

Zeitschrift:	Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie
Band:	76 (1996)
Heft:	1
Artikel:	A new silicate dissolution procedure for isotope studies on garnet and other rock forming minerals
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DOI:	https://doi.org/10.5169/seals-57688

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A new silicate dissolution procedure for isotope studies on garnet and other rock forming minerals

by Thomas F. Nägele¹ and Balz S. Kamber^{1,2}

Abstract

A new silicate digestion technique, based on sequential acid treatment ($\text{HBr} \rightarrow \text{HF-HNO}_3 \rightarrow \text{HNO}_3$), is presented. The main features are: (i) only "off the shelf" equipment is needed, (ii) it avoids HClO_4 and H_2SO_4 , (iii) precipitates which may coat residual grains and inhibit total dissolution are removed by ultrasonic agitation, (iv) cations which are likely to form fluorides in the course of dissolution are largely extracted from the silicates before HF is applied, thus minimising the danger of laboratory fractionation (of e.g. Sm/Nd or U/Pb) and incomplete spike-sample equilibration, (v) the procedure can be optimised for specific silicates (or mineral chemistries), (vi) thanks to the use of transparent beakers the state of dissolution can be traced without interrupting the process and residual fluorides are easily detected and (vii) blank contribution is easily traced. This technique is an alternative to steel jacketed Teflon® bomb digestion and an improvement over traditional closed vial approaches.

Keywords: isotope analysis, silicate dissolution, sequential acid treatment, fluoride precipitation.

Introduction

Absolute age determination of garnet has become a widely used technique since the early work of VAN BREEMEN and HAWKESWORTH (1980), particularly so, since MEZGER et al. (1989) showed that garnet may, apart from a high Sm/Nd ratio, also possess a favourable U/Pb ratio. Indeed, Sm/Nd and Pb/Pb or U/Pb geochronology on not only garnet, but also other rock forming minerals like staurolite, sphene, pyroxene, aluminosilicates has had a considerable impact on our understanding of tectono-metamorphic processes (e.g. MEZGER et al., 1989; VANCE and O'NIIONS, 1990; BURTON and O'NIIONS, 1991; KAMBER et al., 1995; LANZIOTTI and HANSON, 1995). Many laboratories are now able to apply the Rb/Sr, Sm/Nd, Pb/Pb and U/Pb techniques to small sample amounts as required to address first-order problems in metamorphic petrology like heating, cooling-, exhumation- and burial rates. Through this wider application of traditional techniques to rock forming minerals with low U, Pb, Rb, Sr and

REE concentrations, a number of problems of apparent age interpretations have appeared, e.g. nature of isotopic closure and influence of submicroscopic inclusions. In addition, these issues are clouded by error sources in the technical procedures themselves, which mainly concern two aspects: (i) characterisation of samples in the light of possible isotopic heterogeneities (e.g. zonations, fluid and solid inclusions rich in either the parent or daughter elements) and (ii) the problem of complete sample dissolution and spike equilibration. This report reviews the most commonly applied dissolution techniques for comparison and proposes a new dissolution procedure for rock forming silicates, which should eliminate the second error source.

Review of commonly applied dissolution techniques

Complete dissolution of the investigated mineral fraction and equilibration with the spike is one of

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Tab. 1 Compilation of silicate digestion techniques.

author(s)	method	mineral(s)	T (°C)	duration	acid(s)	remarks
VON QUADT and GEBAUER (1993)	bomb	garnet, pyroxene, rutile, sillimanite	?	?	HF–HNO ₃ –HClO ₄	1 day treatment in cold HF (open beaker) prior to dissolution
ZHOU and HENSEN (1995)	bomb	garnet	220	?	HF–HNO ₃	garnets were "oxidised" in 180 °C conc. HNO ₃ for 12 h, prior to digestion
KAMBER et al. (1995)	bomb	garnet	185	5 days	HF–HNO ₃	
LANZIOTTI and HANSON (1995)	bomb	kyanite, garnet, anatase	225	3–10 days	HF–HNO ₃	0.3 ml capsules in Parr® bombs
ibid.	vial	staurolite	?	1–3 days	HF–HNO ₃ –H ₂ SO ₄	ground into a powder prior to digestion
MEZGER et al. (1989)	vial	garnet	150	6–24 hours	HF–HNO ₃ –H ₂ SO ₄	dried at 200 °C for 10–15 hours
COHEN et al. (1989)	vial	garnet, clinopyroxene	?	?	HF–HNO ₃	residual fluorides destroyed with HNO ₃
THÖNI and JAGOUTZ (1992; pers. comm.*)	vial	garnet, epidote, rutile, pyroxene, amphibole, staurolite	110*	2–7 days, rutile and staurolite > 1 month*	HF–HClO ₄	leached minerals kept in cold HF–HClO ₄ prior to dissolution. Residual fluorides destroyed with 6 M HCl*
MABOKO and NAKAMURA (1995)	vial	garnet, clinopyroxene	110	≥ 12 hours	HF–HNO ₃	residual fluorides destroyed in HCl

the fundamental needs to reduce analytical uncertainties and produce reliable isotope data. Most framework, sheet or chain silicates are dissolved applying HF–HNO₃ mixtures. A number of silicates, in particular ortho silicates (i.e. zircon, olivine and garnet) however, are not easily dissolved by conventional acid treatment. Here we review the most commonly applied procedures to disintegrate resistant minerals. An overview is given in table 1.

STEEL-JACKETED TEFLON® BOMB UNDER ELEVATED TEMPERATURE AND PRESSURE

The classical approach (KROGH, 1973) to dissolve zircon is a combined HF–HNO₃ attack at elevated temperature (220 °C, up to 250 °C using the improved approach by PARRISH, 1987) and pressure. The sample is placed in a Teflon® container which is mantled by a steel jacket. This technique has shown to be very efficient in both conventional and single grain U/Pb geochronology but also to dissolve resistant orthosilicates (e.g. VON QUADT and GEBAUER, 1993; ZHOU and HENSEN, 1995; KAMBER et al., 1995; LANZIOTTI and HANSON, 1995) and whole rock powders (e.g. NÄGLER

et al., 1992). However, its application to methods other than U/Pb on accessory minerals has, in our view, some limitations. Due to the generally low abundance of the studied elements, greater amounts of ordinary rock-forming minerals need to be dissolved in order to get sufficient ion yields (e.g. 20–50 mg of garnet for U/Pb analysis as compared to less than 1 mg of zircon). This requires the use of Teflon® containers with a much higher volume which tend to leak more easily, and are more susceptible to contamination. Moreover, the dissolution process can not be visually observed and only after the usually empirically determined attack time is it possible to examine the degree of disintegration. Finally Teflon® bomb dissolution is time-consuming and requires special, usually custom made, equipment which is not easily obtainable to many laboratories.

CLOSED SAVILLEX® VIAL DISSOLUTION ON A HOT PLATE

According to the amount of sample which is to be dissolved 7, 14 or even 60 ml Savigex® screw-top vials are also used commonly for sample disintegration. A number of studies report successful

dissolution of e.g. garnet (and other resistant minerals) using various inorganic acid mixtures (Tab. 1 gives an overview), usually at temperatures between 140 and 170 °C. Although some authors found an HF–HNO₃ mixture sufficient (e.g. COHEN et al., 1988 or MABOKO and NAKAMURA, 1995) most laboratories add either HClO₄ (e.g. THÖNI and JAGOUTZ, 1992) or H₂SO₄ (e.g. MEZGER et al., 1989) to facilitate complete disintegration at such comparatively low temperatures. Apart from being hazardous, these acids have very high boiling temperatures and their complexes are not easily transformed into chlorides for column chemistry. The translucent bottom of Savillex® beakers allows for optical inspection of the dissolution progress. However, depending on sample composition, the dissolved material may not remain in solution but form whitish to greenish precipitates (e.g. MEZGER et al., 1989), most likely fluorides and/or chlorates, in which residual silicate material may be hidden.

LITHIUMTETRABORIDE FUSION

VOCKE et al. (1987) applied a flux dissolution using graphite crucibles to whole rock samples of the Roffna gneiss. Although reported blanks are higher than for samples dissolved in Teflon® bombs, this technique may, under best conditions, serve as an alternative to acid dissolution. To our knowledge, no isotopic study of ordinary rock forming silicates has however used the technique yet.

When comparing the capabilities of the acid based techniques and their modifications it becomes evident, that the main three pitfalls of silicate dissolution (incomplete dissolution, incomplete spike-sample homogenisation and erroneous aliquotting due to laboratory fractionation) are linked to the problem of fluoride precipitation. Many rock-forming-silicates, in contrast to zircon, contain divalent cations which easily form fluorides. Calcium in particular may rapidly produce fluorite in spite of the presence of HNO₃. The main effects of fluoride precipitation are:

(i) They may coat undissolved silicate from the acid and thus inhibit further dissolution. In case of bomb dissolution, residual silicate is only recognised after opening the bomb.

(ii) In case fluorides grow before the total amount of silicate is dissolved they predominantly incorporate tracers from the spike. In order to prevent calculation of false Sm/Nd, Rb/Sr and U/Pb ratios these precipitates need to be quantitatively destroyed after evaporation of the

HF–HNO₃ mixture. Also when the sample is spiked after dissolution, gels and precipitates have to be avoided as they may even fractionate rare earth elements. Concentrated HCl (or HClO₄) is added to convert the sample into chloride form. However, even under a binocular, traces of remaining fluorides are hard to find in white Teflon® bombs, which are required for high temperature dissolution. Moreover, precipitates formed at temperatures in excess of 180 °C are very hard to re-dissolve. POLLER (1994) identified Al–Mg–Na–F compounds in 6 N HCl resistant residues of bomb attacked orthogneiss samples. Indeed, e.g. Na₃AlF₆ is insoluble in HCl (WEAST et al., 1990).

(iii) Fluoride gels strongly fractionate REE (COHEN et al., 1988) and possibly U/Pb (MEZGER et al., 1989). If the sample is to be aliquotted after digestion, it is thus essential to avoid the presence of fluorides or equivalent gels. COHEN et al. (1988) have measured a Sm/Nd ratio of ~ 10 in an Al-rich gel. Two approaches are taken to ensure correct aliquotting. The digested sample can repeatedly be treated with HCl or HClO₄, and finally, remaining precipitates are discarded after centrifuging, assuming no fractionation of the analysed elemental ratios. Alternatively the sample is dissolved in hot (up to 120 °C) HCl and aliquotted while still at high temperature. This approach produces less reliable weighing. If the sample solution is loaded onto the chromatographic column when still hot (MEZGER et al., 1989), precipitates may form on top of the resin bed and complicate chromatography.

In conclusion, resistant silicates, rich in cations prone to form fluorides should ideally not be dissolved with HF, or these cations should be largely removed from the lattice prior to HF attack.

A new dissolution technique based on sequential acid treatment

Here a dissolution technique is presented which is based on our experience with the step wise Pb/Pb leaching procedure of FREI and KAMBER (1995). We found that when mineral fractions of e.g. garnet, clinopyroxene or sphene are subjected to sequential leaching with strong HBr and HNO₃ prior to final dissolution with HF the mineral grains are totally bleached. This, and the observed mass loss (FREI, 1995, personal communication), implies that metal ions like Fe or Mn, but probably also Ca, Mg or Na, are extensively leached from the original silicates. FREI and KAMBER (1995, page 263, Tab. 1) described that the remaining colourless residue can be dissolved

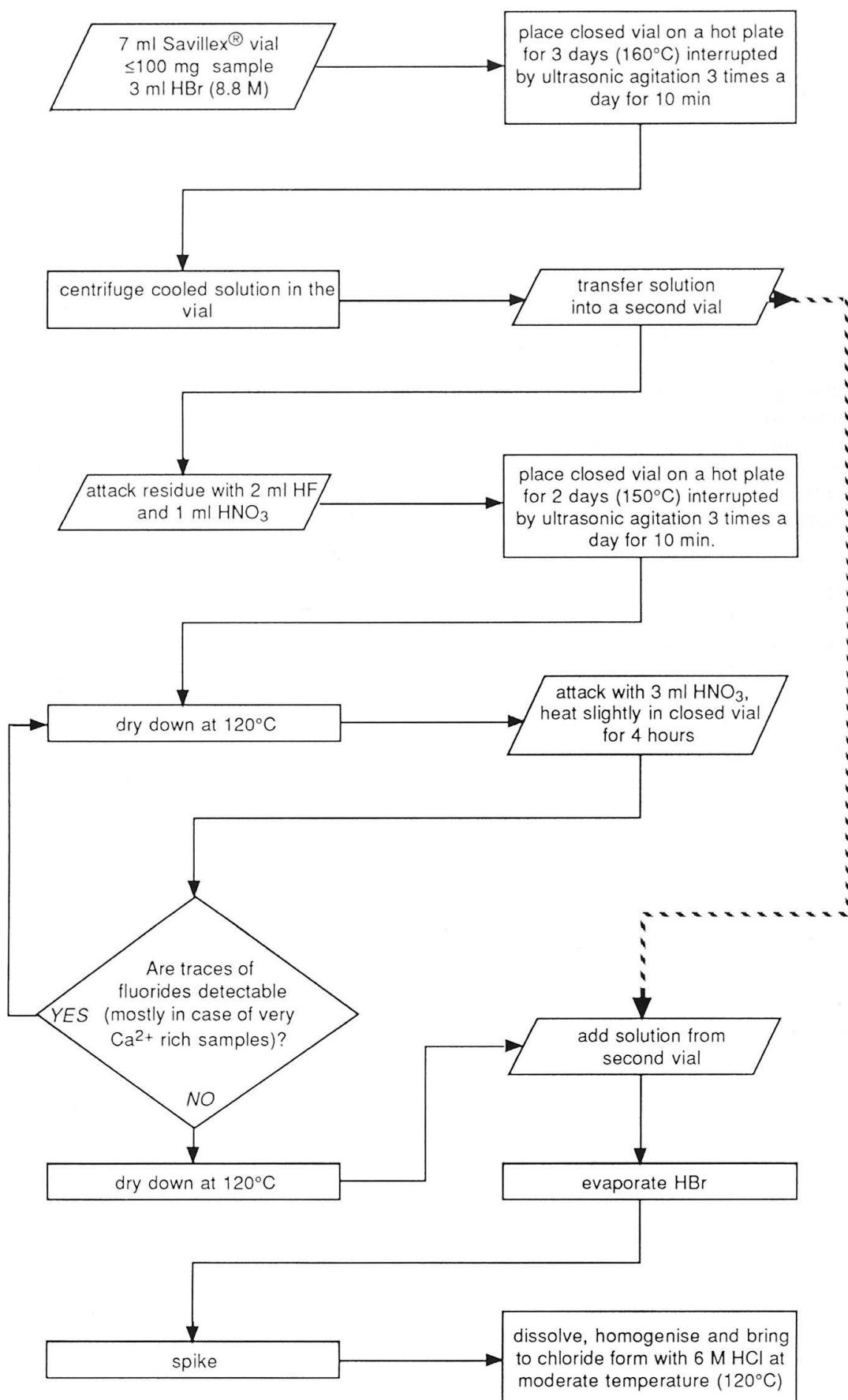


Fig. 1 Flow chart of the procedure.

within 48 h on a hot plate. In this study we have modified sequential leaching for the purpose of designing a fast, easy and reliable dissolution procedure, which only involves "off the shelf" equipment.

The proposed procedure is illustrated on a flow chart on figure 1. Up to 100 mg of pure sample (grain size up to 250 μm) is weighed into a 7 ml Savillex® screw top vial. 3 ml concentrated HBr (8.8 M) are added. The closed beaker is placed on a hot plate (160 °C). Within the first few hours, the colour of the acid will turn from light yellow to dark brown or even black due to chemical reactions and Br_2 release. During the 3 days heating process the beaker is put into an ultrasonic bath 3 times a day, 10 minutes each. Afterwards the still closed vial is centrifuged for 10 minutes at 4000 rpm. The solution is transferred into a 15 ml Savillex® vial using a pipette. The residue is attacked with 2 ml HF and 1 ml HNO_3 and heated to 150 °C for 2 days, again interrupted by ultrasonic agitation 3 times a day. This step will dissolve the silicates, typically within less than 2 days. The solution is evaporated at 120 °C. Another 3 ml HNO_3 are added and the sealed vial is slightly heated for several hours. If fluorides remain (mostly in case of high Ca^{2+} minerals, note that the transparent vial bottom allows for optical inspection), the solution is dried and the HNO_3 treatment is repeated. After complete dissolution and evaporation, the HBr solution from the second vial is added to the residue, HBr is evaporated. The sample is now ready to be spiked and/or separated into aliquots. If ^{205}Pb and ^{150}Nd tracers are added to the dried sample they can easily be homogenised in 6 M HCl at moderate temperatures (120 °C). As fluorine was completely removed beforehand, no new fluorides will form. In case the sample has to be aliquotted, dissolution is achieved with few ml of 6 M HCl (even when heated to 120 °C no precipitation will be found during cooling) and can be split.

The blank contribution largely stems from the acids, because handling is minimal (note that we centrifuge in the vial itself). Using single distilled HF, HNO_3 and HBr, the Nd blank of the attack is ≤ 100 pg. For Pb analyses, double or triple dest. acids must be applied. Care must be taken to distil a low Pb blank HBr. For 50 mg samples (requiring 50% less HBr) a total procedure Pb blank of 120 pg was determined.

Summary

The presented dissolution procedure constitutes an alternative to Teflon® bomb attack and an im-

provement over traditional closed vial techniques. Its main features are:

(i) It applies "off the shelf" equipment (i.e. commercial vials, hot plate, ultrasonic bath and centrifuge).

(ii) It avoids the hazardous acid HClO_4 and the high boiling temperature H_2SO_4 .

(iii) Precipitates which coat residual grains can be removed by agitating in an ultrasonic device. This step is recommended to facilitate HF dissolution of silicates in general.

(iv) Cations that are likely to form fluorides are largely extracted from the silicates before HF is applied, reducing the potential of fluoride formation to a minimum. The absence of such cations facilitates complete dissolution during the HF- HNO_3 attack without the need for more hazardous acids. Because the critical metal ions (largely contained in the HBr solution) are only added to the residue after its conversion to the nitrate form, the danger of fluoride gel formation is minimal. This is a significant improvement over high temperature dissolution typified by precipitates, which are very hard to re-dissolve, even in concentrated HNO_3 or HCl.

(v) The sequence and amount of acids as well as the exposure times can empirically be optimised to the specific silicate (or mineral composition).

(vi) The transparency of the vial allows first to quite sensitively follow the state of dissolution without interrupting the process and second, when placed on a dark surface, to easily detect traces of remaining fluoride.

(vii) Tracing blank contribution is easier than with big Krogh type bombs, especially if a centrifuge is used which allows to directly place vials.

Acknowledgements

We would like to thank R. Frei and J.D. Kramers for sharing their expertise in silicate dissolution. The careful reviews by A. Gilg and M. Thöni are gratefully acknowledged. This work was supported by the SNF, grant 20-40442-94.

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Manuscript received November 21, 1995; minor revision accepted January 10, 1996.