A single-column extraction chemistry for isotope dilution U-Pb dating of carbonate

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Declaration of interest: None

ABSTRACT

U-Pb dating can provide age constraints on carbonate minerals from a wide range of geological settings. A major practical limitation, however, is the need for rapid and efficient extraction of Pb and U from large numbers of typically low-Pb (≤10 ng/g) calcite samples, while maintaining low blanks (~10 pg Pb) and high Pb-U yields and purity. Here we describe a well-tested ion exchange procedure able to extract Pb and U from large (up to 200 mg) calcite samples using a single pass over a mini-column filled with small (~0.1 ml) volumes of AG1-X8 anion exchange and Eichrom TRU-resins. This 'stacked resin' technique halves the time spent on elemental extractions and provides MC-ICPMS-ready Pb and U fractions in a single day. The method results in considerable savings in laboratory time and allows higher sample throughput, without negative impacts on data quality. It is ideally suited for high-precision U-Pb dating of speleothems where large numbers of samples need to be processed, but it is equally adaptable to calcites from other settings. While not explored as part of this work, the stacked resin technique should also be applicable to other carbonates (dolomite, ankerite, siderite).

KEYWORDS: U-Pb dating, carbonate, isotope dilution, geochronology, speleothem, chromatography

1. INTRODUCTION

Carbonate minerals are ubiquitous in the geological record, occurring as major or minor components in many rocks and geological settings. Although few carbonates contain >1 ppm of U, the depositional U/Pb ratios are often very high, such that carbonates – in particular calcite and calcite rocks – have been employed in U-Pb and Pb-Pb isotope geochronological studies for decades. This includes studies of fossils and corals (Smith and Farquhar, 1991; Russell, 1995; Getty et al., 2001; Denniston et al., 2008), marine cements (Jones et al., 1995; Becker et al., 2002; Rasbury et al., 2004), marine carbonate concretions (Israelson et al., 1996), lake carbonates (Cole et al., 2004), dolomites (Hoff et al., 1995; Luczaj and Goldstein, 2000), pedogenic carbonate (Winter and Johnson, 1995; Rasbury et al., 2000) and hydrothermal carbonate (DeWolf and Halliday, 1991; Sturchio et al., 1998; Coveney et al., 2000;).

Calcite U-Pb dating has also greatly extended the utility of speleothems (stalagmites, flowstones) both as chronometers and as palaeoclimate archives. Speleothems are usually protected from post-deposition modification (i.e. deformation, compaction, weathering) and thus the open-system disturbances which may influence other carbonates (e.g. Jahn and Cuvellier, 1994), making them robust recorders of palaeo-climate (Bar-Matthews et al., 1997; Tremaine et al., 2011), hominin evolution (Pickering et al., 2010, 2019) and geomorphology (Richards et al., 1994; Bosak, 2002**)** beyond the nominal ~600ka limit of the U-Th technique (Woodhead and Pickering, 2012).

The recent advent of *in situ* analytical methodologies for the dating of carbonate materials has also seen remarkable success (Roberts and Walker, 2016; Goodfellow et al., 2017; Nuriel et al., 2017; Parrish et al., 2018). Ongoing technical improvements (e.g. Drost et al., 2018) suggest that the technique will likely see rapid uptake in many fields of carbonate U-Pb geochronology, in particular studies requiring chronological histories at a high spatial resolution (Woodhead and Petrus, under review). It is also likely, however, that isotope dilution techniques will remain the benchmark for high accuracy dating, as they have in the field of U-Pb zircon dating (e.g. Schoene, 2014) where *in situ* methods have a strong presence (e.g. Gehrels et al., 2008).

The 'Achilles heel' of the carbonate isotope dilution methodology is, of course, the large amount of time and effort involved in extracting U and Pb from the sample matrix for analysis – an issue of particular importance where large numbers of samples are required in order to obtain landscape-scale chronologies in long-lived systems (e.g. Woodhead et al., 2019). Furthermore, while the U-Th technique can produce radiometric ages from single aliquots, U-Pb dating usually requires >5 aliquots to generate robust isochrons (e.g. Engel et al., 2019) and therefore requires substantially more analyses to produce a single age. As a potential method for accelerating U-Pb isotope dilution analyses, here we describe a rapid procedure for the liquid ion exchange resin chromatography (referred to as "extraction chemistry") of spiked U and Pb from large (up to 200 mg) carbonate samples using a single ion exchange column operated using the readily available HBr, HCl, and HCl-HF acids. The technique combines the advantages of the well-established and widely-used extraction schemes based on AG1-X8 anion resin for Pb (e.g. Manhes et al., 1984; Kamber and Gladu, 2009) and Eichrom TRU-resin for U (e.g. Luo et al., 1997) but explores the consequences of combining the two protocols into one sequential extraction procedure. The two resins are stacked within a single miniature PTFE column of the type used for Pb isotope geochemical studies in many laboratories. In our experiments with large speleothem calcite samples, this combination of resins performed better than other single-column U-Pb extraction techniques (e.g. Krogh 1973; Paquette and Pin, 2001) and produced Pb and U fractions ready for analysis after a single pass and within a single working day. Solution mode ICP-MS results to date indicate that this "stacked resin" column can replace sequential U-Pb extraction procedures that use the same resins in separate columns, thus reducing sample processing times by around 50%.

2. EXPERIMENTAL METHODOLOGY

Sampling of speleothems for isotope dilution U-Pb dating was achieved by drilling out small cubes from sawn and polished stalagmite or flowstone samples (e.g. Woodhead et al., 2006). The resulting material (~100 mg) was briefly reacted with 1M HCl within clean, disposable polystyrene beakers to remove potentially contaminated surficial layers (at most a few mg). The rinsed samples were air-dried, weighed into a Savillex PFA beaker, immersed in distilled water, and dissolved via step-wise addition of 6M HCl at room temperature. After addition of a ^{233}U-^{205}Pb tracer, the spike-sample mix was equilibrated (100°C, 3 hours) and eventually dried, prior to column chemistry.

The miniature Teflon columns used here were made from PTFE heat-shrinkable tubing (4:1 shrinking ratio, Mauritz Communication & Electronics, Germany) prepared to provide a 30 mm long resin reservoir (internal diameter 4 mm) stoppered with two polyethylene frits (Reichelt Chemietechnik GmbH, Germany, 30 µm pore size) and a 7 ml acid reservoir (30x15 mm, with an 18 mm long taper). Columns were placed within individual column holders (inverted 100 ml polycarbonate beakers with a hole drilled in the base) and mounted on multi-position "lazy-Susan" style stands. Multiple column stands allow up to ~30 samples to be processed simultaneously within a normal sized clean air workstation. Ion exchange resins (AG1-X8, 100-200 mesh; TRU-resin, 100-150 µm; Prefilter resin, 100-150 µm) were obtained from Eichrom Industries (Lisle, Illinois, USA). All resins were batch-cleaned using 6M HCl and water (for AG1-X8), and 6M HCl, 0.1M HCl – 0.1M HF mix and 0.05M HNO_3 (for TRU and Prefilter-resin) prior to use. All acids used in contact with beakers, columns and samples were prepared from highly purified starting reagents: HBr (Seastar Baseline), HCl and HNO_3 (Merck AR, purified in a 2-stage quartz sub-boiling still or a Savillex DST-1000 acid purification system), HF (Merck AR, purified in a four-stage sub-boiling Savillex PFA elbow still). High-purity (18.2 MΩ/cm) water was produced in an Elga Purelab Ultra water purification system. All work was performed in a HEPA filtered exhausting clean air cabinet within a class 350 HEPA-filtered clean room (Australian metric Standard 1386, equivalent to US imperial Class 10,000 standard).

Elemental analyses of column fractions were carried out on an Agilent 7700x quadrupole-ICP-MS, following procedures adapted from Kamber et al. (2003). Isotope dilution U-Pb isotopic analyses were conducted using a Nu Instruments 'Plasma' multi-collector ICP-MS, with sample uptake via a 0.1 ml/min Glass Expansion MicroMist glass nebulizer and Nu Instruments DSN100 desolvation system. Typical instrument sensitivity ranged from 300-400 Volts/ppm. Spiked U fractions dissolved in 2% HNO_3 (~10 ppb U) and corrected for mass bias by internal normalization to the spike-corrected natural $^{238}U/^{235}U$ ratio using the exponential law. Instrumental mass bias in Pb isotope runs was corrected by standard-sample bracketing with SRM981, using the SRM981 composition reported in Woodhead (2002). All data reduction was performed using the method of Schmitz and Schoene (2007).

3. STACKED RESIN COLUMNS

The original extraction technique for speleothem U-Pb dating in our laboratory (Woodhead et al., 2006) was a 2-stage, 2-day procedure. On day 1, Pb would be extracted from the sample solution on a 12 x 4 mm column of AG1-X8 (100-200 mesh) anion exchange resin, using 0.6M HBr to wash off matrix elements (incl. U) and 6M HCl to elute Pb. On day 2, the U-bearing sample matrix produced on day 1 (dried down overnight) would be redissolved and loaded onto a 12 x 4 mm bed of Eichrom TRU-resin in 1.5M HNO_3, followed by further washing with 1.5M HNO_3 and 3M HCl, and finally the collection of U using a mixed 0.3M HCl-0.1M HF solution. This technique was well suited to the ubiquitous organic impurities in speleothem calcite and produced analysis-ready Pb and U fractions of high purity and yield (>95%), with column blanks of ~5 pg Pb and <5 pg U.

Combining the two resins into a single column should produce the same results in half the time, since only a single column set-up, elution and sample dry-down is required. However, potential unresolved problems include the effects of HBr and HCl-HF on the exchange characteristics of the stacked TRU-resin and anion exchange resin, respectively, and perhaps increased Pb and U blanks. To examine these issues, elution patterns (HBr, HCl, HCl-HF mix) of layered test columns loaded with test solution made from Pb-rich speleothems doped with U and Th were mapped by ICP-MS.

3.1 Loading and elution of stacked resin columns

Teflon mini-columns were loaded (in water) with Eichrom TRU-resin to produce a 12-15 mm tall resin bed, followed by the addition of a 12-15 mm AG1-X8 anion resin bed (approximately 150 – 200 µl of each resin). The reverse stacking sequence was also tested. The settled resin beds were pre-cleaned with 6M HCl, mixed 0.3M HCl - 0.1M HF, more HCl, and then water, followed by a conditioning step of HBr (Table 1).

After the addition of 1 ml of 0.6M HBr to the beakers, the spiked calcite samples were capped and briefly heated to re-dissolve the sample. After cooling, the entire sample solution was pipetted onto the column and allowed to sink into the resin bed. Next, the calcite matrix elements were eluted with three further 1 ml washes of 0.6M HBr. Pb and U were then sequentially stripped from the column in 4x 0.5 ml of 6M HCl and 3x 1 ml of 0.3M HCl-0.1M HF mix, respectively, collected in 7 ml Savillex PFA beakers, and dried.

3.2 Elution patterns

Elution patterns observed from the U-Th-doped (original conc. U 0.1-1ppm, Th <0.1 ppb), Pb-rich test speleothem (100 mg calcite equivalent test solutions) are shown in Fig.1. This figure shows a typical elution pattern for a column with AG1-X8 as the top layer but elution patterns observed for test columns with AG1-X8 as the bottom layer were identical. The main matrix elements Ca and Mg, the minor Sr and Ba components, and Al (which may be present in clay-bearing speleothem calcite)

were rapidly removed from the resin during loading in HBr and quantitatively (>99%) eluted after three additional HBr washes. The light rare earth elements (La, Ce, Pr) and Y were also removed at this stage, as was 35-40% of the Th. Elution of Pb occurred almost exclusively during the 6M HCl stage where 98% of all Pb was recovered. The Pb fractions contained small remnants (<0.07%, or 3-30 μg) of Ca, La, Ce, Pr and Y, as well as 4-12% of the Th. Uranium was quantitatively (>99%) eluted in the HCl-HF step, which also contained 50-60% of the Th.

3.3 Procedural blanks

Pb blanks for the chemical procedure were measured for both the sequential and stacked resin methods by passing 4x 1.0 ml of 0.6M HBr over cleaned (Section 3) AG1-X8 resin or stacked AG1-X8 and Eichrom TRU resins, respectively, in lieu of a sample. Any blank Pb was then collected using 4x 0.5 ml of 6M HCl, dried in clean air, redissolved in HNO_3 running solution, and analysed via MC-ICP-MS (Section 2.1). Uranium blanks were produced from a similar but separate experiment from cleaned TRU resin or the combined resin protocol (including all cleaning steps) and collected using 3x 1ml of the HCl-HF mixture. Blank amounts were calculated using the largest representative isotopic signal intensities (i.e. ^{208}Pb and ^{238}U signals) calibrated to standards of known concentration: in this way we can measure approximately 3 pg of U or Pb within ~20% uncertainty. In these experiments all U blank analytes (both stacked and sequential) were below the detection threshold and therefore prescribed a conservative default value of 5 ± 50% pg of ^{238}U. Five AG1-X8 only eluates (i.e. the sequential resin technique) generated an average total Pb blank of 4.3 ± 3 pg Pb. Six eluates from the stacked resin columns produced an average total Pb blank of 11.8 ± 5 pg; the stacked resin produced on average a Pb blank three times larger than the sequential resin, which is not surprising given the much larger resin bed to which the sample is exposed in the stacked resin. Both techniques produce some variation in Pb blank and this uncertainty must be propagated through the isotope dilution calculations. Therefore, in applying the Pb blank corrections to all isotope dilution results we used conservative values of 4.5 ± 50% (2σ) pg Pb for the sequential resin method and 12 ± 50% pg Pb for stacked resins. This increased Pb blank amount is important only for samples with extremely small Pb contents (e.g. Godeau et al., 2018), such as those with <0.01 ppb of Pb.

3.4 Comparison of final U-Pb ratios: stacked resin vs sequential columns

The above elution and column blank tests suggested that U-Pb isotope results from the stacked resin columns should be closely comparable to those from the original sequential columns. To test this we processed two speleothems with typically low total Pb contents (<1 ng) over both column types: sample NS is relatively old (~4Ma) and relatively un-radiogenic, while sample RS is young (0.7Ma) and highly radiogenic. For each sample, ~200mg of material were dissolved, spiked, dried, re-dissolved in HBr, and then split equally amongst each column type. This division ensured that each column received identical sample load (0.35 ng Pb for sample RS; 0.19 ng for sample NS). If both column types performed equally well in terms of Pb-U yield and purity, and if column blank estimates are accurate, then the U-Pb results should be indistinguishable within analytical uncertainties. In all cases, the U-Pb results from stacked and sequential columns significantly overlapped within their analytical uncertainties (Table 2**).** In general, the larger Pb blank estimates for the stacked resin columns resulted in larger analytical uncertainties compared to the sequential resins. When viewed on the Tera-Wasserbug Concordia (Figure 2), the increased dependence on Pb blank created slightly more correlated U-Pb uncertainty envelopes for the stacked resin columns. However, accounting for this increased Pb blank has produced virtually identical isotope dilution U-Pb results between the two techniques.

4. DISCUSSION

The elemental elution patterns observed for the stacked resin columns preserved most elution features of the component AG1-X8 and TRU-resins (e.g. Luo et al., 1997; Kamber and Gladu, 2009). The major calcite matrix elements (Ca, Mg), and some key minor components (Sr, Ba, REE-Y), were quickly removed from the column during loading and washing with dilute HBr, without any detectable loss of Pb and U. This implies that TRU-resin tolerated sample loading in HBr without reducing its capacity to retain U. The original protocol employed 4x 1 ml of HBr (incl. loading) which proved adequate for handling ~100 mg calcite samples. For larger samples, or for those particularly rich in organics, additional HBr washes have been applied without obvious effects on Pb-U retention. One major departure from the established elution pattern of TRU-resin loaded with 1.5M HNO_3 (Luo et al., 1997) was the partial loss of Th during the last HBr wash (Fig.1). This was only noticed because the test speleothem used in the elution experiments was doped with Th; typical speleothems have very low Th contents (e.g., Whitehead and Ditchburn., 1999).

The elution of Pb from the stacked resin columns was very consistent in all test runs, with ~98% of the Pb recovered after 4x 0.5 ml of 6M HCl: as expected from an AG1-X8-only column. The 6M HCl used to collect Pb is well outside the molarity range [0.5 -3M HCl] for U-stripping on the TRU-resin (Paquette and Pin, 2001) and causes no discernible loss in U yield. The Th leakage observe in our experiments with Th-doped calcite solution (Fig. 1) would not present an issue in typical low-Th speleothems. In all experiments the Pb fractions were very pure and well-suited to MC-ICPMS analysis: <0.1% of Ca and <1% of the other calcite relevant elements were found in the HCl fractions. In absolute terms, the combined HCl fractions from a stacked resin column loaded with 100 mg calcite contained no more than 30 μg of matrix elements. Total Pb signals and peak shapes observed in the Nu Plasma were comparable with those of pure SRM981 Pb, implying that the stacked resin Pb fraction purity produced no degraded peak shape artefacts.

Elution of U from the stacked resin column was also very consistent. Over 99% of U removal occurred during the 0.3M HCl + 0.1M HF step of the elution sequence (Fig.1). Virtually no matrix elements (<0.1% of Ca and <1% of minor matrix elements, e.g. Sr) were eluted at this stage and, as mentioned above, co-elution of Th observed in the column tests would not be an issue for typical speleothems. Experience gained during routine operation of the stacked resin columns suggests the following measures to be beneficial: (i) mixing the TRU-resin with Prefilter-resin helps to suppress organic material leaking from the TRU resin (such leakage is well-documented for Eichrom Sr-resin, e.g. Paquette and Pin, 2001); and (ii) drying a drop of conc. HNO_3 onto the U extracts improves re-dissolution in the 2% HNO_3 run solution.

The technique described here was inspired by, and has much in common with, Paquette and Pin (2001) who combined minute quantities of Eichrom Sr and TRU-resin to extract Pb-U from zircons. However, our unpublished tests of an upscaled version of their Sr/TRU-resin column for large speleothem samples failed to produce consistent U-Pb results: the combination of AG1-X8 anion resin and TRU-resin performed better in our experiments. Similarly, we believe that our protocol has advantages over the combined U-Th-Pb extraction method for speleothem calcite proposed by Mason et al. (2013). The latter utilises near-concentrated acetic acid as a primary reagent and also requires additional cleaning columns after the main separation. Other single-column U-Pb extraction techniques, notably the well-established technique of Krogh (1973), have proven to be highly versatile. Although designed for small (~1 mg or less) zircon samples, the technique can also be used for small samples of other minerals, such as monazite, titanite, rutile, xenotime and apatite (e.g. Corfu and Noble, 1992). Our tests with a scaled-up Krogh-type AG1-X8 anion resin column, however, show that Pb is not extracted strongly in 3.0M HCl compared to 0.6M HBr, consistent with Pb partitioning data (Kamber and Gladu, 2009), suggesting that this is not an efficient protocol for handling large matrix loads. In contrast, the value of our mixed resin protocol described here is in its ability to accommodate the larger sample sizes (100 mg+) which are required where mineral Pb contents are very low, as in speleothems and other carbonates.

5. CONCLUSIONS

The new stacked resin technique is a simple and effective procedure for extracting clean Pb and U fractions from large calcite samples. These fractions run well on a MC-ICPMS, producing consistent U-Pb results and ages. So far the technique was only tested for a calcite matrix, and it is not known if the technique can handle other matrix types.

Our test results suggest the new stacked resin technique should perform well for Ca and Mg carbonates, as well as for witherite ($BaCO_3$) and strontianite ($SrCO_3$). As the tests did not include Fe, the performance for Fe-bearing carbonates (siderite, ankerite) on the mixed resin bed is unclear. Iron is not strongly extracted onto AG1-X8 in dilute HBr and strong HCl, and should thus elute quickly from this resin, like Ca and Mg. However, we are not aware of data relevant to Fe uptake on TRU-resin in dilute HBr, and thus this resin's ability to extract U during sample loading and washing in dilute HBr. This will be an area for further work which will establish if the new stacked resin technique can handle all major carbonate types. This would provide a convenient separation technique for applications of U-Pb dating to a wide range of carbonates.

Acknowledgments

We would like to thank two anonymous reviewers for their help and insight in improving this manuscript. This research was facilitated by Australian Research Council grant FL160100028 to JDW.

Figure 1) Elution patterns of Pb, Th, U, Ca, Al, Mg, Sr, Ba and La in a U-Pb doped speleothem calcite samples (0.1 g of solid) from a stacked bed of Eichrom TRU (below) and AG1-X8 anion resin (above) using dilute HBr, strong HCl and dilute HCl/HF mix. Elution peak heights were normalized to 100% of element loaded. Stacking the two resins into a single column preserved the retention quality of each composite resin. The dominant matrix element, Ca, as well as Mg-Al (panel A) and trace elements Sr, Ba, La (panel B), were eluted in dilute HBr (left). Lead (centre) and U (right) were only eluted in 6M HCl and HCl-HF mix, respectively. Thorium showed a bimodal elution across all three acids; in practice, this is unlikely to be a problem as carbonates tend to have very low Th contents. Note that x-axis shows test fraction numbers, not acid volume; the actual recipe adopted in this laboratory is shown in Table 1.

Figure 2) U-Pb isotopic results from doped-speleothem analyses using both the sequential resin (red) and "stacked resin" (black) techniques. Isotopic ratios are displayed upon the Tera-Wasserburg (T-W) Concordia commonly used for young, Pb-rich speleothems (see Woodhead et al., 2012). Two different, isotopically homogenous test solutions were evenly split and processed by the two techniques. Isotopic ratios were produced after applying a Pb blank of 4.5 ± 2.25 pg for sequential resins and 12 ± 6 pg for the new stacked resin technique. U-Pb results from both techniques were very similar, though with a systematic increase in uncertainty for stacked resin results resulting from the larger Pb blank.

Table 1) The proposed "stacked resin" protocol for U-Pb isotope dilution analyses of large carbonates.

Table 2) Isotopic results from isotope dilution U-Pb solution-mode ICP-MS analyses using both the sequential resin (seq) and proposed "stacked resin" (stack) techniques. Errors are shown as 2σ percent values.

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Figure 1

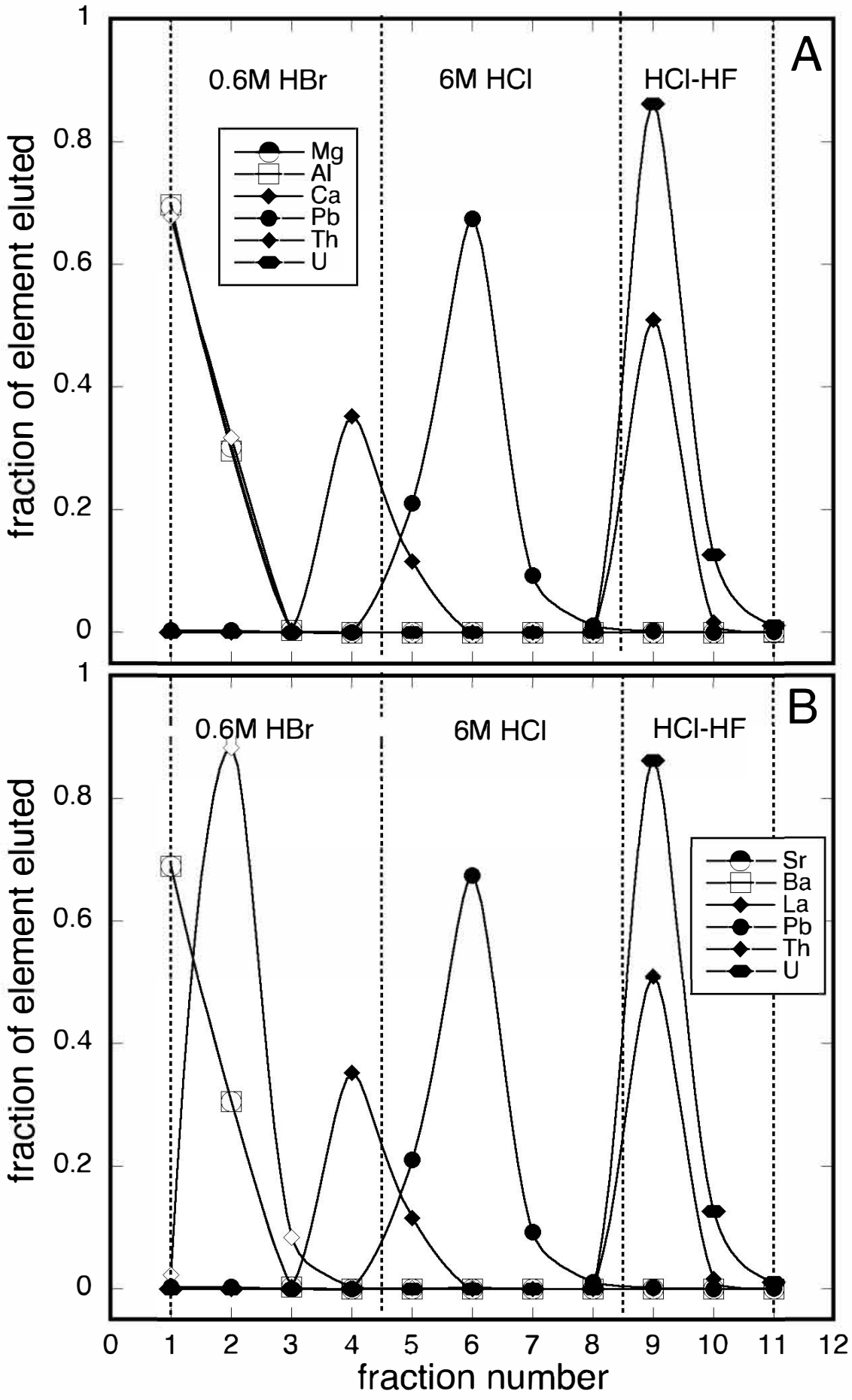
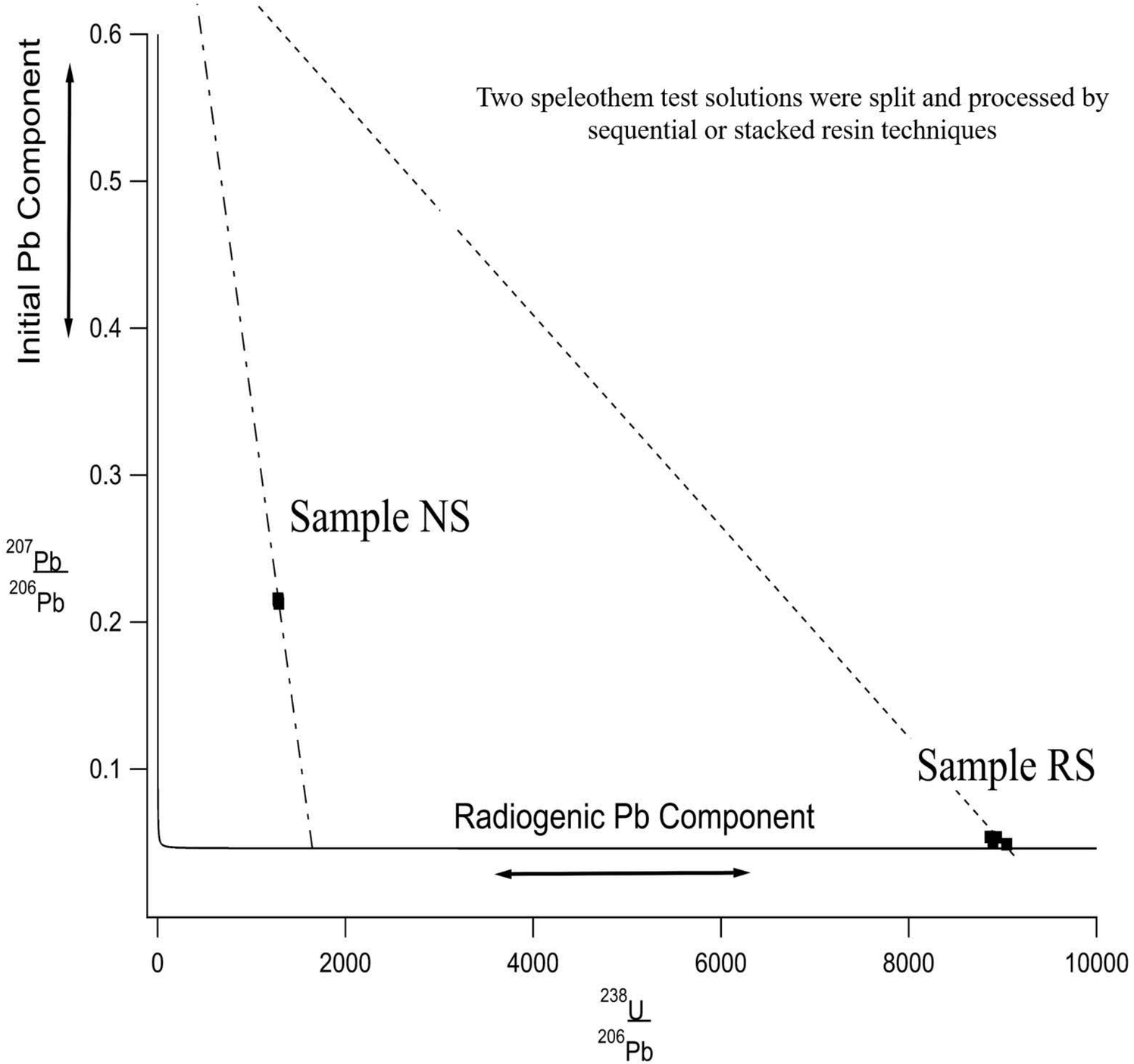
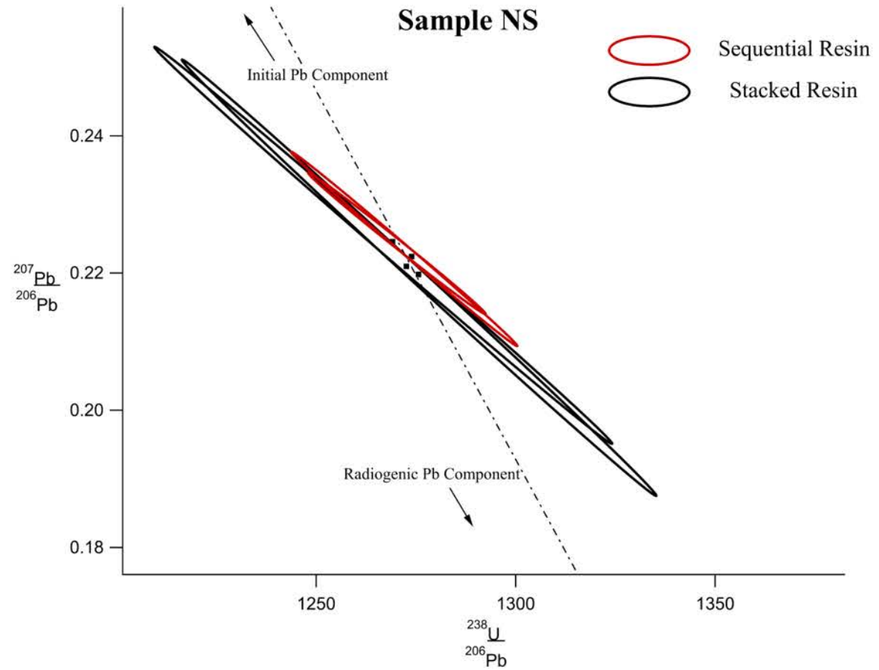

A
0.6M HBr
6M HCl
HCl-HF
Mg
Al
Ca
Pb
Th
U
fraction of element eluted
B
0.6M HBr
6M HCl
HCl-HF
Sr
Ba
La
Pb
Th
U
fraction of element eluted
fraction number

Figure 2


Two speleothem test solutions were split and processed by sequential or stacked resin techniques
Initial Pb Component
Sample NS
Sample RS
Radiogenic Pb Component
207Pb/206Pb
238U/206Pb
0.6
0.5
0.4
0.3
0.2
0.1
0
2000
4000
6000
8000
10000


Sample NS
Sequential Resin
Stacked Resin
Initial Pb Component
Radiogenic Pb Component
207Pb/206Pb
238U/206Pb
0.24
0.22
0.20
0.18
1250
1300
1350

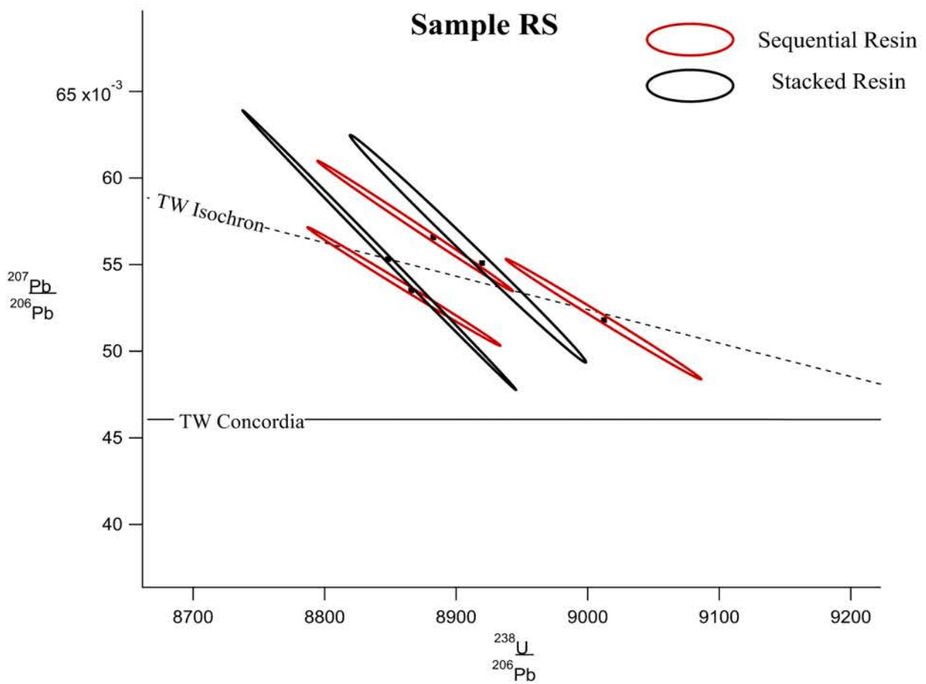

Sample RS
Sequential Resin
Stacked Resin
TW Isochron
TW Concordia
207Pb/206Pb
238U/206Pb
65 x10-3
60
55
50
45
40
8700
8800
8900
9000
9100
9200

Table 1

Click here to download Table: Table 1.pdf

Stacked Resin Protocol for U-Pb Extraction from Calcite

Pack Resins	Below	12 - 15 mm height	Eichrom True + Prefilter resin mixture (1:1) in water[1]
	Above	12 - 15 mm height	AG1-X8 anion resin
Clean Resins			
Removes Pb from AG1-X8 resin	2x	2 ml	6M HCl
Removes U from TRU + Pre-filter mix resin	3x	1 ml	0.1M HCl + 0.1M HF mixture
Removes released Pb (if any) from cleaning TRU + Pre-filter mix	1x	1 ml	6M HCl
Removes remaing HF acid, avoids creating insoluble fluorides	1x	0.1 ml	Water
Conditioning and Dissolution			
Conditions the resins for sample loading	1x (onto resin)	1 ml	0.6M HBr
Dissolve sample residue in HBr, cap, and heat for 1 hour at 100°C	1x (onto sample)	1 ml	0.6M HBr
Load Sample			
Pour the dissolved samples onto the resins[2]			
Wash Out Matrix			
Removes calcite matrix from resins, retains U and Pb[3]	3x	1 ml	0.6M HBr
Pb Collection			
Removes Pb fraction, does not effect U	4x	0.5 ml	6M HCl
U Collection			
Removes U fraction	3x	1 ml	0.1M HCl + 0.1M HF mixture

[1] *Allow resin to settle* [2] *Allow to cool before loading* [3] *More washes for organic rich samples*

Table 2

Sample	Procedure	Weight (mg)	U ppm	Pb ppm	$^{238}U/^{206}Pb$	2σ%	$^{207}Pb/^{206}Pb$	2σ%	ρ
RS1	seq	117.3	32.7	0.003	8882.6	0.64	0.0566	5.02	-0.46
RS2	seq	117.3	32.9	0.003	9012.4	0.64	0.0518	5.21	-0.49
RS3	seq	117.3	32.5	0.003	8865.9	0.64	0.0535	5.01	-0.49
RS4	stack	117.3	32.7	0.003	8919.7	0.97	0.0551	12.45	-0.83
RS5	stack	117.3	32.5	0.003	8848.2	0.99	0.0553	12.37	-0.81
NS1	seq	96.8	1.38	0.002	1269.1	1.38	0.225	3.91	-0.98
NS2	seq	96.8	1.38	0.002	1273.9	1.38	0.222	3.96	-0.98
NS3	stack	96.8	1.38	0.002	1272.6	3.34	0.221	10.33	-0.96
NS4	stack	96.8	1.38	0.002	1275.6	3.34	0.220	10.34	-0.98

	Weight (pg)	2σ%	$^{206}Pb/^{204}Pb$	2σ%	$^{207}Pb/^{204}Pb$	2σ%
Applied Pb Blank - seq	4.5	50	17.05	0.4	15.5	0.4
Applied Pb Blank - stack	12	50	17.05	0.4	15.5	0.4
Applied ^{238}U Blank	5	50				

Highlights for A single-column extraction chemistry for isotope dilution U-Pb dating of carbonates

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- Isotope dilution analyses will likely remain the standard for precision and accuracy in carbonate U-Pb studies.
- The “stacked resin” chromatography reduces analysis time by factor of two.
- Loading samples in dilute HBr did not adversely affect U retention on TRU-resin.
- Larger resin beds increased Pb blank (4.5 pg Pb to 12 pg Pb).
- Protocol increases isotope dilution sample throughput while still utilizing acids and resins common to geochemical labs.