barite removal methods in two ways. First, it might not introduce bias into the sample, in contrast to both of the other two methods. Second, it requires less time than the sodium carbonate solution technique. If future research shows that the DTPA and potassium carbonate solution technique does not affect isotopic systems in zircon, this method appears to be a favorable alternative to both milling and boiling in sodium carbonate solution.

INTRODUCTION

Detrital zircon dating and chemical analysis provide important data for investigations of continental tectonics, improving our understanding of subjects such as stratigraphy, paleogeography, magma production in arcs, continental crust generation and preservation, orogenic history, and hydrocarbon exploration (Gehrels, 2014; Pujols et al., 2018). Most analytical techniques require isolation of zircon grains. Barite ($BaSO_4$) interferes with zircon separation because the two minerals have similar densities and magnetic susceptibilities (Murakami et al., 1991; Rosenblum and Brownfield, 1999; Schmidt et al. 2009; Shahab et al., 2016) and because barite has low solubility during boiling at atmospheric pressure in the strong acids commonly used in geology laboratories (O'Neil, 2013).

Two methods in current use for barite removal from detrital zircon have potentially serious drawbacks. As the final step in zircon separation, geologists in many laboratories remove barite using a ball mill. A problem with this method is that milling the barite and zircon mixture breaks and causes loss of both minerals, not only the barite (Martin et al., 2021). Loss of zircon can introduce bias into the sample because the lost grains are no longer available for analysis (Slama and Kosler, 2012). Breakage of grains into multiple fragments can cause bias even if the pieces are retained because dates from each fragment will be treated as coming from individual detrital grains, which is incorrect because those fragments actually were just one detrital grain in the sedimentary rock. To avoid the breakage and loss caused by mechanical comminution of the grains, Martin et al. (2021) developed a chemical method to remove barite from zircon. The heart of this method is conversion of the barite to barium carbonate by boiling in an aqueous solution of sodium carbonate. The resulting barium carbonate grains can be picked out of the sample by hand or dissolved using nitric or hydrochloric acid. One drawback to the sodium carbonate method is that it takes much more time. Whereas milling takes about fifteen minutes not including preparation and cleanup, the grains must be boiled in sodium carbonate solution for four hours, followed by removal of the barium carbonate for an hour, plus setup and cleanup. Additionally, boiling in sodium carbonate solution for four hours followed by concentrated nitric acid for one hour slightly decreased the U-Pb isotopic age of standard reference zircon crystal interiors, suggesting that this technique might affect the U-Pb isotopic system in zircon even at the more dilute concentrations of sodium carbonate and nitric acid required to dissolve barite (Martin et al., 2021).

To avoid the shortcomings of these two barite removal methods, we optimized an alternative procedure for chemical removal of barite from zircon. This technique requires boiling the zircon and barite mixture in an aqueous solution of DTPA and potassium carbonate for only one hour. We also report the results of examinations of attacks on barite and zircon surfaces by the DTPA plus potassium carbonate solution, as well as a test of the efficacy of this method on a zircon plus barite separate from a barite-bearing sandstone.

DTPA BACKGROUND

DTPA is an aminopolycarboxylic acid with chemical formula $C_{14}H_{23}N_3O_{10}$. Its conjugate base is an effective chelating agent because it forms up to eight bonds with the metal cation – one bond with each of its three nitrogen atoms and five carboxylate groups (Jin et al., 1991; Martell and Hancock, 1996). In solution, water molecules also can bond to the metal ion as necessary (Jin et al., 1991; Martell and Hancock, 1996). Aqueous solutions of DTPA have been used in petroleum production since the 1990s to dissolve barium sulfate scale in oilfield equipment as well as pore-clogging barium sulfate in productive formations (Paul and Fieler, 1992). Complete deprotonation of the DTPA molecule, which increases its ability to dissolve barium sulfate, requires an aqueous solution with a pH of at least 11 (Putnis et al., 2008). Using potassium hydroxide rather than sodium hydroxide to achieve this pH results in greater barium sulfate dissolution (Bageri et al., 2017). Potassium carbonate added to the aqueous DTPA solution aids barium sulfate dissolution (Bageri et al., 2017; Mahmoud et al., 2018). DTPA does not break down quickly in the natural environment and it is present in surface water in and around many countries (Nozaki et al., 2000; Sykora et al., 2001; Birka et al., 2016).

EXPERIMENTAL DESIGN

We conducted the experiments with DTPA solution in four phases. We used the results from each previous phase to modify the procedures in the next round of experiments. We obtained pelletized potassium hydroxide and powdered DTPA from a commercial supplier. We also obtained an approximately 1 cm-long natural barite crystal from a commercial supplier and crushed it in an alumina mortar and pestle to produce sand-size grains. We did not sieve the barite particles. We used these grains for the experiments in phases I, II, and III. Experiments took place on a laboratory benchtop, not in a fume hood. In the following subsections we describe the procedures we used for the experiments in each phase.

Phase I

The goal of the Phase I experiments was to test the extent of barite dissolution in DTPA solution at various conditions (Table 1). We measured the mass of barite removed during boiling in 0.5 M versus 0.1 M DTPA solution, with 6 weight percent potassium carbonate present or absent, and for 60 versus 30 minutes. We performed the experiments according to the following procedure.

1. Prepare 250 mL of an aqueous solution of potassium hydroxide using deionized water. We used concentrations of 2, 1, 0.8, and 0.5 M for experiments 6B, 7, 8, and 9, respectively.
2. Add powdered DTPA to achieve the desired concentration, which was 0.5 M for experiment 6B and 0.1 M for the other experiments.
3. For all experiments except 9, add 6 weight percent potassium carbonate.
4. Use a paper testing strip to ensure the pH is at least 11.5.
5. Place approximately 0.2 g of barite sand in a small glass beaker. Dry in an oven at 70 °C for 1 hour.
6. Weigh the dry barite.
7. Place the dried, weighed barite in the 250 mL DTPA (plus potassium carbonate if applicable) solution. Add two small pebble-size quartz grains to nucleate bubbles.
8. Boil the solution on a hotplate at atmospheric pressure for the desired time, which was half an hour for experiment 8 and one hour for the other experiments. We did not stir the solutions.
9. Remove the remaining barite from the solution by pouring onto filter paper. Rinse the barite with an aqueous solution of potassium hydroxide, then rinse with deionized water.
10. When dry, place the barite in a small glass beaker. Dry the barite in an oven at 70 °C for 1 hour.
11. Weigh the dry barite.

Phase II

Phase II entailed repeating experiment 7 five times to test the amount of barite dissolved. All experiments in Phase II followed the procedures for Phase I except that the concentration of the potassium hydroxide solution described in step 1 was 0.5 M.

Phase III

The purpose of the Phase III experiments was to determine the extent to which the DTPA treatments developed in phases I and II physically affected the surfaces of barite and zircon. For this experiment, we obtained a cm-long zircon crystal from a commercial supplier. Experimental conditions are given in Table 1. We obtained backscattered and secondary electron images of barite crystal surfaces before and after the DTPA treatment using an FEI Quanta 200 scanning electron microscope. We used an FEI Quanta 250 FEG to image the zircon crystal surface before and after treatment with the DTPA solution.

Phase IV

In the Phase IV experiment, we tested the DTPA plus potassium carbonate procedure on a natural sandstone sample. We collected a 3 kg sample of Alamar Formation sandstone from outcrops near Galeana, Nuevo Leon, Mexico (sample location: 24.69706 °N, 100.10147 °W). At this location, the Alamar Formation contains abundant barite, both as veins and disseminated throughout the sandstone (Kesler et al., 1988; Kroeger and Stinnesbeck, 2003). Approximately 2 kg of the sample was disaggregated by hand using a stainless steel mortar and pestle. Grains were finer than 250 μm after disaggregation. Clay and silt size particles were eliminated by hand panning in water, magnetic grains were removed using a Frantz magnetic barrier separator, and grains less dense than 2.8 g/cm^3 were removed using LST Heavy Liquid (aqueous solution of lithium heteropolytungstates). The resulting barite and zircon mixture was boiled in DTPA and potassium carbonate solution following the procedures given for our Phase I experiments and the conditions listed in Table 1. The concentration of potassium hydroxide solution for step 1 was 0.5 M. We examined the dense mineral separate using a stereoscopic microscope before and after the DTPA plus potassium carbonate solution treatment.

RESULTS

The results of the Phase I and II experiments are given in Table 1. In the Phase I experiments, the proportion of barite removed ranged from 96% to 69%. The experiment without potassium carbonate dissolved the least amount of barite; boiling for only 30 minutes removed the second lowest amount. In the Phase II experiments, which repeated experiment 7, the proportion of barite removed ranged from 95% to 85%. The mean proportion of barite dissolved in experiments 7 and 11-15 was 92±8% (2 s.d.).

We propagated the errors from the mass measurement on the laboratory balance into the calculated proportion of barite removed. For all experiments in phases I and II, this uncertainty is 0.5% of the barite removed at the two standard deviation level.

The results of the Phase III experiments are shown in figures 1 and 2. Boiling in DTPA and potassium carbonate solution caused the development of micrometer scale scallops and sub-micrometer scale pits on the surfaces of the barite crystals. In contrast, boiling in DTPA plus potassium carbonate solution had no detectable effect on the surface of the zircon crystal.

Microscopic examination of the natural sample used for the Phase IV experiment prior to the DTPA plus potassium carbonate treatment revealed zircon and large barite crystals and few other minerals. After treatment with DTPA plus potassium carbonate, no barite grains were observed; the remaining sample was nearly 100% zircon grains.

The appearance of the DTPA plus potassium carbonate solution was similar before and after all the experiments. Barite dissolution did not create residues that noticeably coated remaining grains or the interiors of the beakers or that greatly increased the viscosity of the solution. No such residues were observed in examinations of rinsed remaining grains using the stereoscopic or scanning electron microscopes.

DISCUSSION

In all of our Phase I and II experiments, the DTPA solution dissolved more than two thirds of the initial mass of the barite (Table 1). Adding six weight percent potassium carbonate to the solution increased the mass of barite dissolved in one hour of boiling by approximately twenty weight percent. Boiling for sixty rather than thirty minutes increased the mass of barite removed by about eight weight percent. We therefore conclude that both adding potassium carbonate and boiling for sixty minutes are preferred when using DTPA solution to dissolve barite.

Using 0.1 M DTPA solution rather than 0.5 M solution slightly increased the mass of barite dissolved, from 88% (one experiment with 0.5 M solution) to 92±8% (six experiments with 0.1 M solution). In addition to this small increase, another reason to prefer the 0.1 M solution is that its preparation requires five times less DTPA powder and using less of a reagent is desirable for both economic and environmental reasons.

A 0.5 M potassium hydroxide solution was sufficient to prepare a 0.1 M DTPA plus 6 weight percent potassium carbonate solution with a pH greater than 11.5. We did not determine the minimum potassium hydroxide concentration necessary to maintain this pH. However, we recommend using the smallest possible amount of solid potassium hydroxide to prepare the solution in order to use no more of this reagent than necessary.

Boiling DTPA solution attacked the surfaces of barite crystals, resulting in scallops and pits on the surfaces (Fig. 1). This result is similar to that shown in Dunn and Yen (1999) and Putnis et al. (2008). In contrast, zircon crystal surfaces were not attacked by boiling DTPA plus potassium carbonate solution at the resolution of several nanometers provided by the secondary electron images. The absence of effects on the zircon crystal surfaces indicates that an aqueous solution of 0.1 M DTPA plus six weight percent potassium carbonate did not attack zircon aggressively enough to dissolve entire grains or major parts of grains, as it did for barite.

Our experiment on the Alamar Formation natural sandstone sample demonstrated that the DTPA plus potassium carbonate procedure effectively removes barite from a mixture of barite and detrital zircon. The absence of detectable residues on the beakers or remaining grains from all experiments suggests that the method, which includes rinsing after the dissolution step, does not contaminate the surfaces of grains. Although we did not test whether boiling in DTPA plus potassium carbonate solution affected isotopic systems in zircon, the absence of physical attacks larger than a few nanometers on a zircon crystal surface is an encouraging sign that these chemicals may not greatly affect zircon. In contrast to milling in a ball mill, the DTPA plus potassium carbonate procedure may not introduce bias into the detrital zircon separate, and the new protocol takes about one fifth the time as the sodium carbonate solution method developed by Martin et al. (2021). Therefore, pending tests of its effects on isotopic systems in zircon, we suggest that the DTPA plus potassium carbonate solution procedure developed in this paper may be an advantageous replacement for other barite removal methods.

Pyrite is another mineral that commonly persists with detrital zircon after density and magnetic separation. Boiling the pyrite and zircon mixture in nitric acid is a pyrite removal technique used in many laboratories. An aqueous solution of DTPA and potassium carbonate also dissolves pyrite (Ahmed et al., 2019). The DTPA plus potassium carbonate technique described here thus offers the possibility of one-step removal of both barite and pyrite.

One downside of the DTPA plus potassium carbonate solution method is that it produces a small amount of chemical waste that must be disposed of and that does not break down easily. Another drawback is that this method takes forty-five minutes longer than milling, not including preparation and cleanup time. However, if the DTPA and potassium carbonate solution method were used to dissolve both barite and pyrite simultaneously, the treatment duration would be similar to the total time needed to remove both minerals using the two independent steps currently employed in many laboratories.

IMPLICATIONS

Fundamental conclusions in many Earth Science disciplines are built on data from geochemical analyses of detrital zircon. In all of these applications, it is important to minimize bias introduced into the sample during separation and analysis of the zircon. Milling a detrital zircon and barite mixture to remove the barite can introduce bias by breaking the barite along with the zircon grains (Martin et al., 2021). The alternative offered by Martin et al. (2021), boiling in sodium carbonate solution, has two drawbacks: (1) This procedure takes five hours plus preparation and cleanup, and (2) It might affect the U-Pb isotopic system in zircon. The DTPA plus potassium carbonate solution technique described in this paper does not break or cause the loss of zircon and takes only one hour plus preparation and cleanup. It thus offers a time-efficient means to remove barite without introducing bias into the sample. Pending tests of the effects of the DTPA plus potassium carbonate technique on isotopic systems in zircon, this method of barite removal thus appears to be superior to both milling and boiling in sodium carbonate solution. The possibility of simultaneously dissolving both barite and pyrite increases the appeal of the technique. The procedure also could be used for isolating zircon from barite-bearing igneous rocks. It is potentially widely applicable in the Earth Sciences.

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FIGURE CAPTIONS

1. Secondary electron images of the surfaces of barite crystals. (A) Before treatment. (B) After boiling in 0.1M DTPA solution (experiment 1B). Boiling in DTPA solution caused the development of microscopic scallops and pits on the surface of the barite crystal. The scale is the same for both images.
2. Secondary electron images of the same portion of the surface of a zircon crystal. (A) Before treatment. (B) After boiling in 0.1M DTPA solution plus 6 weight percent potassium carbonate. This treatment did not cause any detectable change to the surface of the zircon crystal. The scale is the same for both images.

TABLES

1. Conditions and results of experiments.

TABLE 1. SET-UP AND RESULTS OF EXPERIMENTS

Experiment Number	Concentration of DTPA solution (M)	6 weight % K_2CO_3 added?	Boiling time (min)	Barite mass before boiling (g)	Barite mass after boiling (g)	Proportion barite dissolved (%)
Phase I						
6B	0.5	yes	60	0.2003	0.0247	88
7	0.1	yes	60	0.2011	0.0088	96
8	0.1	yes	30	0.2010	0.0330	84
9	0.1	no	60	0.2010	0.0625	69
Phase II: Repetitions of experiment 7						
11	0.1	yes	60	0.2015	0.0208	90
12	0.1	yes	60	0.2015	0.0298	85
13	0.1	yes	60	0.2017	0.0105	95
14	0.1	yes	60	0.2017	0.0135	93
15	0.1	yes	60	0.2017	0.0152	92
Phase III: Physical attacks on barite and zircon surfaces						
1B	0.1	no	480	-	-	-
zircon	0.1	yes	60	-	-	-
Phase IV: Natural sample						
10	0.1	yes	60	-	-	-

Notes

1. The volume of DTPA solution was 250 mL for all experiments except 1B, for which it was 30 mL.
2. The 2-sigma uncertainty in the proportion of barite dissolved, propagated from the uncertainty in the mass measurements, is 0.5% barite dissolved.

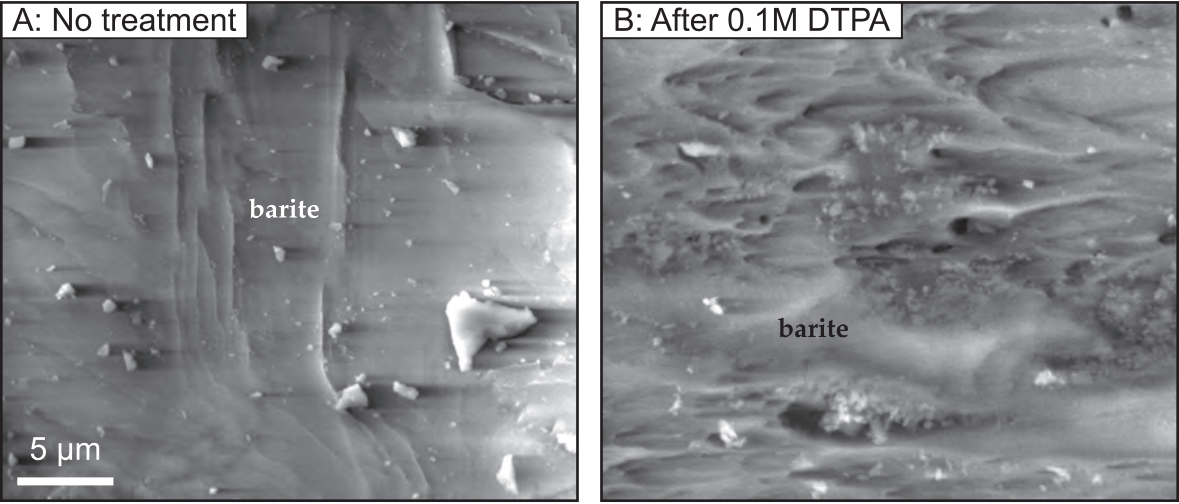

Figure 1 (Martin and Rocha-Estopier)

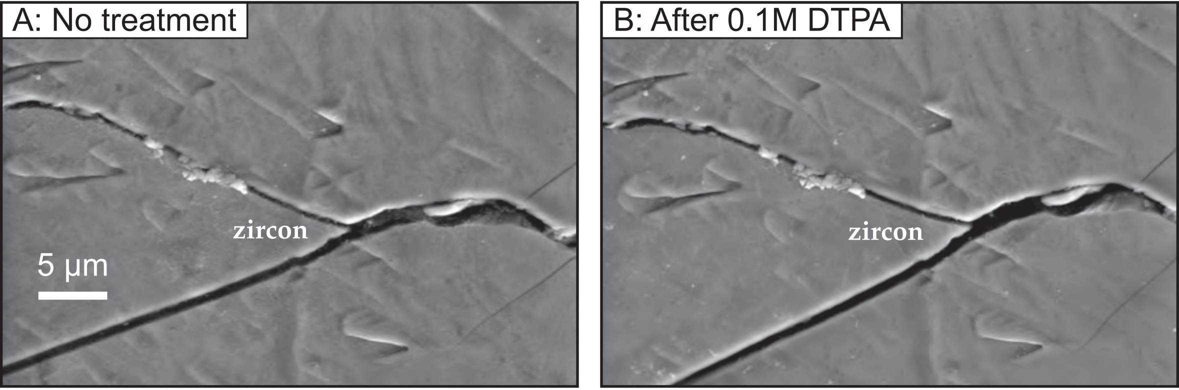

Figure 2 (Martin and Rocha-Estopier)