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

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1 1 **A single-column extraction chemistry for isotope**
2 2 **dilution U-Pb dating of carbonate**

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1 **ABSTRACT**

2 U-Pb dating can provide age constraints on carbonate minerals from a wide range of geological
3 settings. A major practical limitation, however, is the need for rapid and efficient extraction of Pb and
4 U from large numbers of typically low-Pb (≤ 10 ng/g) calcite samples, while maintaining low blanks
5 (~10 pg Pb) and high Pb-U yields and purity. Here we describe a well-tested ion exchange procedure
6 able to extract Pb and U from large (up to 200 mg) calcite samples using a single pass over a mini-
7 column filled with small (~0.1 ml) volumes of AG1-X8 anion exchange and Eichrom TRU-resins.
8 This ‘stacked resin’ technique halves the time spent on elemental extractions and provides MC-
9 ICPMS-ready Pb and U fractions in a single day. The method results in considerable savings in
10 laboratory time and allows higher sample throughput, without negative impacts on data quality. It is
11 ideally suited for high-precision U-Pb dating of speleothems where large numbers of samples need to
12 be processed, but it is equally adaptable to calcites from other settings. While not explored as part of
13 this work, the stacked resin technique should also be applicable to other carbonates (dolomite,
14 ankerite, siderite).

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

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18 **1. INTRODUCTION**

19
20 Carbonate minerals are ubiquitous in the geological record, occurring as major or minor components
21 in many rocks and geological settings. Although few carbonates contain >1 ppm of U, the
22 depositional U/Pb ratios are often very high, such that carbonates – in particular calcite and calcite
23 rocks – have been employed in U-Pb and Pb-Pb isotope geochronological studies for decades. This
24 includes studies of fossils and corals (Smith and Farquhar, 1991; Russell, 1995; Getty et al., 2001;
25 Denniston et al., 2008), marine cements (Jones et al., 1995; Becker et al., 2002; Rasbury et al., 2004),
26 marine carbonate concretions (Israelson et al., 1996), lake carbonates (Cole et al., 2004), dolomites
27 (Hoff et al., 1995; Luczaj and Goldstein, 2000), pedogenic carbonate (Winter and Johnson, 1995;
28 Rasbury et al., 2000) and hydrothermal carbonate (DeWolf and Halliday, 1991; Sturchio et al., 1998;
29 Coveney et al., 2000;).

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

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

1 The ‘Achilles heel’ of the carbonate isotope dilution methodology is, of course, the large
2 amount of time and effort involved in extracting U and Pb from the sample matrix for analysis – an
3 issue of particular importance where large numbers of samples are required in order to obtain
4 landscape-scale chronologies in long-lived systems (e.g. Woodhead et al., 2019). Furthermore, while
5 the U-Th technique can produce radiometric ages from single aliquots, U-Pb dating usually requires
6 >5 aliquots to generate robust isochrons (e.g. Engel et al., 2019) and therefore requires substantially
7 more analyses to produce a single age. As a potential method for accelerating U-Pb isotope dilution
8 analyses, here we describe a rapid procedure for the liquid ion exchange resin chromatography
9 (referred to as “extraction chemistry”) of spiked U and Pb from large (up to 200 mg) carbonate
10 samples using a single ion exchange column operated using the readily available HBr, HCl, and HCl-
11 HF acids. The technique combines the advantages of the well-established and widely-used extraction
12 schemes based on AG1-X8 anion resin for Pb (e.g. Manhès et al., 1984; Kamber and Gladu, 2009)
13 and Eichrom TRU-resin for U (e.g. Luo et al., 1997) but explores the consequences of combining the
14 two protocols into one sequential extraction procedure. The two resins are stacked within a single
15 miniature PTFE column of the type used for Pb isotope geochemical studies in many laboratories. In
16 our experiments with large speleothem calcite samples, this combination of resins performed better
17 than other single-column U-Pb extraction techniques (e.g. Krogh 1973; Paquette and Pin, 2001) and
18 produced Pb and U fractions ready for analysis after a single pass and within a single working day.
19 Solution mode ICP-MS results to date indicate that this “stacked resin” column can replace sequential
20 U-Pb extraction procedures that use the same resins in separate columns, thus reducing sample
21 processing times by around 50%.

2. EXPERIMENTAL METHODOLOGY

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

31 The miniature Teflon columns used here were made from PTFE heat-shrinkable tubing (4:1
32 shrinking ratio, Mauritz Communication & Electronics, Germany) prepared to provide a 30 mm long
33 resin reservoir (internal diameter 4 mm) stoppered with two polyethylene frits (Reichert
34 Chemietechnik GmbH, Germany, 30 µm pore size) and a 7 ml acid reservoir (30x15 mm, with an 18
35 mm long taper). Columns were placed within individual column holders (inverted 100 ml
36 polycarbonate beakers with a hole drilled in the base) and mounted on multi-position “lazy-Susan”
37 style stands. Multiple column stands allow up to ~30 samples to be processed simultaneously within a
38 normal sized clean air workstation. Ion exchange resins (AG1-X8, 100-200 mesh; TRU-resin, 100-
39 150 µm; Prefilter resin, 100-150 µm) were obtained from Eichrom Industries (Lisle, Illinois, USA).
40 All resins were batch-cleaned using 6M HCl and water (for AG1-X8), and 6M HCl, 0.1M HCl – 0.1M
41 HF mix and 0.05M HNO₃ (for TRU and Prefilter-resin) prior to use. All acids used in contact with
42 beakers, columns and samples were prepared from highly purified starting reagents: HBr (Seastar
43 Baseline), HCl and HNO₃ (Merck AR, purified in a 2-stage quartz sub-boiling still or a Savillex DST-
44 1000 acid purification system), HF (Merck AR, purified in a four-stage sub-boiling Savillex PFA
45 elbow still). High-purity (18.2 MΩ/cm) water was produced in an Elga Purelab Ultra water
46 purification system. All work was performed in a HEPA filtered exhausting clean air cabinet within a
47 class 350 HEPA-filtered clean room (Australian metric Standard 1386, equivalent to US imperial
48 Class 10,000 standard).

1 Elemental analyses of column fractions were carried out on an Agilent 7700x quadrupole-
2 ICP-MS, following procedures adapted from Kamber et al. (2003). Isotope dilution U-Pb isotopic
3 analyses were conducted using a Nu Instruments ‘Plasma’ multi-collector ICP-MS, with sample
4 uptake via a 0.1 ml/min Glass Expansion MicroMist glass nebulizer and Nu Instruments DSN100
5 desolvation system. Typical instrument sensitivity ranged from 300-400 Volts/ppm. Spiked U
6 fractions dissolved in 2% HNO₃ (~10 ppb U) and corrected for mass bias by internal normalization to
7 the spike-corrected natural ²³⁸U/²³⁵U ratio using the exponential law. Instrumental mass bias in Pb
8 isotope runs was corrected by standard-sample bracketing with SRM981, using the SRM981
9 composition reported in Woodhead (2002). All data reduction was performed using the method of
10 Schmitz and Schoene (2007).

11 12 3. STACKED RESIN COLUMNS

13 The original extraction technique for speleothem U-Pb dating in our laboratory (Woodhead et al.,
14 2006) was a 2-stage, 2-day procedure. On day 1, Pb would be extracted from the sample solution on a
15 12 x 4 mm column of AG1-X8 (100-200 mesh) anion exchange resin, using 0.6M HBr to wash off
16 matrix elements (incl. U) and 6M HCl to elute Pb. On day 2, the U-bearing sample matrix produced
17 on day 1 (dried down overnight) would be redissolved and loaded onto a 12 x 4 mm bed of Eichrom
18 TRU-resin in 1.5M HNO₃, followed by further washing with 1.5M HNO₃ and 3M HCl, and finally the
19 collection of U using a mixed 0.3M HCl-0.1M HF solution. This technique was well suited to the
20 ubiquitous organic impurities in speleothem calcite and produced analysis-ready Pb and U fractions of
21 high purity and yield (>95%), with column blanks of ~5 pg Pb and <5 pg U.

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

28 3.1 Loading and elution of stacked resin columns

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

34 After the addition of 1 ml of 0.6M HBr to the beakers, the spiked calcite samples were capped
35 and briefly heated to re-dissolve the sample. After cooling, the entire sample solution was pipetted
36 onto the column and allowed to sink into the resin bed. Next, the calcite matrix elements were eluted
37 with three further 1 ml washes of 0.6M HBr. Pb and U were then sequentially stripped from the
38 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
39 ml Savillex PFA beakers, and dried.

40 3.2 Elution patterns

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

1 were rapidly removed from the resin during loading in HBr and quantitatively (>99%) eluted after
2 three additional HBr washes. The light rare earth elements (La, Ce, Pr) and Y were also removed at
3 this stage, as was 35-40% of the Th. Elution of Pb occurred almost exclusively during the 6M HCl
4 stage where 98% of all Pb was recovered. The Pb fractions contained small remnants (<0.07%, or 3-
5 30 µg) of Ca, La, Ce, Pr and Y, as well as 4-12% of the Th. Uranium was quantitatively (>99%)
6 eluted in the HCl-HF step, which also contained 50-60% of the Th.

7 3.3 Procedural blanks

8 Pb blanks for the chemical procedure were measured for both the sequential and stacked resin
9 methods by passing 4x 1.0 ml of 0.6M HBr over cleaned (Section 3) AG1-X8 resin or stacked AG1-
10 X8 and Eichrom TRU resins, respectively, in lieu of a sample. Any blank Pb was then collected using
11 4x 0.5 ml of 6M HCl, dried in clean air, redissolved in HNO₃ running solution, and analysed via MC-
12 ICP-MS (Section 2.1). Uranium blanks were produced from a similar but separate experiment from
13 cleaned TRU resin or the combined resin protocol (including all cleaning steps) and collected using
14 3x 1ml of the HCl-HF mixture. Blank amounts were calculated using the largest representative
15 isotopic signal intensities (i.e. ²⁰⁸Pb and ²³⁸U signals) calibrated to standards of known concentration:
16 in this way we can measure approximately 3 pg of U or Pb within ~20% uncertainty. In these
17 experiments all U blank analytes (both stacked and sequential) were below the detection threshold and
18 therefore prescribed a conservative default value of 5 ± 50% pg of ²³⁸U. Five AG1-X8 only eluates
19 (i.e. the sequential resin technique) generated an average total Pb blank of 4.3 ± 3 pg Pb. Six eluates
20 from the stacked resin columns produced an average total Pb blank of 11.8 ± 5 pg; the stacked resin
21 produced on average a Pb blank three times larger than the sequential resin, which is not surprising
22 given the much larger resin bed to which the sample is exposed in the stacked resin. Both techniques
23 produce some variation in Pb blank and this uncertainty must be propagated through the isotope
24 dilution calculations. Therefore, in applying the Pb blank corrections to all isotope dilution results we
25 used conservative values of 4.5 ± 50% (2σ) pg Pb for the sequential resin method and 12 ± 50% pg Pb
26 for stacked resins. This increased Pb blank amount is important only for samples with extremely small
27 Pb contents (e.g. Godeau et al., 2018), such as those with <0.01 ppb of Pb.

28 3.4 Comparison of final U-Pb ratios: stacked resin vs sequential columns

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

45 4. DISCUSSION

1 The elemental elution patterns observed for the stacked resin columns preserved most elution features
2 of the component AG1-X8 and TRU-resins (e.g. Luo et al., 1997; Kamber and Gladu, 2009). The
3 major calcite matrix elements (Ca, Mg), and some key minor components (Sr, Ba, REE-Y), were
4 quickly removed from the column during loading and washing with dilute HBr, without any
5 detectable loss of Pb and U. This implies that TRU-resin tolerated sample loading in HBr without
6 reducing its capacity to retain U. The original protocol employed 4x 1 ml of HBr (incl. loading) which
7 proved adequate for handling ~100 mg calcite samples. For larger samples, or for those particularly
8 rich in organics, additional HBr washes have been applied without obvious effects on Pb-U retention.
9 One major departure from the established elution pattern of TRU-resin loaded with 1.5M HNO₃ (Luo
10 et al., 1997) was the partial loss of Th during the last HBr wash (Fig.1). This was only noticed
11 because the test speleothem used in the elution experiments was doped with Th; typical speleothems
12 have very low Th contents (e.g., Whitehead and Ditchburn., 1999).

13 The elution of Pb from the stacked resin columns was very consistent in all test runs, with
14 ~98% of the Pb recovered after 4x 0.5 ml of 6M HCl: as expected from an AG1-X8-only column. The
15 6M HCl used to collect Pb is well outside the molarity range [0.5 -3M HCl] for U-stripping on the
16 TRU-resin (Paquette and Pin, 2001) and causes no discernible loss in U yield. The Th leakage observe
17 in our experiments with Th-doped calcite solution (Fig. 1) would not present an issue in typical low-
18 Th speleothems. In all experiments the Pb fractions were very pure and well-suited to MC-ICPMS
19 analysis: <0.1% of Ca and <1% of the other calcite relevant elements were found in the HCl fractions.
20 In absolute terms, the combined HCl fractions from a stacked resin column loaded with 100 mg
21 calcite contained no more than 30 µg of matrix elements. Total Pb signals and peak shapes observed
22 in the Nu Plasma were comparable with those of pure SRM981 Pb, implying that the stacked resin Pb
23 fraction purity produced no degraded peak shape artefacts.

24 Elution of U from the stacked resin column was also very consistent. Over 99% of U removal
25 occurred during the 0.3M HCl + 0.1M HF step of the elution sequence (Fig.1). Virtually no matrix
26 elements (<0.1% of Ca and <1% of minor matrix elements, e.g. Sr) were eluted at this stage and, as
27 mentioned above, co-elution of Th observed in the column tests would not be an issue for typical
28 speleothems. Experience gained during routine operation of the stacked resin columns suggests the
29 following measures to be beneficial: (i) mixing the TRU-resin with Prefilter-resin helps to suppress
30 organic material leaking from the TRU resin (such leakage is well-documented for Eichrom Sr-resin,
31 e.g. Paquette and Pin, 2001); and (ii) drying a drop of conc. HNO₃ onto the U extracts improves re-
32 dissolution in the 2% HNO₃ run solution.

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

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2 **5. CONCLUSIONS**
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6 4 The new stacked resin technique is a simple and effective procedure for extracting clean Pb and U
7 5 fractions from large calcite samples. These fractions run well on a MC-ICPMS, producing consistent
8 6 U-Pb results and ages. So far the technique was only tested for a calcite matrix, and it is not known if
9 7 the technique can handle other matrix types.

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11 8 Our test results suggest the new stacked resin technique should perform well for Ca and Mg
12 9 carbonates, as well as for witherite (BaCO_3) and strontianite (SrCO_3). As the tests did not include Fe,
13 10 the performance for Fe-bearing carbonates (siderite, ankerite) on the mixed resin bed is unclear. Iron
14 11 is not strongly extracted onto AG1-X8 in dilute HBr and strong HCl, and should thus elute quickly
15 12 from this resin, like Ca and Mg. However, we are not aware of data relevant to Fe uptake on TRU-
16 13 resin in dilute HBr, and thus this resin's ability to extract U during sample loading and washing in
17 14 dilute HBr. This will be an area for further work which will establish if the new stacked resin
18 15 technique can handle all major carbonate types. This would provide a convenient separation technique
19 16 for applications of U-Pb dating to a wide range of carbonates.
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26 **19 Acknowledgments**
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36 25 Figure 1) Elution patterns of Pb, Th, U, Ca, Al, Mg, Sr, Ba and La in a U-Pb doped speleothem calcite
37 26 samples (0.1 g of solid) from a stacked bed of Eichrom TRU (below) and AG1-X8 anion resin
38 27 (above) using dilute HBr, strong HCl and dilute HCl/HF mix. Elution peak heights were normalized
39 28 to 100% of element loaded. Stacking the two resins into a single column preserved the retention
40 29 quality of each composite resin. The dominant matrix element, Ca, as well as Mg-Al (panel A) and
41 30 trace elements Sr, Ba, La (panel B), were eluted in dilute HBr (left). Lead (centre) and U (right) were
42 31 only eluted in 6M HCl and HCl-HF mix, respectively. Thorium showed a bimodal elution across all
43 32 three acids; in practice, this is unlikely to be a problem as carbonates tend to have very low Th
44 33 contents. Note that x-axis shows test fraction numbers, not acid volume; the actual recipe adopted in
45 34 this laboratory is shown in Table 1.
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49 35 Figure 2) U-Pb isotopic results from doped-speleothem analyses using both the sequential resin (red)
50 36 and "stacked resin" (black) techniques. Isotopic ratios are displayed upon the Tera-Wasserburg (T-W)
51 37 Concordia commonly used for young, Pb-rich speleothems (see Woodhead et al., 2012). Two
52 38 different, isotopically homogenous test solutions were evenly split and processed by the two
53 39 techniques. Isotopic ratios were produced after applying a Pb blank of 4.5 ± 2.25 pg for sequential
54 40 resins and 12 ± 6 pg for the new stacked resin technique. U-Pb results from both techniques were very
55 41 similar, though with a systematic increase in uncertainty for stacked resin results resulting from the
56 42 larger Pb blank.
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59 43 Table 1) The proposed "stacked resin" protocol for U-Pb isotope dilution analyses of large carbonates.
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1 Table 2) Isotopic results from isotope dilution U-Pb solution-mode ICP-MS analyses using both the
2 sequential resin (seq) and proposed “stacked resin” (stack) techniques. Errors are shown as 2σ percent
3 values.

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Figure 1

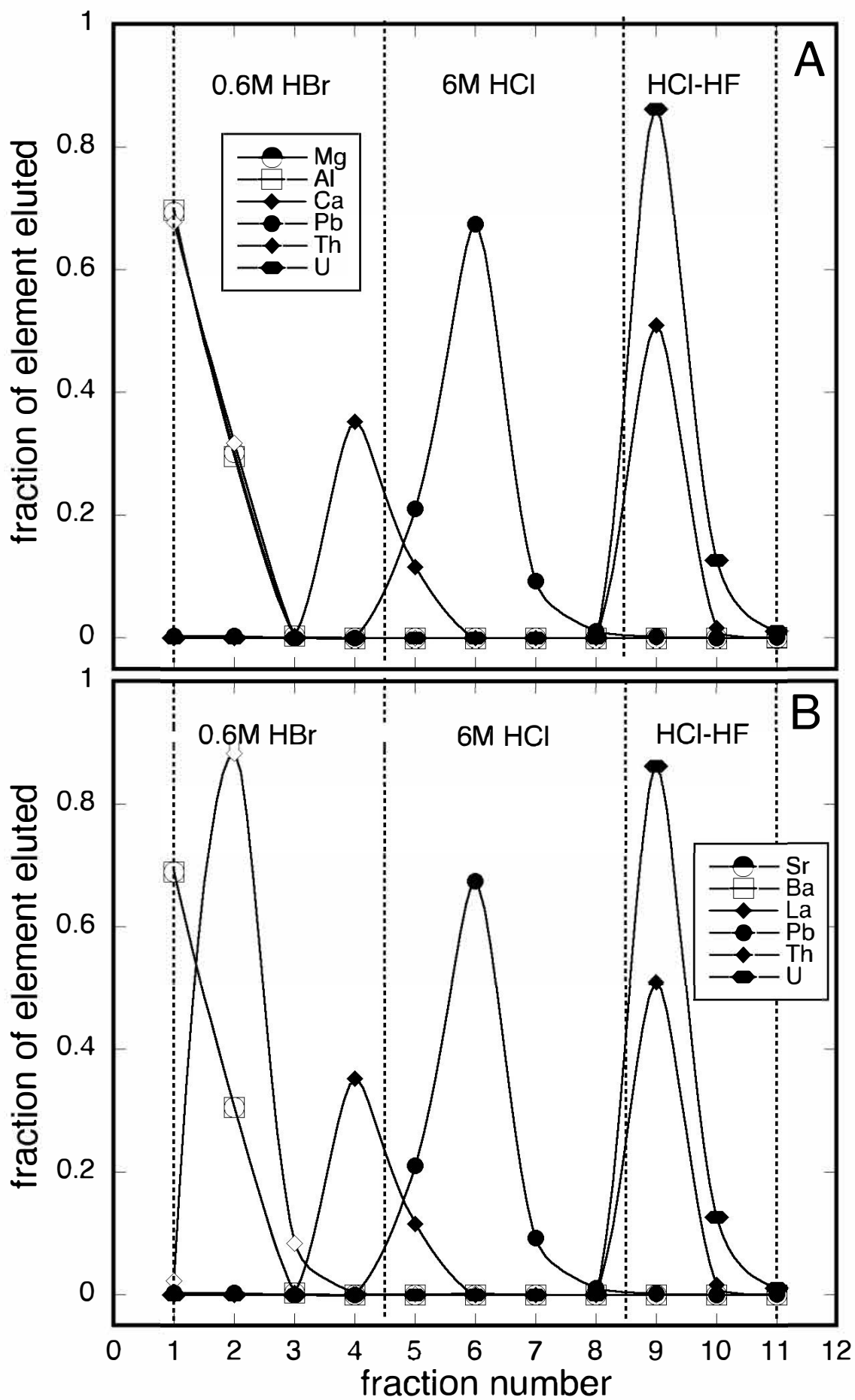


Figure 2

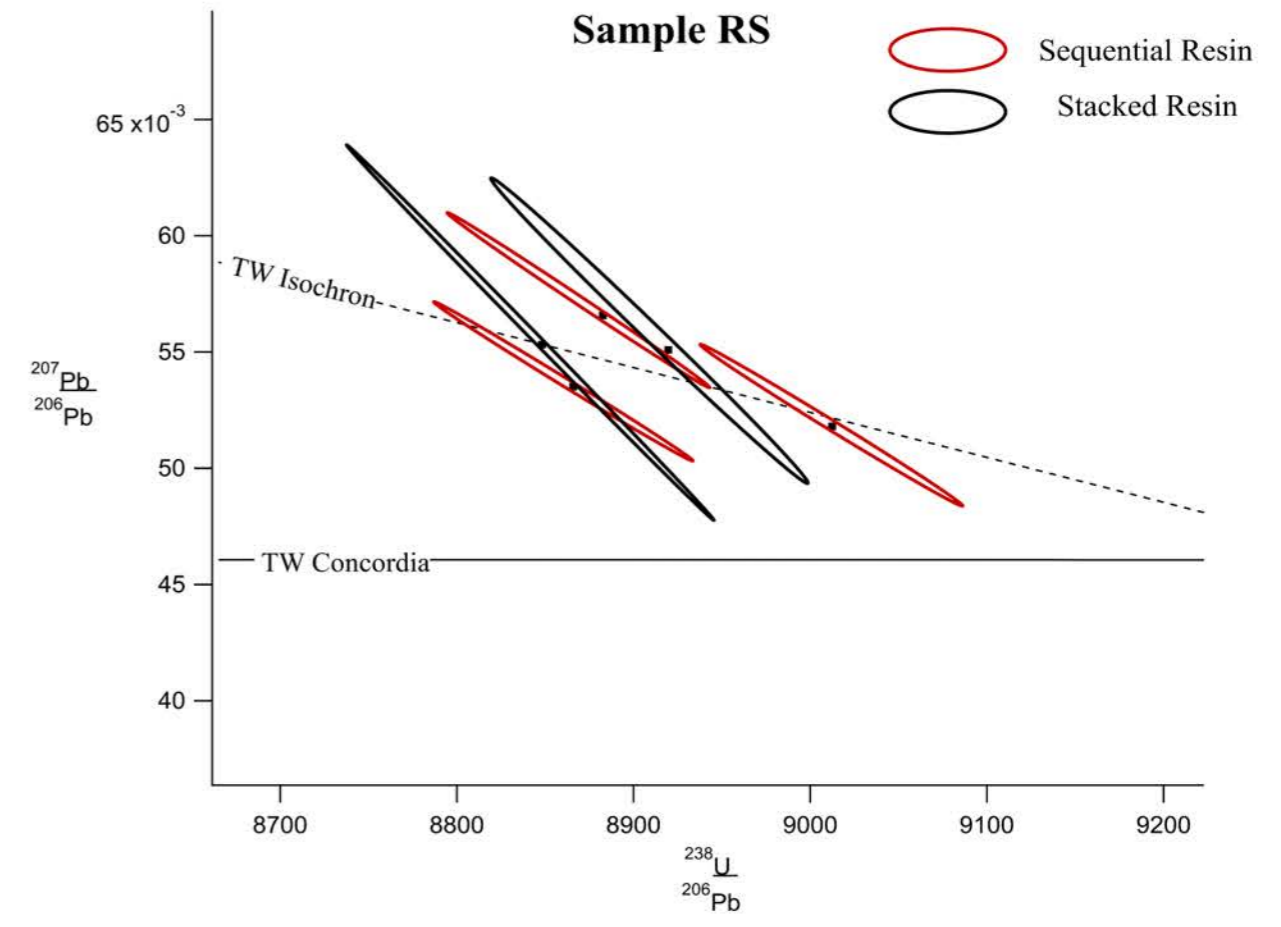
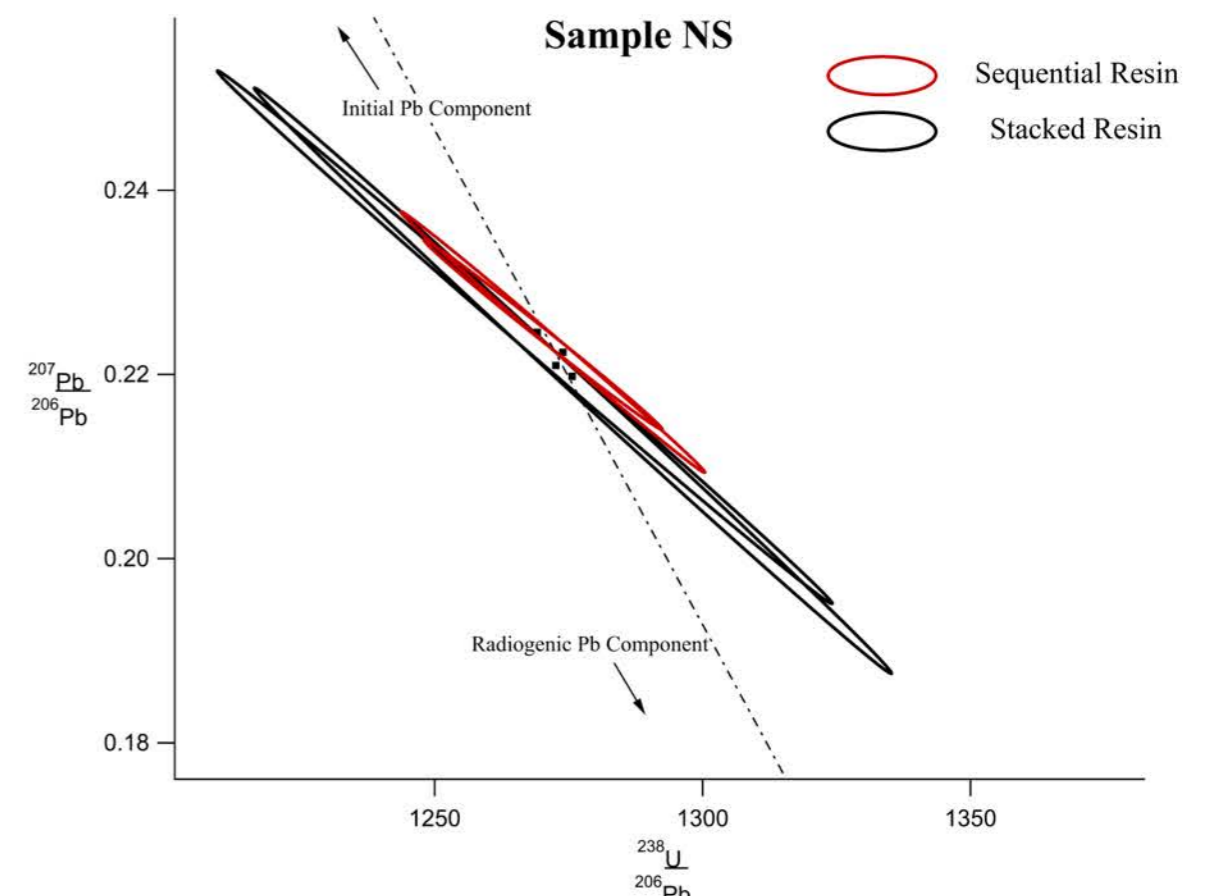
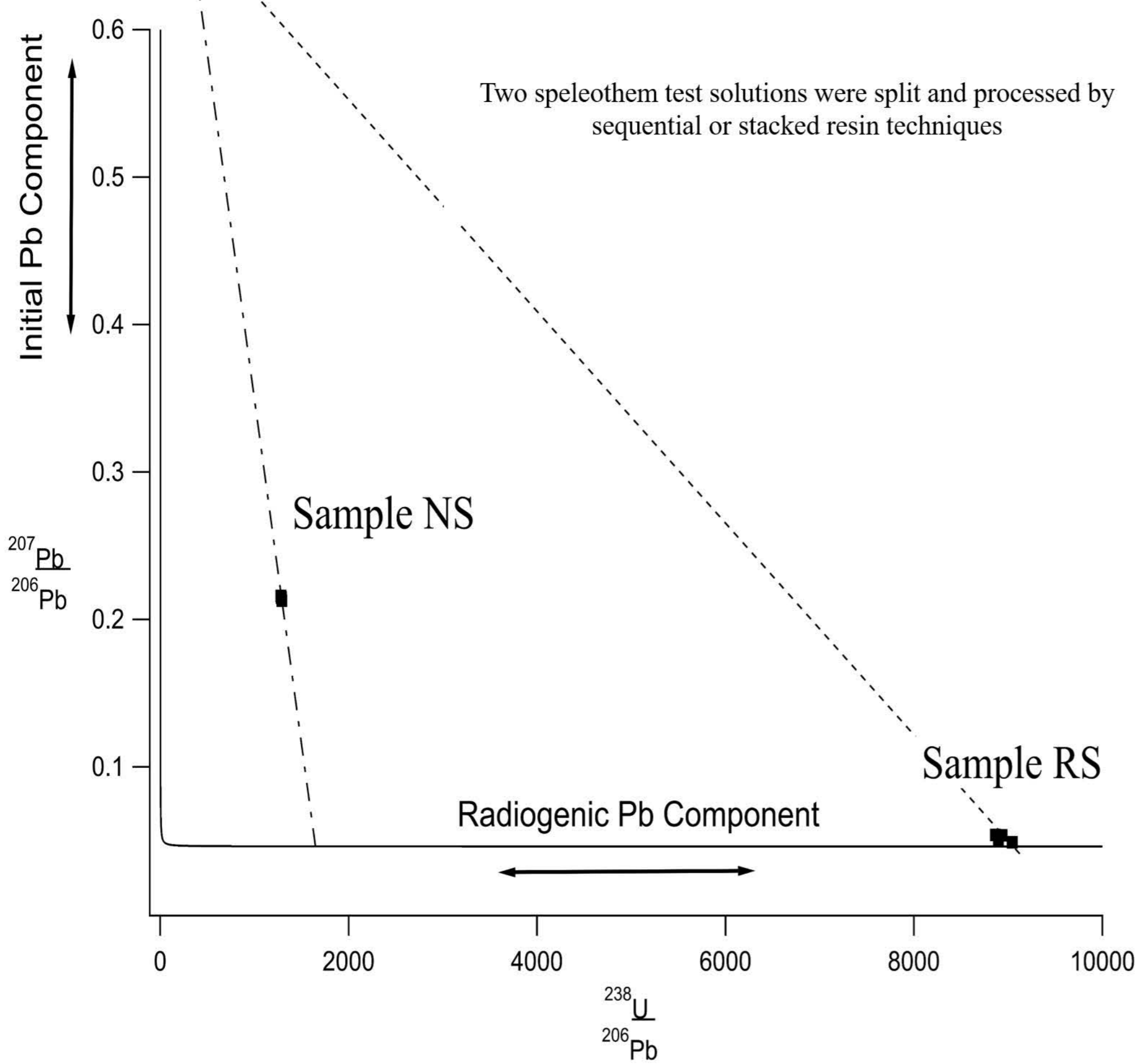


Table 1 Click here to download Table: Table 1.pdf			
Stacked Resin Protocol for U-Pb Extraction from Calcite			
Pack Resins	Below	12 - 15 mm height	Eichrom True + Prefilter resin mixture (1:1) in water ¹
	Above	12 - 15 mm height	AG1-X8 anion resin
Clean Resins			
Removes Pb from AG1-X8 resin	2x	2 ml	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 remaining 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			

Sample	Procedure	Weight (mg)	U ppm	Pb ppm	$^{238}\text{U}/^{206}\text{Pb}$	2 σ %	$^{207}\text{Pb}/^{206}\text{Pb}$	2 σ %	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)	2 σ %	$^{206}\text{Pb}/^{204}\text{Pb}$	2 σ %	$^{207}\text{Pb}/^{204}\text{Pb}$	2 σ %		
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.