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Uranium-series dating of gypsum speleothems: methodology and examples.

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Abstract:

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The analytical problems of dating gypsum speleothems with the U-series technique are reviewed. Gypsum speleothems are, in general, very low in U content, challenging the limits of detection methods. Various approaches to dissolving gypsum and isolation of actinides from the matrix include ion-pairing dissolution with magnesium salts and using nitric acid. The most precise dating technique is Thermal Ionization Mass Spectrometry (TIMS), combined with Fe(OH)₃ scavenging and anionic exchange chromatography. Less satisfactory, but much quicker, is direct retention of actinides from HNO₃ by means of TRU resin and MC-ICP-MS detection. We have tested these methods on gypsum speleothems from the Sorbas karst in Spain and from the Naica caves in Mexico.

Keywords: *Uranium series dating, gypsum, cave, methodology*

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INTRODUCTION

Uranium-series dating of speleothems is standard procedure in speleological science and in palaeoclimatic research (Ford & Williams, 2007; Ivanovich & Harmon, 1982). Carbonate speleothems are widespread in space and time and have generally enough uranium to allow determination of isotopic ratios of the element itself and its radiogenic daughters. In principle, all spelean secondary minerals can be used for dating, provided that their initial isotopic composition is known and that they contain enough actinides for reliable determination. In spite of this, most of the attention has been on calcite speleothems, for which there are numerous standard procedures available.

Gypsum speleothems are a rarely used, if they can

be successfully dated, a potentially excellent source of palaeoenvironmental and geomorphic information. For instance, many gypsum karsts, like *Sorbas* in southern Spain (Calaforra, 1998), the *Gypsum area* near Bologna in Italy (Forti & Rossi, 2003) and the New Mexico gypsum karst (Calaforra & Forti, 1994) contain gypsum speleothems (Klimchouk *et al.*, 1997). There is also a great variability in gypsum speleothems with regards to their size, external shape, internal structure and development. Davis (2000) reports from Lechuguilla Cave (New Mexico, USA) gypsum stalactites, columns, hairs, "Candelieres" (up to 6 m long), flowers and needles (>1 m long). Korshunov and Shavrina (1998) focus on cryogenic gypsum speleothems and describe gypsum powder (formed after ice sublimation), gypsum yozh (with spherical, hemispherical, flat or amorphous shape, with development closely related to clay deposits), and spherical porous yozh with an unclear genesis. Gypsum trays have been reported by Calaforra & Forti (1994) and Doran & Hill (1998) as clusters of popcorn or grape coralloids ending in a flat surface. Gypsum nests has been described by Maltsev (1997) at Geophysicheskaya Cave, Turkmenistan, as a funnel-shaped mass of thousands of oriented gypsum needles with a hollow interior. Gypsum crusts in lava tubes have recently been dated by U-series technique (Dillon, 2009). Also, northern caves, even in relatively cold and wet regions like north Norway, contain evaporitic gypsum crusts (Lauritzen, 2002; Onac & Lauritzen, 1995). It is evident that dating of these various cave minerals can give valuable information

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for understanding their formation and of the environment they were formed in. The purpose of this paper is to give a review of various methods that are practically useful for bringing gypsum into solution in manageable volumes, and of isolation and separation techniques for actinides and their measurement by radiometric and mass spectrometric techniques.

PRACTICAL ASPECTS OF U- SERIES DATING

Detection of actinides for U-series dating is at present based on wet chemistry where the sample is decomposed in sufficient amount to yield detectable levels of the analyte. In general, the amount of sample required, the choice of decomposition method and the volume and further handling of the resulting solution depend on the uranium content and mineralogy of the sample (Bock, 1979; Novozamsky *et al.*, 1995).

For dating of carbonate speleothems, the mineral is brought into solution by means of acids (HCl, HNO₃), which means that "solubility" can theoretically attain 10 – 15 moles L⁻¹, so that large amounts of sample in any case can be dissolved in manageable volumes of liquid. The amount of sample required depends on its U content and on the technique used. Modern techniques have extremely low detection limits compared to the classic α -particle counting. As spelean calcite commonly contains 0.1 - 1 ppm U, 5 – 20 g samples were prepared for α -particle counting, 0.5 – 2 g for TIMS (Thermal Ionization Mass Spectrometry), and 0.05 - 0.2 g for ICP-MS (Ionization Coupled Plasma - Mass Spectrometry) analyses. With the latter two techniques, sample size and reagent volumes are no problem when it comes to carbonates. Isolation of actinides from the concentrated [Ca²⁺] solutions involves destruction of potential organic chelators either by dry ignition (600 °C, prior to dissolution) or wet oxidation with HClO₄ or H₂O₂, followed by ferric hydroxide scavenging. Actinides are then separated from Fe³⁺ and each other by ion exchange before determination. However, gypsum speleothems poses additional challenges rooted in their solubility and U content. First, in gypsum speleothems, the routinely low U content makes that sample size vs. volume of solute required, which are manageable for carbonates, become cumbersome. Second, the isolation and separation of actinides considering the large volumes of solute required may pose additional problems. In the U-series dating laboratory in Bergen we have tested various approaches to these issues.

The solubility of gypsum in water

When it comes to actinide extraction from gypsum (CaSO₄·2H₂O) speleothems, a problem of its limited solubility arises for two reasons. First, gypsum speleothems often have very low uranium content, which is probably caused by the correspondingly low ion pairing affinity between UO₂²⁺ and SO₄²⁻, causing UO₂²⁺ to stay in solution rather than being adsorbed on growing gypsum surfaces. Typically, gypsum crystals, like those in the Naica caves, contain U at the ppb (10⁻⁹) level. Second, the solubility of gypsum in water is limited to 2.4 g L⁻¹ (CRC Handbook of

Chemistry and Physics, 1970) and has a maximum at about +40 °C (Figure 1). In order to get sufficient intensity of the relevant atomic masses, like ²³⁰Th, - the isotope which measures the actual age and is often the minimum factor - gypsum amounts of up to 10 g or more must be dissolved. For pure water, this would require some 4.5 – 5 L in order to bring it into complete solution. For a TIMS sample, which is generally larger, and in particular, for α -particle counting technique, the resulting volumes would not be practically manageable.

Enhanced gypsum solubility by ion pairing

In general, gypsum solubility increases with solute content (e.g. brines) (Klimchouk, 2000). The effect is largely governed by ion pairing of foreign cations and anions with SO₄²⁻ and Ca²⁺, respectively. This lowers the activity of these ions so that more gypsum can dissolve. The effect is formidable, in particular with magnesium chloride and nitrate (Figure 1). For instance, in a 2 mole L⁻¹ solution of Mg(NO₃)₂, the solubility of gypsum is raised from 2.4 g L⁻¹ to 14 g L⁻¹, an increase of 580%. This means that 10 g gypsum can dissolve in a volume of 720 mL. With the addition of large amounts of salts to the sample, there is a danger of contamination, so that *pro analysi* or purer qualities (*Suprapur*[®]) must in any case be pre-cleaned for actinides by adjusting pH and using an appropriate ion exchanger, either in column or batch mode.

Yield experiments in gypsum dissolution

In a study of gypsum balls from Sorbas caves (southern Spain), carried out in 1999-2000 at Bergen University, we tested the addition of MgCl₂ on gypsum solubility (Figure 2). A practical optimum was found using 50 g MgCl₂·6H₂O in 450 mL H₂O (0.55 mol L⁻¹), which could dissolve 7 g gypsum speleothem. Beyond this ratio, increasing the amount of MgCl₂·6H₂O would lead to the precipitation of epsomite (MgSO₄·7H₂O). In a neutral or only slightly acidic solution, actinides - and Th in particular - would plate out on insoluble particles and on the walls of glassware. In order to retain Th in solution, pH needs to be below ~1. Some gypsum speleothems contain detrital components, like air-borne dust or floodwater silt, that are not relevant to the age of the speleothem formation (often much older). Strong acid could in principle attack these particles, which are most likely carbonate and clay, and thereby contaminate the digest with non-authigenic U and Th. This is linked to the well-established allogenic ²³⁰Th contamination problem of so-called "dirty" calcites (Przybyłowicz *et al.*, 1991; Schwarcz, 1980; Schwarcz & Latham, 1989). It is therefore necessary to find a compromise between risking authigenic ²³⁰Th to plate out (at high pH) and contamination of non-authigenic ²³⁰Th to dissolve from detrital surfaces (at low pH). Hence, a series of tests was performed on the MgCl₂ procedure to investigate the effects of pH on the resulting ages and on the chemical yield of U and Th through the procedure. At the time when these experiments were done, we

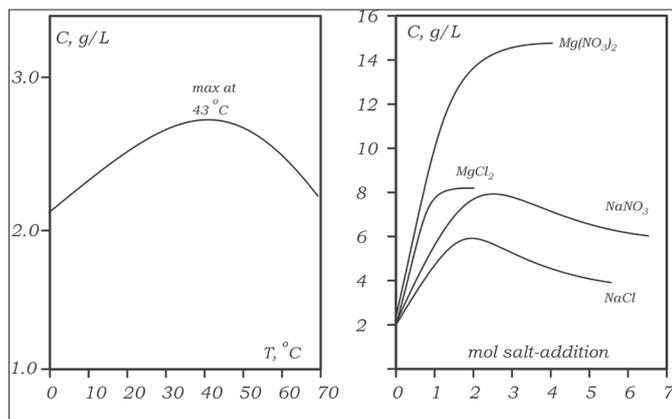


Fig. 1. Solubility of gypsum. Left: Gypsum solubility in pure water as a function of temperature. Right: Gypsum solubility as a function of concentration of other salts. Magnesium chloride and nitrate have a very strong effect on gypsum solubility. (Modified after Klimchouk, 2000)

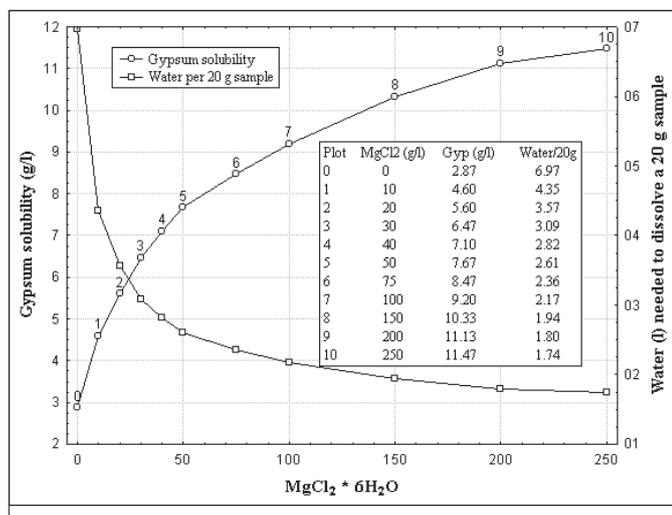


Fig. 2. Solubility of gypsum in solution with different concentrations of MgCl₂ · 6H₂O. Further experiments with speleothems used 50 g of MgCl₂ · 6H₂O per 7g of gypsum sample.

found it convenient to assess chemical yields by using α -particle counting which measures the total recovery from the chemistry. Two different speleothem samples (from Sorbas) having ages of approximately 10 and 20 kyr respectively, were chosen for testing. They were mechanically cleaned, and each was crushed to a fine powder and homogenized. Two different protocols were followed (Figure 3): in procedure A, aliquots of the powdered samples were dissolved in 0.55 M MgCl₂ to which HCl had been added to pH<1, and then filtered. In procedure B, acidification was done after dissolution and filtration. Spike (²²⁸Th/²³²U) was added to the solution during dissolution. Chemical isolation followed the normal protocol for α -particle counting (Gascoyne, 1980), where actinides were scavenged on Fe(OH)₃, Fe³⁺ removed by ether extraction, then U and Th were separated and purified by anion exchange chromatography. U and Th were electroplated on steel disks and counted separately. Further experiments tried acidification to pH=1.5 and pH=2.0. The chemical yields from these experiments are shown in Figure 4.

U yields are generally higher than Th yields, as is common in all preparation procedures. Both U and Th yields were not significantly different from average

yields of more than 3,000 carbonate analyses in this laboratory; they are always variable due to sample and operator variability. There was, however, a significant effect on Th yields, where acidification after filtration gave more variable and often quite low yields. Using HCl to lower the pH to 1.5 during gypsum dissolution gave the most consistent results and is therefore the preferred approach (Figure 4).

The low chemical yields also affect the resulting ages. Due to lower yields, counting statistics are worse, giving larger errors (Figure 5). Acidification prior to, or after, filtration did not change the radiometric ages of each sample, but dates become more precise with high yields. Due to this effect, the two samples could only be chronologically distinguished when the samples were dissolved at pH=1.5. A similar effect was found when dating a gypsum ball from Sorbas in southern Spain (Figure 6). The ball is some 10 cm in diameter and consists of alternating pure white and detrital (grey) bands due to episodes of flooding or aeolian dust being adsorbed onto the speleothem. Growth bands imply that the sample grew radially (Figure 6c). Two very large subsamples had to be taken for accommodating the low sensitivity of alpha dating, yielding overlapping ages, but with inverted stratigraphic distribution (Figure 7). Re-sampling of the other half of the gypsum ball with much smaller subsamples and TIMS dating (see below) yielded much more precise dates in correct stratigraphic order (Figure 7). This example also demonstrates the need for repeated dating along sequences with a precise technique so that chronological trends can be tested; single dates can be deviant for various reasons of random subsample properties and operator skill.

Application to TIMS techniques

When we adapted this technique for application to TIMS, we have tested two different dissolution protocols: (1) using MgCl₂ · 6H₂O (16 g was required to dissolve ~2 g of gypsum in 200 mL H₂O) and (2) using 2M Mg(NO₃)₂ at pH 1.5 (which has about the double dissolution capacity for gypsum than 0.55M MgCl₂). In both cases the samples were spiked (²²⁹Th, ²³³U and ²³⁶U) and acidified by addition of a few drops of Suprapur[®] HNO₃. The dissolution took place at a controlled temperature of 25°C. Further purification involved standard procedures (Lauritzen & Lundberg, 1999) of Fe(OH)₃ scavenging, followed by the separation of Fe³⁺ by ion exchange (nitrate eluant). Actinides were further separated on anion exchange columns in HCl and HBr media before being dissolved in H₃PO₄ or HNO₃ and loaded on zone-refined Re filaments prior to measurements.

TIMS detection

TIMS measurements were done on a Finnigan MAT 262 RPQ instrument with the ion counter in dynamic mode, at the Department of Earth Science, Bergen University. We have tried several methods of ionization. U can be run as a metal without addition or with graphite on the filament, or as oxide from a silica bed. Th is always run as a metal from a graphite

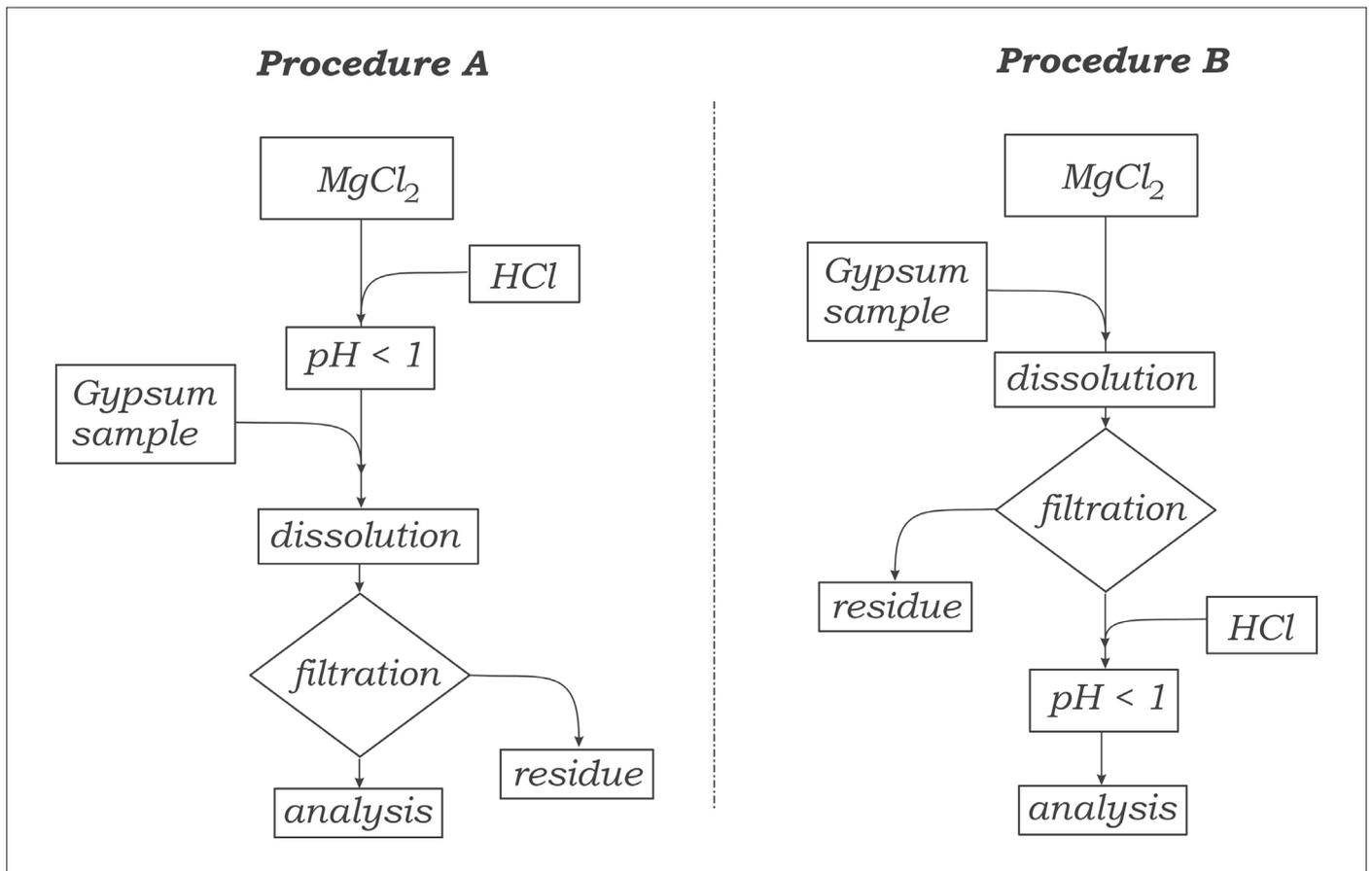


Fig. 3. Two different laboratory procedures tested to optimize the dissolution process for gypsum samples. They differ in the moment when conc. HCl is added to the solution.

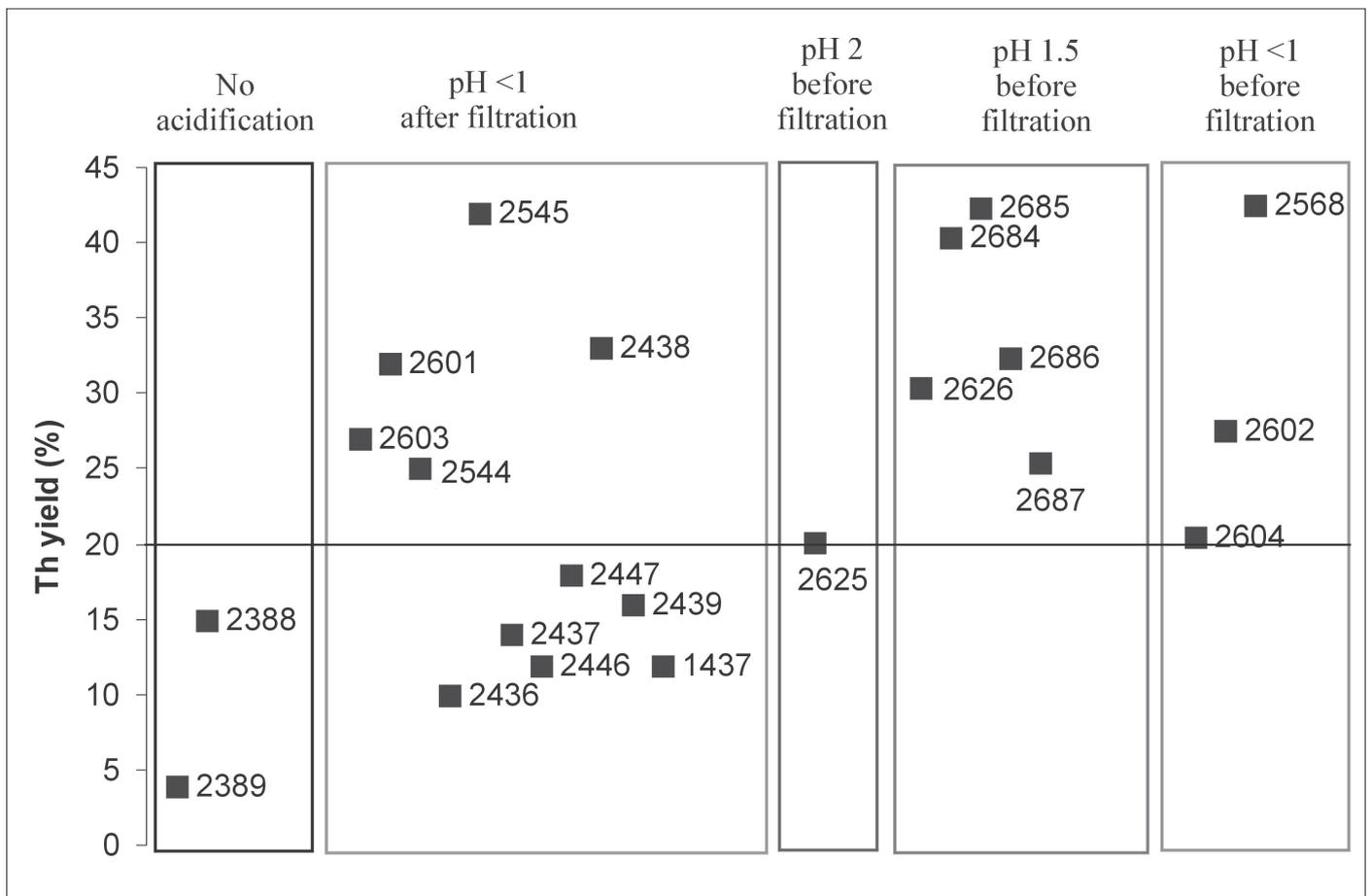


Fig. 4. Effect of different chemical situations on the Th yields. See text for discussion. Numbers refer to the Bergen Quaternary U-series lab's alpha counting journal.

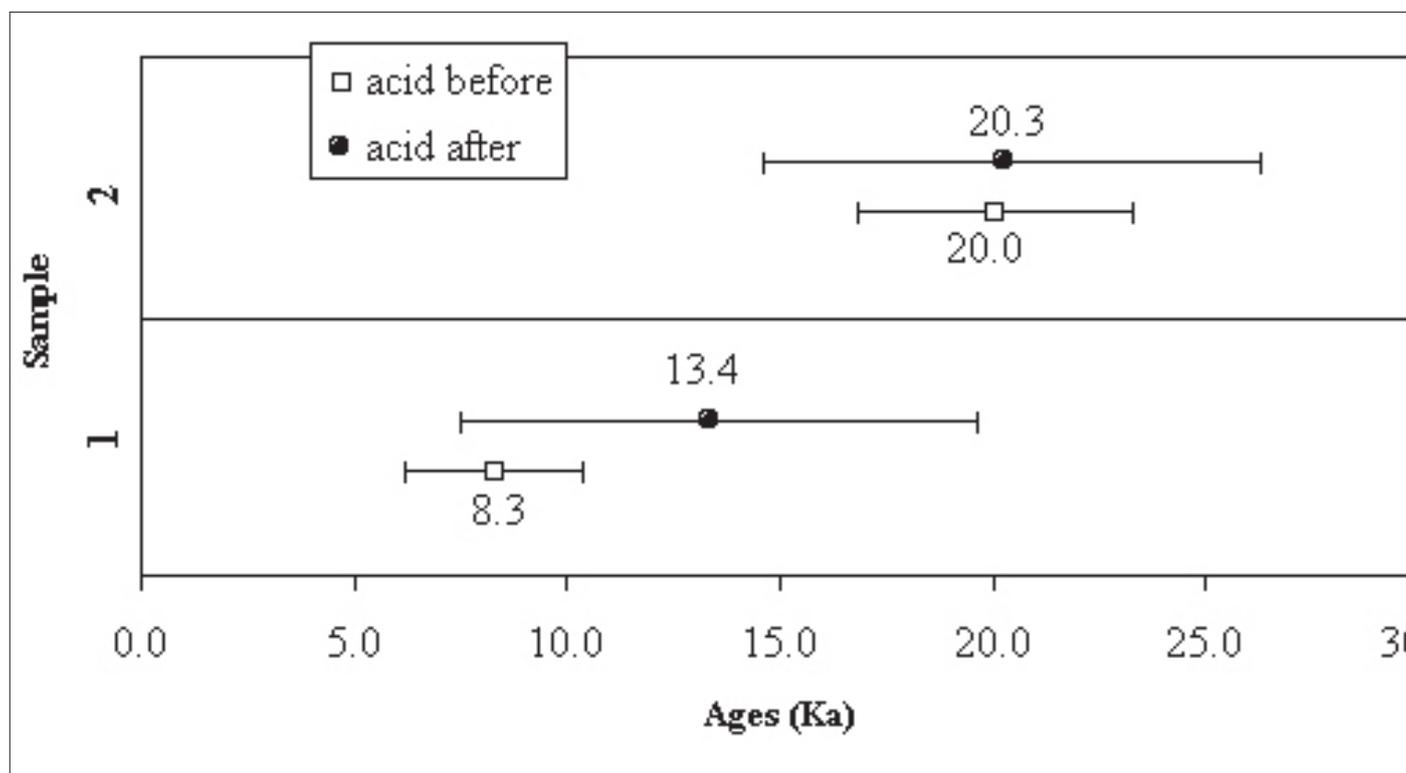


Fig. 5. Comparison of the ages obtained for two different gypsum samples (1 and 2) and two acid treatments (before and after filtering), i.e. four age determinations. When acid is added after dissolving, the errors become so big that the ages are not statistically different; but when acid is added before dissolving, the errors are smaller and the ages can be distinguished.

bed due to the extremely low volatility of its oxide. U was run at 1650 – 1775 °C; Th at 1750 – 1850 °C in separate runs. Mass abundances of ^{236}U , ^{235}U , ^{234}U , ^{233}U , ^{229}Th , ^{230}Th , ^{232}Th were measured and converted to mass ratios. The first protocol worked satisfactorily on one Naica sample with about 4 ppb U (Lauritzen *et al.*, 2008) with reproducibilities of 0.26% for $^{234}\text{U}/^{238}\text{U}$ and 1.62% for $^{230}\text{Th}/^{234}\text{U}$ (2σ). The second protocol was successfully tested for the outer part of the gypsum crystal from Espadas Cave (Table 1), with ~0.2 ppm ^{238}U . In this case the reproducibility was ~0.2% for $^{234}\text{U}/^{238}\text{U}$ and 1.2% for $^{230}\text{Th}/^{234}\text{U}$ (2σ). Blank tests were done to check for contamination on both MgCl_2 and $\text{Mg}(\text{NO}_3)_2$ and they showed no ^{230}Th . However, considering the very low U concentrations of gypsum samples, blank tests must be routinely done.

Application to ICP-MS techniques

ICP-MS has an even lower detection limit than TIMS and, in order to minimize contamination from reagents, we have simplified the procedures further. First, introduction of new, actinide-specific resins (Peterson *et al.*, 2007; Yang, 2009), like the Eichrom TRU resin, simplify the chemical workup procedure. The TRU resin contains a phosphate/phosphine-based liquid ion exchanger supported on an inert substrate (Amberlite XAD-7). Actinides are selectively retained directly from 1M HNO_3 . Matrix ions (SO_4^{2-} and Ca^{2+}) can then be washed out with 1M HNO_3 , followed by conversion of the eluant from a nitrate to a chloride base and subsequent elution of actinides by dilute HCl/HF . This procedure is recommended by Hellstrom (2003) and we have adapted it from him. In order to avoid both the scavenger step and

addition of large amounts of magnesium salts, we tested the solubility of gypsum directly in 1M HNO_3 and found that up to 10 g gypsum can be dissolved in 600 mL acid. After spiking and equilibration, the actinides can be retained on a small column. The only drawback is the relatively large volume that needs to be passed through the column, which is a time-consuming process. (Also, we do not know if the retention is optimal with such large amount of eluant). After washing and elution, the solution was dried down with HNO_3 and then dissolved in 2% HNO_3 for analysis.

ICP-MS detection

Isotopic measurements were performed on a Nu Plasma HR multicollector ICP-MS with a U-Pb collector block at the Department of Geology, University of Oslo. Analyses were done in dry plasma using a DSN-100 desolvating nebuliser with a sample uptake rate of 0.1 mL/min. Uranium and thorium were dissolved in 2% v/v HNO_3 prior to analysis.

The mixed uranium and thorium solution was analysed in two separate procedures. First, Uranium isotopes with mass 236, 235, 234 were determined in ion counters and Thorium with mass 232 in a Faraday cup. The second procedure measures Thorium mass 229 and 230 in an ion counter. Tailing from 238 and 232 was corrected by measuring half masses and using an exponential interpolation. Fractionation of the instrument has been determined on a daily basis by analysing mass 235 and 238 of a natural uranium solution in Faraday cups using $^{238}\text{U}/^{235}\text{U} = 137.88$. Early attempts on measuring fractionation by analysing $^{236}\text{U}/^{233}\text{U}$ were abandoned due to problems

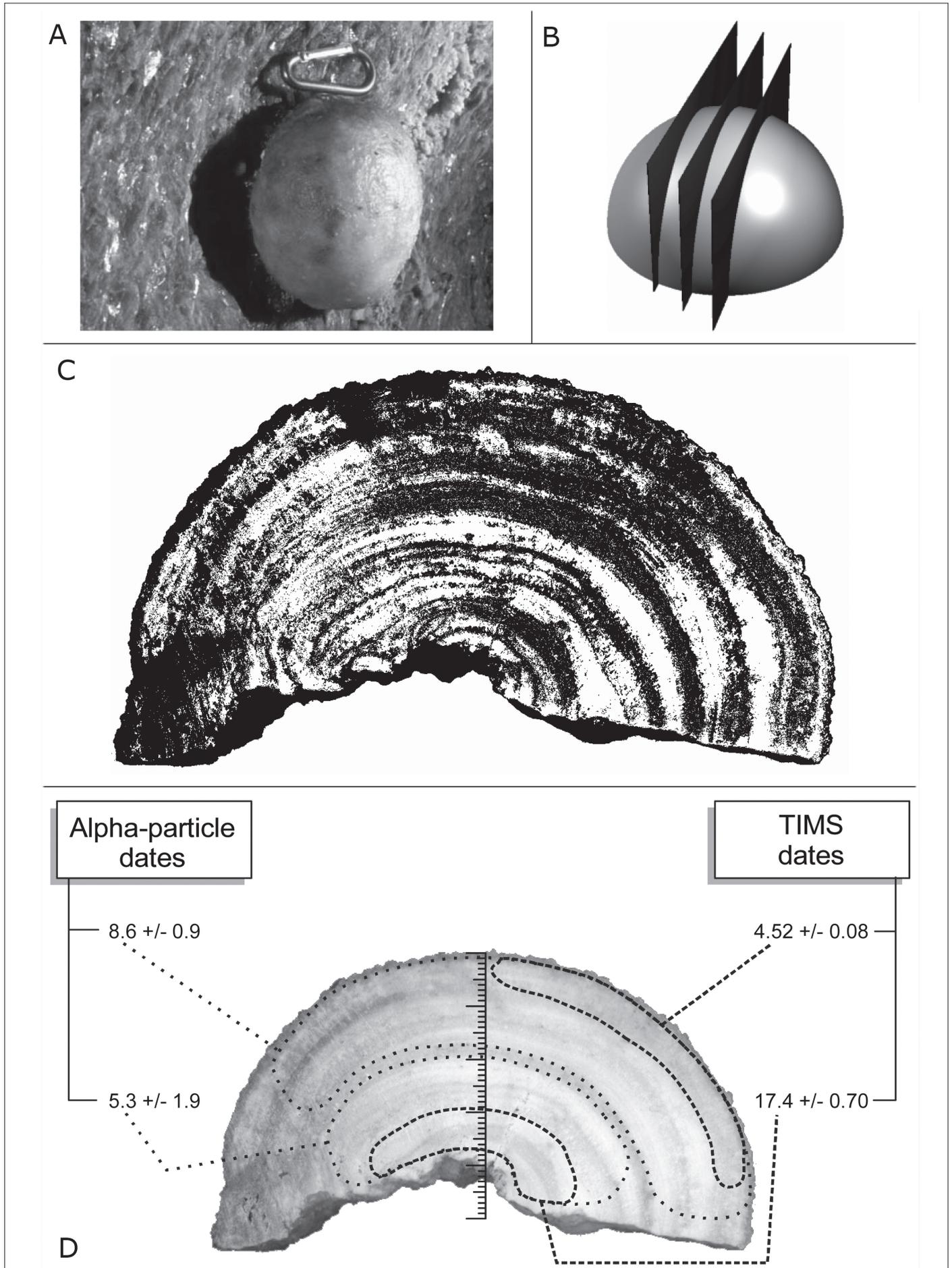


Fig. 6. Gypsum ball from the Sorbas karst, southern Spain. A) photo of in situ ball on the cave wall. B) section done for analysis. C) Structure of layers inside the speleothem. Dark bands contain dust, while lighter ones are made of more pure gypsum. D) Ages obtained with alpha particle spectrometry and mass spectrometry for the same speleothem.

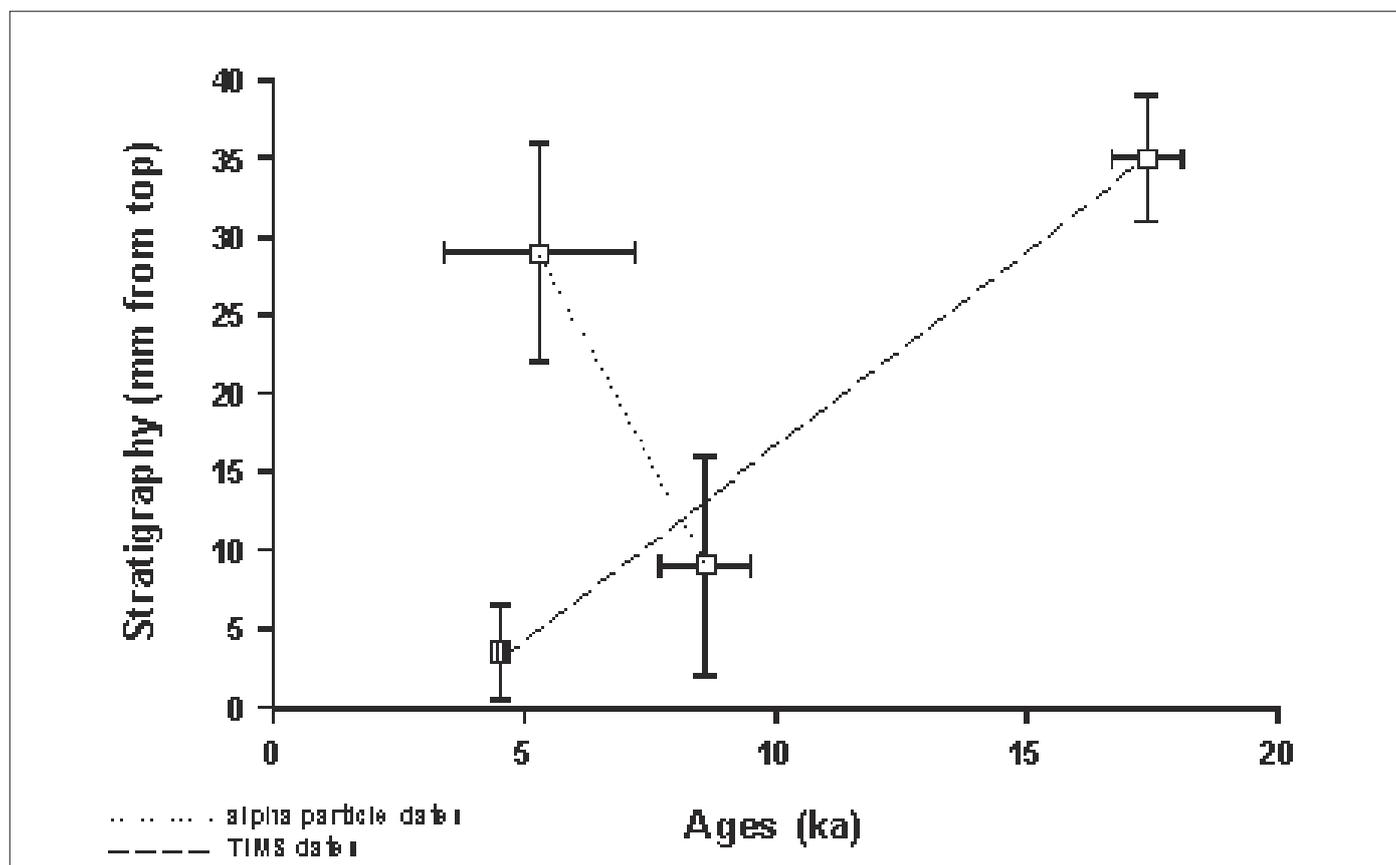


Fig. 7. Gypsum ball from Sorbas (see figure 6). Stratigraphy vs. age for the samples obtained. α -particle dates yield large errors (1σ) and overlapping ages that also appear inverted with stratigraphy. TIMS dates are, in spite of low U content, much more precise (2σ) and in correct stratigraphic order.

with hydride formation from ^{232}Th . The reproducibility of each measured $^{234}\text{U}/^{238}\text{U}$ ratio was 0.11% (2σ).

Repeated analyses of BR5 (a high Uranium speleothem powder standard used in Bergen) gave an age of 125.862 ± 1.546 kyr ($n = 12$), with a reproducibility of measured $^{234}\text{U}/^{238}\text{U}$ ratio of 0.59% (2σ). Age determinations were based on measured atomic mass ratios of $^{235}\text{U}/^{236}\text{U}$, $^{235}\text{U}/^{234}\text{U}$, $^{236}\text{U}/^{234}\text{U}$, $^{232}\text{Th}/^{229}\text{Th}$; and $^{229}\text{Th}/^{230}\text{Th}$. Data reduction, error optimization and propagation were done using tailored software (Lauritzen and Lundberg, 1997) which has been rewritten for the Windows environment.

Example analyses on Naica gypsum crystals

Sample description

The Naica mine (Chihuahua, Mexico) is well-known for the dimension and purity of gypsum crystals that fill several natural cavities cut by its galleries (Foshag, 1927). The Naica caves were discovered at different levels inside the mine and observations suggest that these crystals grew in three different environments (deep phreatic, epiphreatic and sub-aerial) until the caves were dewatered in 1985 (Forti *et al.*, 2009a). We have analysed one selenite sample from each of the three most important caves (Figure 8): *Cueva de las Espadas* (Cave of the Swords at the -120 m level), *Ojo*

Table 1. ICP-MS and TIMS Uranium series dates of Naica cave crystals.

Ulab No	ID sample	Cave	Method	U (ppm)	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$	Age, kyr	$2\sigma+$	$2\sigma-$	Corr. age ¹	$2\sigma+$	$2\sigma-$
850	N01-1	Ojo	ICPMS	0.0010	1.05741 ± 0.0129	0.87149 ± 0.0133	7 ± 0.49	213.700	12.53	11.03	191.018	13.75	12.50
853b	N07-10	Cristales	ICPMS	0.0002	1.33974 ± 0.0933	0.82823 ± 0.1406	12 ± 1.85	168.838	101.14	51.80	158.526	101.64	51.96
858	ESP1-1	Espadas	ICPMS	0.0460	2.36105 ± 0.0109	0.44666 ± 0.0773	19 ± 18.62	60.457	0.07	0.07	57.010	1.77	1.77
863b	ESP1-2	Espadas	ICPMS	0.1625	2.97474 ± 0.0294	0.13186 ± 0.0334	29 ± 7.43	15.209	4.14	4.02	14.491	4.15	4.03
796	ESP-surf	Espadas	TIMS	0.2000	3.42787 ± 0.00671	0.24131 ± 0.00289	949 ± 20	7.874	0.04	0.04	7.863	0.04	0.04
788	N1	Cristales	TIMS	0.0038	0.76927 ± 0.0020	0.30282 ± 0.0049	10 ± 0.17	40.071	0.82	0.81	34.544	0.82	0.81

¹Correction for detrital ^{230}Th contamination, assuming "world mean" initial $^{230}\text{Th}/^{232}\text{Th}$ of 1.5, (Richards & Dorale, 2003).

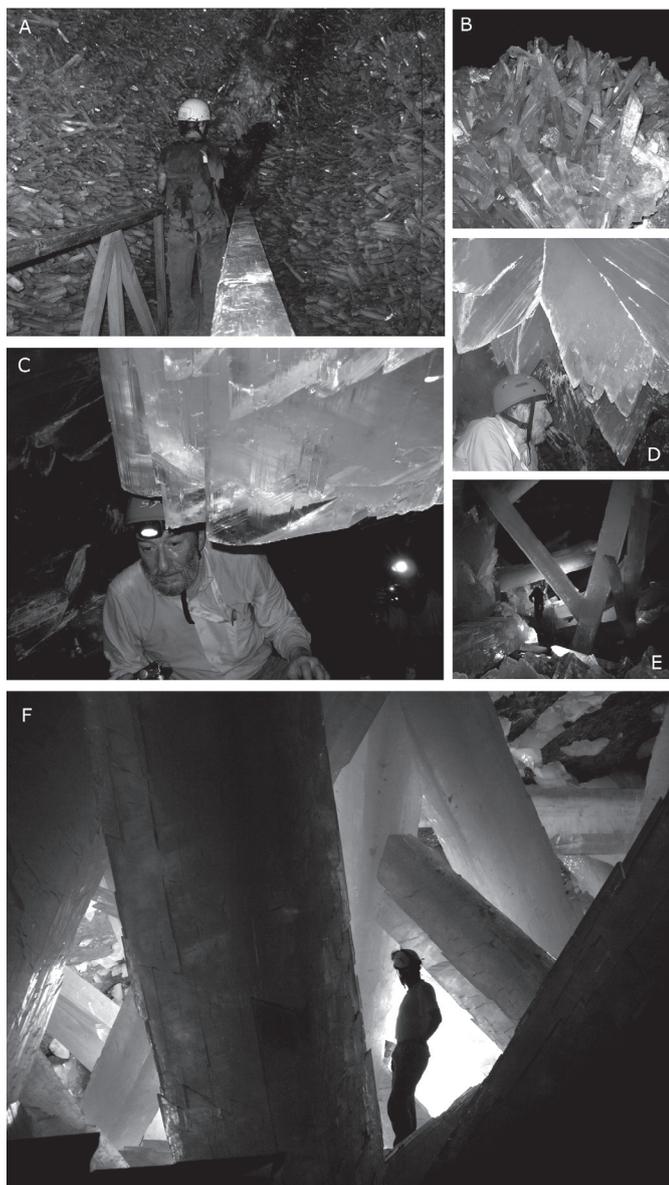


Fig. 8. The three most important caves of Naica mine: the main gallery of Cueva de las Espadas (Swords Cave) (A) at the -120 level and a detail of its gypsum crystals (B); transparent (C) and pyramid (D) shaped selenite crystals grown in Ojo de la Reina (Queen's Cave); Cueva de los Cristales (Crystals Cave) hosts the largest known gypsum crystals of the world, in single prismatic shape (E) (F) (Photo L. Sanna - Archivio La Venta & S/F).

de la Reina (Queen's cave, at the -290 m level), and *Cueva de los Cristales* (Crystals cave, at the -290 m level).

All observed 'giant' crystal specimens of Naica caves are euhedral and are composed of gypsum, except for the subaqueous spar carbonate layered grown in Espadas cave that are covered by aragonite (Forti et al., 2009b). This sample (Figure 9A) is a smaller spar, about 6 cm across, covered with several 1 cm - thick aragonite layers (Forti, 2007). The Reina sample (Figure 9B) is composed of loosely bound lamina of completely transparent gypsum, collected at the base of a crystal wall. The Cristales sample (Figure 9C) is about 40 cm across consisting of a slice cut perpendicularly through a broken crystal. The dated subsample was collected close to the centre of the slice, 13 cm from the outer surface of the crystal.

RESULTS

According to the first analyses (Table 1), the gypsum displays low uranium concentrations and a relatively high background thorium level, but possibly within reliable age range. Ages were corrected for detrital thorium content assuming an initial $^{230}\text{Th}/^{232}\text{Th}$ ratio of 1.5 (Richards & Dorale, 2003). We found significant differences in ages between samples. The oldest crystal is the sample from Ojo de la Reina (191 ± 13 kyr): this may approach the commencement of gypsum growth at the -290 m level. The central part of a giant selenite of *Cristales* yielded an imprecise age in the range of 106 - 260 kyr. The sample was taken close to a central zone of large fluid inclusions, but if we assume that the gypsum was intact and that it grew continuously until the cave was drained. The corresponding growth rate (for 13 cm of accumulation) is then in the range of 0.5 to 1.22 mm/kyr, slightly less than the rate (1.45 mm/kyr) previously found for the outer 50 mm (Lauritzen et al., 2008), and suggests that the crystal growth rate might have changed through time. The analytical results also suggest that the Uranium content of the growing gypsum has increased with time (Figure 10). The oldest samples (age > 100 kyr) have lowest U content, less than 10 ppb, samples around 10 kyr display the highest U concentrations, greater than 0.1 ppm. This trend suggests that a similar increase in the U content of the mother liquor (groundwater) occurred through time.

The base of the *Espadas* spar (57 ± 1.7 kyr) is more recent than the crystals found in the deeper caves. The age is also in accordance with the groundwater model of the area, where a late rise in groundwater might have formed the relatively smaller and more complex crystals in the *Espadas* cave (Forti et al., 2009a). A subsequent aragonite layer, taken 2 mm above the gypsum surface dated at 15 ± 2 kyr; a third subsample taken right beneath the surface of the speleothem and TIMS-dated yielded an age of 7.9 ± 0.1 kyr. These ages indicate that: (1) the genesis of these minerals are related to groundwater oscillations and corresponding aeration of the cave in an epiphreatic environment and (2) the precision is apparently improved by using iron scavenging, anionic exchange chromatography and TIMS detection.

CONCLUSIONS

In this work, we have given a review of analytical problems in dissolving gypsum and the extraction of actinides from gypsum speleothems for Uranium-series dating. We have then developed a simple dissolution method for gypsum and adapted a one-stage extraction chromatography step using Eichrom TRU resin with ICP-MS determination of atomic masses. This protocol allows the dissolution of the sample and the separation of U and Th from a sulphate matrix in 2 working days and was successfully applied to the investigation of U-Th isotope compositions in selenite crystals from Naica caves, which have very low U concentration. However, iron scavenging, anionic exchange chromatography and TIMS detection gave the most precise results.

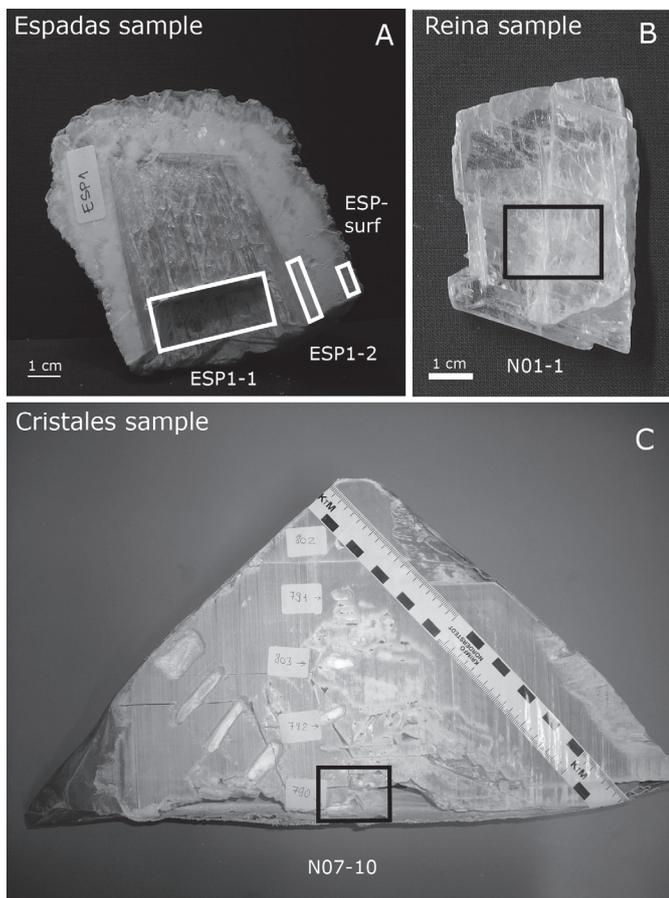


Fig. 9. Subsamples collected on Naica crystals: (A) the spar of Espadas cave is a gypsum crystal covered by aragonite; (B) a lamina of completely transparent gypsum collected at the bottom of a crystal wall in the entrance of Ojo de la Reina; (C) a slice cut perpendicularly through a broken giant selenite crystal of Cristales. Scale in centimeters.

APPENDIX (EXPERIMENTAL)

Recommended chemical procedures

All operations were performed in an overpressured cleanlab or in an overpressured LAF-bench with laminar airflow. All containers were of Teflon, pre-cleaned by boiling in 7M HNO_3 and rinsed in milliQ water. FeCl_3 , for the scavenging alternative, was cleaned by extraction into di-isopropyl ether (DPE) from 9M HCl and back-extraction into 0.1M HCl ; residual DPE was boiled off. Columns were made from disposable polyethylene Pasteur pipettes with a polyethylene frit (porous, sintered material) inserted. Solutions were evaporated on a hotplate in Teflon containers with doubly perforated evaporation closures (Savillex®), through which filtered air was drawn via a manifold directly into a water pump outside the cabinet. Vapour and fumes (HNO_3 , HCl , HF , HClO_4) were then directly absorbed in large amounts of water in a safe manner. In this way, no acid fumes entered the workspace.

All reagents were either of Suprapur® (Merck) (i.e. HBr and HClO_4) or double (sub-boiling) distilled in our laboratory (HNO_3 , HCl , HF).

Sample preparation

Subsamples should be cut with pre-cleaned (acid, water, alcohol) tools; we use a dentist's drill with cutting disks to extract subsamples in one piece or as coarse chips. These coarse pieces were then crushed in a mortar to desired grain size. This procedure minimizes contamination from tools and optimizes grain size (powder) to enhance dissolution.

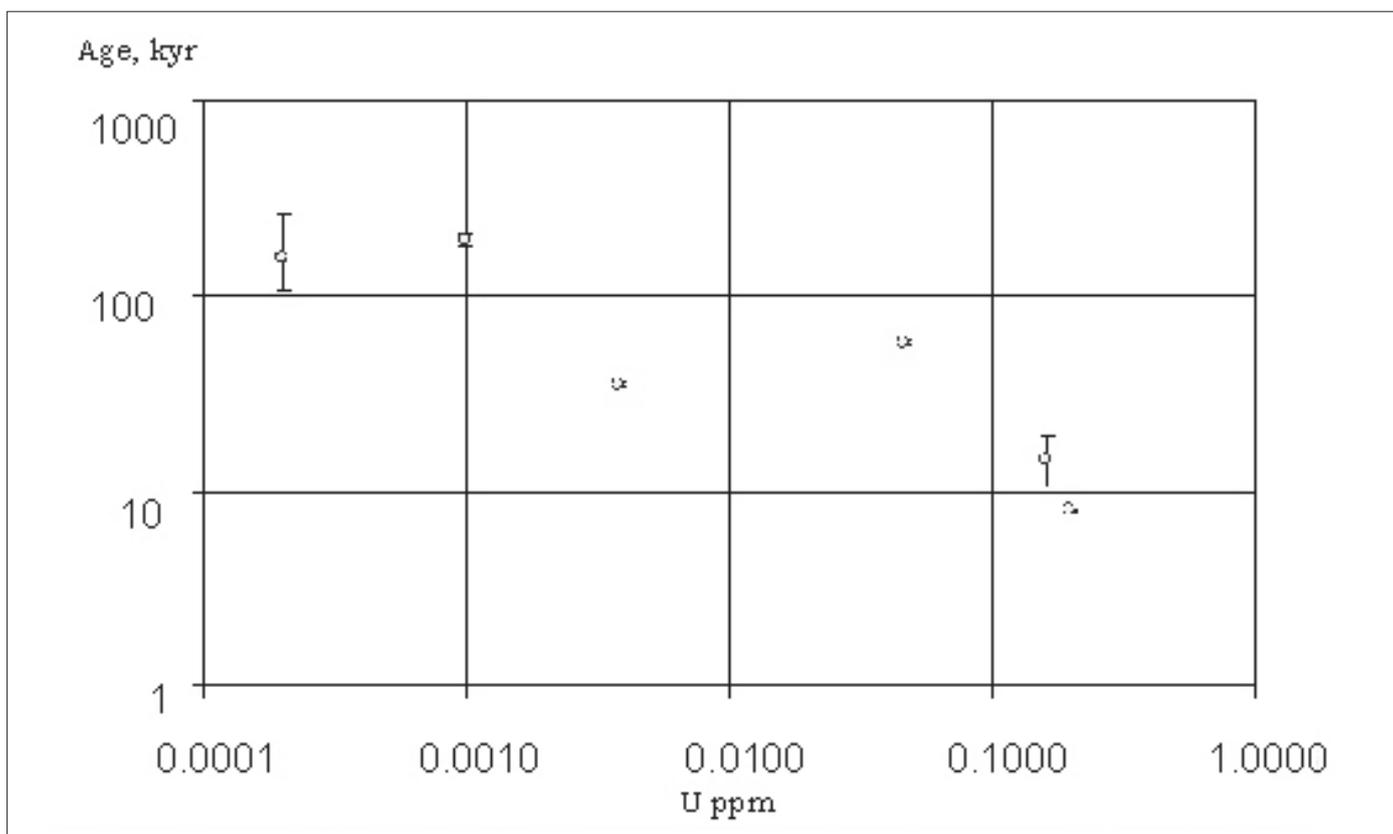


Fig. 10. Age and analytical error as a function of U content of the Naica gypsum crystals. Data from Table 1. Samples older than 100 kyr have very low U concentrations (<10 ppb), whilst the younger samples (ca 10 kyr) display much higher concentrations (>0.1 ppm).

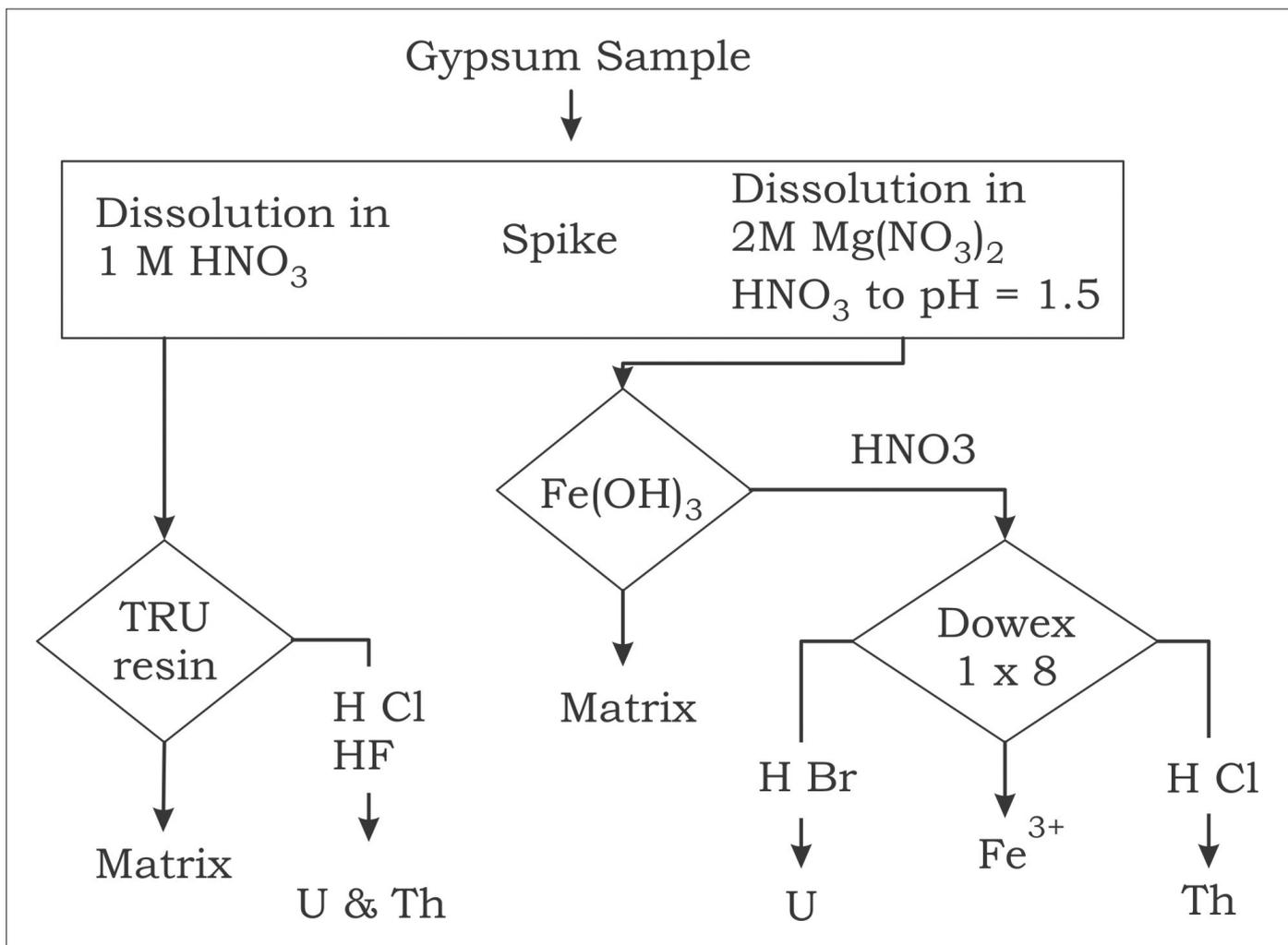


Fig. 11. Flow-chart of the analytical procedures. Left: direct retention by TRU resin (procedure a). Right: iron scavenger approach with anion exchange chromatography (procedure b).

Sample dissolution

Figure 11 depicts the flowchart of our recommended preparation alternatives. In both cases, the finely powdered sample is brought into solution by means of either 1M HNO₃ or in 2M Mg(NO₃)₂ / HNO₃ at pH 1.5. The solution is spiked and equilibrated overnight before further treatment.

Extraction Chromatography (EXC) was performed using TRU-resin™ (Triskem), a non-ionic acrylic-ester polymer comprising a combination of tri-*n*-butylphosphate (TBP) and octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) supported on an inert substrate (Amberlite XAD-7). This resin has a high affinity to tri-, tetra- and hexavalent actinides, extracted as their nitrate complexes (Peterson *et al.*, 2007). Anionic exchange of U and Th was done on Biorad (Dowex) AG 1x8 (200 – 400 mesh) resin, consisting of quaternary ammonium (-NR₃⁺) groups, capable of binding nitrate- and chloride complexes of UO₂²⁺ (e.g. UO₂Cl₄²⁻) and the nitrate complex of Th⁴⁺ in strong HCl or HNO₃, respectively. The complexes can be broken by more dilute HCl and HBr eluants. The nitrate medium is also capable of separating UO₂²⁺ and Th⁴⁺ from Fe³⁺ in HNO₃.

Direct retention on TRU resin.

The clear, centrifuged sample is slowly passed through a column prepared with TRU resin, previously cleaned by several *cv* (column void volume, it is approximately half of the resin volume) 0.1M HCl + 0.2M HF and conditioned with 4 *cv* 1M HNO₃. The column (7.2 x 150 mm) contains 1 mL (240 mg) of Eichrom TRU resin, 100-150 μm particle size, suspended in a few mL of water. After application of the sample, the column was washed with 4 *cv* of 1M HNO₃ in small portions. Then, HNO₃ was replaced by 2 *cv* of 1M HCl, after which U and Th were eluted with 14 *cv* (7 mL) of 0.1M HCl – 0.2M HF. To the eluates were added 1 drop concentrated HNO₃. They were evaporated to complete dryness in Teflon vials. Organics can be removed by adding one drop conc. HClO₄ in the HNO₃ evaporation step, followed by a second HNO₃ treatment. If the procedure is done correctly, the residue is hardly perceptible.

Scavenging and separation of U and Th

During dissolution and spiking, 2 drops of FeCl₃ are added to the solution, corresponding to 100 – 200 mg Fe. After centrifugation, the solution is neutralised with conc. NH₃, using the brown colour of Fe(OH)₃ as an indicator, plus an excess

of 1 mL per 100 mL solution. The final solution will smell of ammonia. After flocculation, $\text{Fe}(\text{OH})_3$ is centrifuged off and washed with 5 - 10 mL water containing one drop diluted ammonia solution. After centrifugation, the precipitate is dried down several times with conc. HNO_3 and finally dissolved in 0.5 mL 7.5M HNO_3 . Iron is eluted from a 1 mL AG 1x8 resin column with a total of 3 - 4 cv 7.5M HNO_3 . (The column is pre-cleaned and conditioned with 6M HCl, followed by 8 cv water and conditioned with 4 cv 7.5M HNO_3). Th is then eluted with 6 cv 6M HCl, whereafter U is eluted with 6 cv 1 M HBr. A second purification step on each fraction is done on 0.25 mL columns with AG 1x8 resin, using the same procedure. Finally, the fractions are evaporated to dryness with one drop concentrated HNO_3 .

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