



Tools for uranium characterization in carbonate samples: case studies of natural U–Pb geochronology reference materials

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Received: 12 June 2020 – Discussion started: 3 July 2020

Revised: 25 November 2020 – Accepted: 1 December 2020 – Published: 16 February 2021

Abstract. Laser ablation U–Pb analyses of carbonate (LAcarb) samples has greatly expanded the potential for U–Pb dating to a variety of carbonate-producing settings. Carbonates that were previously considered impossible to date using isotope dilution methods may preserve radiogenic domains that can be dated using spatially resolved laser ablation geochronology techniques. Work is ongoing to identify reference materials and to consider best practices for LAcarb. In this study we apply standard and emerging characterization tool sets on three natural samples with the dual goal of enhancing the study of carbonates and establishing a new set of well-characterized natural reference materials for LAcarb studies. We start with the existing carbonate reference material WC-1 from the Permian Reef Complex of Texas, building on the published description to offer a deeper look at U and associated trace elements. We consider a tufa sample from the Miocene Barstow Formation of the Mojave Block, California, as a possible secondary calcite reference material due to its well-behaved U–Pb systematics. There are currently no natural dolomite standards. We present an unusual dolomite sample with very well-behaved U–Pb systematics from the Miocene of the Turkana Basin of Kenya as a possible dolomite reference material for LAcarb dating. In addition to using X-ray fluorescence (XRF) mapping and spectroscopy to better understand U in these natural samples, we have analyzed multiple aliquots of each of them for ⁸⁷Sr/⁸⁶Sr

by thermal ionization mass spectrometry (TIMS). The Sr isotope compositions are analytically homogeneous within petrographically homogeneous regions of all three samples, and thus these materials could be used as Sr isotope standards as well. While not part of the current contribution, this combination could streamline simultaneous LA analyses of ⁸⁷Sr/⁸⁶Sr and U–Pb geochronology.

1 Introduction

Carbonates are ubiquitous in the Earth's crust and form from a variety of fluids, often with characteristic isotopic and element ratios (Fig. 1). Carbonate-producing fluids in all crustal levels range from oxygenated to reducing, from low salinity to high salinity, and from low temperature to high temperature. Fluids evolve as they interact with rocks along their flow paths, adding complexity but also providing opportunities to trace these processes with the rock's paragenetic history. Carbonate compositions are highly susceptible to diagenetic alteration, particularly when fluid chemistry and temperature changes affect the thermodynamic stability of carbonate minerals. Mixing of fluids can be particularly corrosive, such as is seen where seawater and fresh water mix in a carbonate platform, or can be responsible for mineral precipitation depending on the saturation state of the combined fluids (Run-

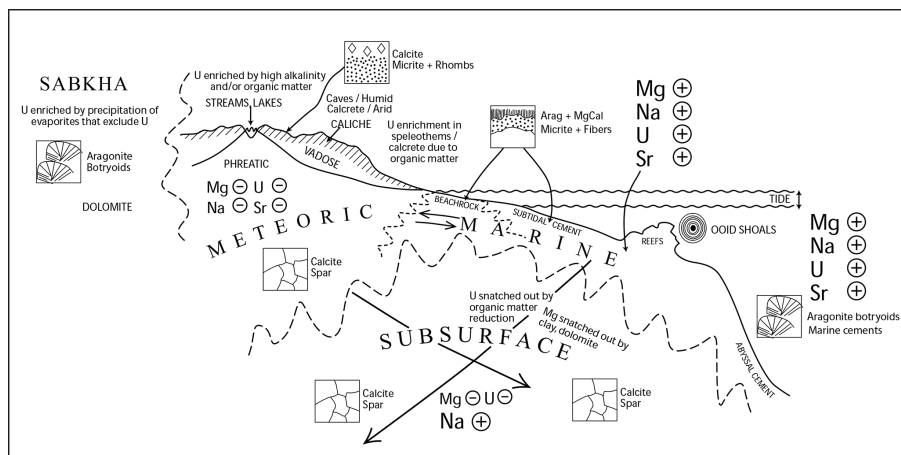


Figure 1. Cartoon of the variety of carbonate-producing environments, with arrows indicating the direction the elements would change through diagenetic alteration (Rasbury and Cole, 2009). We would like to see U concentrations and oxidation states be an important component in understanding fluids and diagenesis.

nells, 1969; Wigley and Plummer, 1976). Thus, introduction of fluids with different chemistries through exposure, uplift, or burial can destroy the original carbonate prior to precipitation of a new carbonate or can alter the carbonates visibly or at a microscopic scale. Therefore, an important part of investigation of carbonates should involve establishing field and petrographic relationships. Standard assessment of field and petrographic relationships between carbonate phases is a prerequisite to developing a detailed rock paragenesis necessary for interpreting the timing and source of depositional and diagenetic fluids interacting with carbonate rocks. Here, we present tools useful for characterizing the incorporation of radiogenic elements – especially uranium, lead, and strontium – into carbonates as a means for relating $^{87}\text{Sr}/^{86}\text{Sr}$ and U–Pb data to carbonate paragenetic frameworks.

It is widely recognized that carbonates are a proxy for the fluids that formed them. Published studies demonstrate the need for careful characterization of carbonates in order to interpret geochemical results in geologically meaningful context, and this same attention to detail is needed to understand U–Pb results. Carbonates have element ratios that are controlled by the composition of the fluid and the partition coefficient (K_d) of the element for the crystal lattice (Banner and Hanson, 1990). Special circumstances are required to have elevated U in calcite because the K_d is less than 0.05 (Reeder et al., 2001; Drysdale et al., 2019; Weremeichik et al., 2017). However, aragonite, which is metastable, does not exclude U. Reeder et al. (2001) and Kelly et al. (2003) suggested that high U contents in a speleothem calcite (which we use as a U^{6+} standard) might have been inherited from high concentrations in primary aragonite and preserved during neomorphic inversion to calcite. No experimental studies for U incorporation have been reported for dolomite, but it is unlikely to have a higher affinity for U than calcite as they have the similar structures and there is more of a size mis-

match with Mg than Ca. Using modern settings and a laboratory understanding of trace element incorporation, we know that U incorporation follows aragonite > high Mg calcite > calcite (Chung and Swart, 1990; Reeder et al., 2001). Seawater has elevated U/Pb, but carbonates forming from seawater have much lower U/Pb, demonstrating that the structure has a much higher affinity for Pb than U (Shen and Boyle, 1988), at least at seawater composition.

No lab experiments have studied U^{4+} incorporation in carbonates, despite several published examples of natural carbonates with reduced U (Sturchio, 1998; Cole et al., 2004) and an additional example that we present in this contribution. Because U^{4+} is immobile in most aqueous fluids, carbonate minerals that incorporate U^{4+} must represent precipitates from poorly understood fluid compositions in depositional or diagenetic environments. Recent work on modern calcite from a deep granite aquifer with a reducing fluid suggests a mechanism for U^{4+} transport (Drake et al., 2018). Experimental work at elevated T has shown that $\text{U}^{6+}\text{Cl}_4^0$ is soluble in acid solutions (Timofeev et al., 2018), and high T experiments of U in hydrocarbons indicate that economic concentrations can be produced via transport in hydrocarbons (Migdisov et al., 2017), but how would these processes result in incorporation in carbonates? There is likely more than one mechanism and this is a fruitful avenue for future research both of synthetic and natural carbonate samples. Understanding U incorporation in carbonates is important for a holistic approach to U–Pb dating, but there is no evidence that the oxidation state of U in carbonates has any control on the reliability of the dating. However, understanding U speciation might elucidate the depositional or diagenetic condition under which the U was incorporated and therefore affect the interpretation of the U–Pb date.

Cement stratigraphy is a powerful approach to establish the relative age relationships of carbonate phases or para-

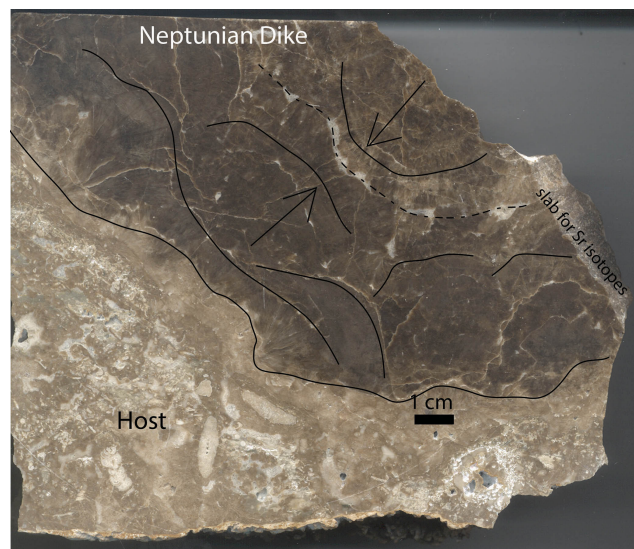


Figure 2. Large hand sample from a Neptunian dike at Walnut Canyon. The lighter brown limestone on the left is the reef rock, with abundant large forams clearly visible. The dark brown botryoids can be seen growing from both sides of this oblique slab through the dike carbonate. Curved lines show approximate botryoid boundaries and arrows point in the growth direction. The dashed line is approximately the center of the dike. A white calcite cement lines many of the botryoids and occurs in the center of the dike. A slab from the host to the center was analyzed for the Sr isotopes presented in this paper.

genesis across a basin. This approach uses relative relationships of cements from the thin-section scale and correlation of these throughout a basin or region (Meyers, 1991, 1974). This field to petrographic approach has been used to select samples for geochemistry, providing fundamental insights into the fluid evolution of basins and degree of rock–water interaction (e.g., Banner and Hanson, 1990), as well as establishing trace and minor element incorporation trends (e.g., Mn/Fe) useful for tracking burial histories (Barnaby and Rimstidt, 1989). Combining microanalytical tools that characterize carbonates at the micrometer to centimeter scale of cement growth zones is often required to understand the origin and timing of various textures in complex samples. Chemical imaging techniques; carbonate staining; and polarized light, fluorescence, electron, and cathodoluminescence microscopy provide spatial context for quantitative microscale analyses of fluid inclusion, ion microprobe, electron microprobe, and laser ablation measurements. Integrated data from such a toolkit enables collection of LA–U–Pb isochrons that reliably dates a single paragenetic event and permits geologically meaningful interpretation of U–Pb ages. U–Pb dating in this context places age constraints on the fluids that can then be tied to testable hypothesis about the origin and changes in the fluids whatever the technique for dating is (Lawson et al., 2018; Quade et al., 2017; Parrish

et al., 2019; Pisapia et al., 2018; Woodhead et al., 2010; Winter and Johnson, 1995; Hoff et al., 1995; Cole et al., 2005; Polyak et al., 2008, 2013; Luczaj and Goldstein, 2000; Brannon et al., 1996; Godeau et al., 2018; Rasbury et al., 2004, 1997; Pagel et al., 2018; Roberts et al., 2020).

Laser ablation mapping (Woodhead et al., 2010, 2007; Piccione et al., 2019; Drost et al., 2018; Roberts et al., 2020), synchrotron XRF mapping (Cole et al., 2004; Piccione et al., 2019; Frisia et al., 2008; Vanghi et al., 2019), PIXE (Ortega et al., 2005, 2003), μ XRF (de Winter et al., 2017), and EMPA (Suzuki et al., 2016) permit tying petrographic observations of different phases to in situ chemical maps of U and other elements that inform fluid chemistry. For the purpose of U–Pb dating, knowledge of the mineral lattice location of U and its oxidation state and speciation provide a fundamental framework for interpreting ages, as well as revealing details of the fluid chemistry (Kelly et al., 2006, 2003; Sturchio, 1998; Cole et al., 2004). In some cases, uranium minerals are encapsulated in calcite, which can protect them from alteration (Suzuki et al., 2016; Ludwig, 1978).

Given that the major element composition of seawater has changed appreciably through time (Hardie, 1996; Lowenstein, 2001; Horita et al., 2002), that meteoric fluid compositions are controlled by water rock interaction (Chung and Swart, 1990; Banner and Hanson, 1990), and that deep brines have evolved since deposition in basins (Musgrove and Banner, 1993), we can imagine that there is no such thing as a typical fluid. A holistic approach to dating carbonates should involve an effort to see back to the fluid or fluids that have been responsible for its formation and how they might have changed through the diagenetic history. This, particularly in the context of how favorable the U concentrations and U/Pb ratios are, will provide an important path towards understanding factors that create favorable carbonate samples for U–Pb dating. The purpose of this contribution is to highlight tools that are available for carbonate characterization relevant to U–Pb dating. These tools build on the more commonly used petrographic approaches, particularly cathodoluminescence (CL) imaging, such as will be demonstrated in the three case studies presented here.

1.1 Mapping uranium

While the U/Pb ratio matters for dating, it is usually the U concentration that limits the potential. Mapping U at low concentrations in carbonates is challenging but necessary to tie U–Pb ages to paragenetic context and to identify datable phases; therefore, the focus here will be on tools that map the distribution of U on the hand-specimen to the thin-section scale. Fission track mapping (Chung and Swart, 1990; Hoff et al., 1995; Rasbury et al., 2000; Cole et al., 2004; Becker et al., 2002; Wang et al., 1998; Luczaj and Goldstein, 2000; Amiel et al., 1973; Haglund et al., 1969; Gvirtzman et al., 1973) can help to map the distribution of U on microscopic to hand-specimen scales. This simply requires making a pol-

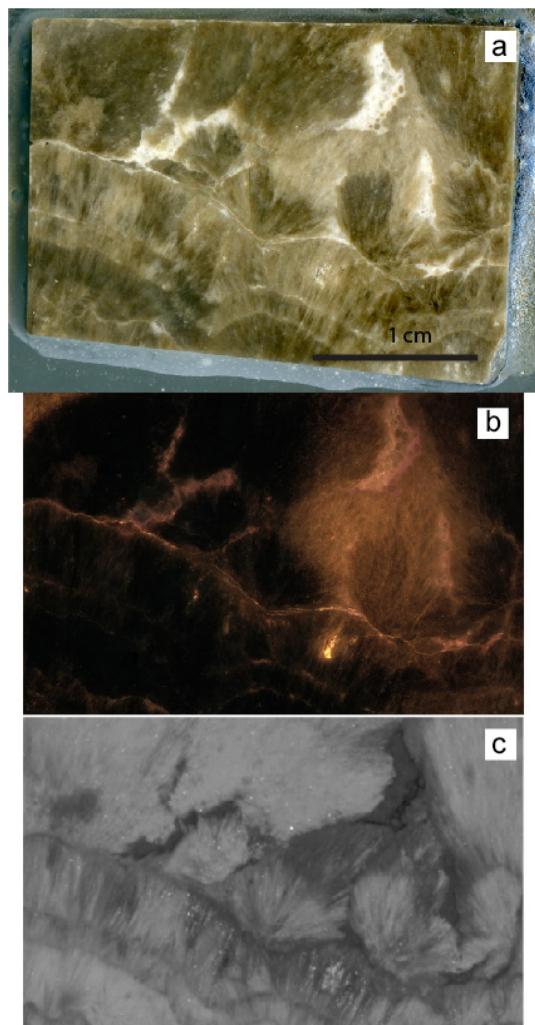


Figure 3. (a) Polished slab from the Walnut Canyon Neptunian Dike sample used in this study to illustrate various tools for characterization. This is approximately 3 cm across. This is a similar size to that being distributed as a reference material (Roberts et al., 2017). Note the variability of color from very dark to light brown and the white veins. The fibrous botryoidal texture is visible even at this scale, and complexities due to veins should be easily avoided when using this as a LAcarb reference material. (b) Photomosaic of 639 CL photos. (c) MicroXRF map of Sr (details in the next figure caption). Areas that are brightly luminescent have low Sr. Boundaries between botryoid layers are luminescent (and white so they are easy to avoid) and should be avoided when using this sample as a standard. This microXRF map of Sr beautifully shows the texture of the sample. We suggest that this easy screening technique could be done on all slabs being used for a LA standard and that using this as a guide for analyses could result in better reproducibility of measurements.

ished slab, placing it on a detector such as Lexan plastic (Chung and Swart, 1990), and sending it to a nuclear reactor. Depending on the flux requested, it typically takes weeks for the samples to be returned due to harmful radioactivity pro-

duced in the reactor. Once back, the detector has to be etched to increase the size of the tracks for visibility and then a comparison to the rock can be made. Thin sections can be used, making it easier to relate the tracks to the exact phases. There is a modest cost for sending samples to a reactor, but this is an under-utilized non-destructive approach. For samples with high U (tens of parts per million), modern high-resolution scanners can image the tracks. For lower-concentration samples, high-magnification microscope images can be stitched together to provide a larger-scale framework for the U distribution.

Autoradiography (Cole et al., 2003; Pickering et al., 2011) offers the opportunity to examine radioactive elements on the hand-specimen scale. Phosphor imaging plates are used in biomedical and biochemical studies to detect samples tagged with radionuclides. While the scanning devices themselves are somewhat costly, phosphor screens can be rented from imaging centers or even purchased at lower cost, making this technique more broadly applicable. Polished hand samples (along with a solid standard) are left to activate the phosphor over time (days to weeks), ideally in a shielded environment. Following exposure, the screens are scanned to produce a digital autoradiograph that provides a map of relative differences in U and Th concentrations directly comparable to the hand specimen (Cole et al., 2003; Pickering et al., 2011). Centimeter-scale regions of higher U (and Th) can then be targeted further with sampling and other finer-scale mapping techniques.

Synchrotron X-ray fluorescence (SXRF) imaging and X-ray absorption spectroscopy (XAS) techniques have the ability to provide information about both the distribution of major and trace elements (including U and Pb) in samples and their valence state and speciation. Using XAS methods it is possible to quantify U valence state at concentrations of a few parts per million. Synchrotron X-ray beamlines are available through a competitive process of general user proposals (Sutton et al., 2002). These brighter sources offer micrometer-sized resolution for low part per million levels of the elements of interest. Emerging tender energy spectroscopy (TES), using the energy range between soft and hard X-ray techniques, allows mapping of elements such as Mg and S that are important in carbonates (Northrup, 2019). In addition to XRF maps that show element distribution and the relationships among elements, spots can be chosen for spectroscopy, providing mineralogy (Mg, Ca) and redox (U, Fe, Mn, etc.).

Bench-top microscale XRF mapping (μ XRF) of major, minor, and trace elements by energy-dispersive spectroscopy permits geochemical characterization of samples at the micrometer to decimeter scale. X-ray-focusing optics, rather than collimation, allow high spatial resolutions (ca. 15–25 μ m) with laboratory X-ray sources. μ XRF has been used for chemical imaging in diverse fields, including material characterization, archeology, and Earth sciences (de Winter et al., 2017; Allwood et al., 2018; Katsuta et al.,

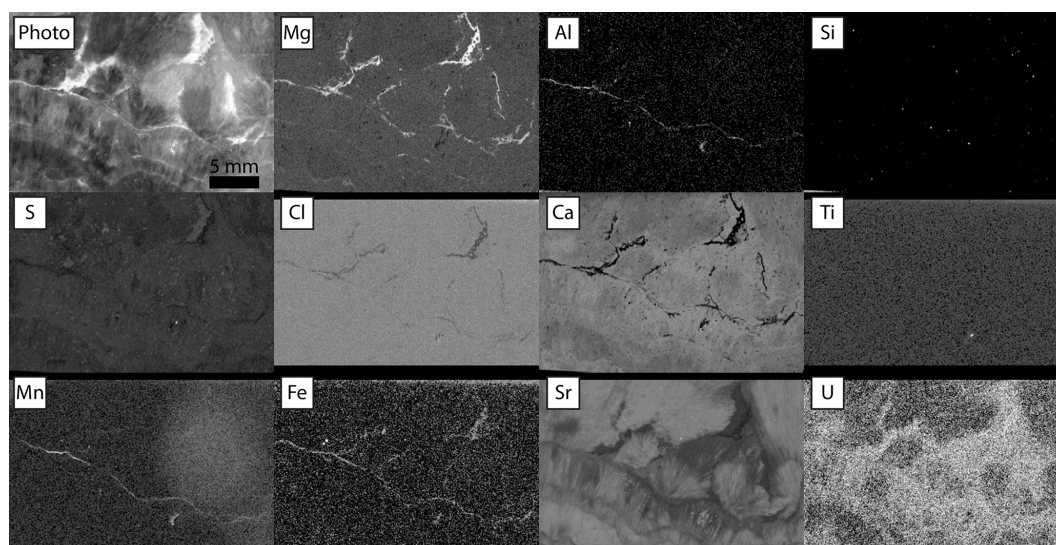


Figure 4. Relative intensities of emission regions for each element detected in Walnut Canyon, imaged at 20 μm pixels with 1.5 SD Gaussian blur. Dwell time was 30 ms per pixel for maps with no incident radiation filter (Mg, Al, Si, S, Ca). Dwell time was 60 ms per pixel for maps with incident radiation filtered with 100 μm Al, 50 μm Ti, 20 μm Cu foil (Cl, Ti, Mn, Fe, Sr, U). Each panel is adjusted in terms of gamma and contrast to emphasize gradients between textures.

2019; Haschke et al., 2014; de Winter and Claeys, 2017), and related instruments will be deployed on interplanetary spacecraft (Williford et al., 2018). Qualitative and semi-quantitative imaging and standard-less analysis is rapid and versatile, but quantitative composition determination of carbonate rocks is challenging due to the X-ray-transparent carbonate matrix (de Winter et al., 2017). As shown here, in some samples with high U concentrations, U abundance can be mapped with appropriate analytical conditions, such as incident radiation filtering, multiple beam dwell passes, acquisition under vacuum, and preparation of thick samples that permit excitation of all available U atoms through the sample depth. Data presented here was acquired using an M4 Tornado (Bruker) operating with a 30 W Rh X-ray tube excited at 50 kV and focused to a 17 μm spot (1σ of incident energy at Mo-K α) on flat, polished, and thick (> 2 mm) samples under 20 hPa vacuum. Fluorescence energy was detected with two 60 mm² XFlash silicon drift detectors (Bruker), energy spectra were deconvolved with Bruker software, and total counts in each emission line region were exported for plotting and visualization using MATLAB (Mathworks).

2 Case studies

We use three natural carbonates that have potential as Laser ablation U–Pb analyses of carbonate (LAcarb) reference materials to illustrate imaging and spectroscopy techniques. We also discuss what is known of the geology and geochemistry to provide context for other samples that might be dated.

2.1 Late Permian marine cement – Permian reef complex

Roberts et al. (2017) offered WC-1 (Walnut Canyon) as a primary standard for LAcarb. This late Permian marine cement sample is reasonably homogeneous with high enough U/Pb and radiogenic enough Pb isotopes to make it a suitable reference material. A brief description of the field relationships and U–Pb characterization were presented in Roberts et al. (2017), but here we expand on this to offer additional insight into the reference material and to highlight characterization techniques that are relevant to any carbonate study. Similar buildups and cements are described from important oil plays in Kazakhstan (Dickson and Kenter, 2014), and comparisons have been made to Precambrian marine aragonite cements (Grotzinger and Knoll, 1995). Cements of this type offer good potential for providing the ages of penecontemporaneous marine diagenesis.

The Permian reef complex, spectacularly exposed in the Guadalupe Mountains of western Texas, stands in relief primarily due to the type of cements that make up WC-1. Neptunian dikes are found parallel to the reef track, filling fractures that resulted from tensional stresses as the reef built out into the Permian Basin (Hunt et al., 2003; Budd et al., 2013; Frost et al., 2013). Early marine cements in the reef and within these Neptunian dikes are primarily botryoidal aragonites and are typically a dark brown color. The dark brown color is from organic matter that is occluded in the carbonate, such that when broken or sawn these cements smell like hydrocarbons (anecdotally this strong smell is a good criterion for selecting carbonates for dating). The cements have

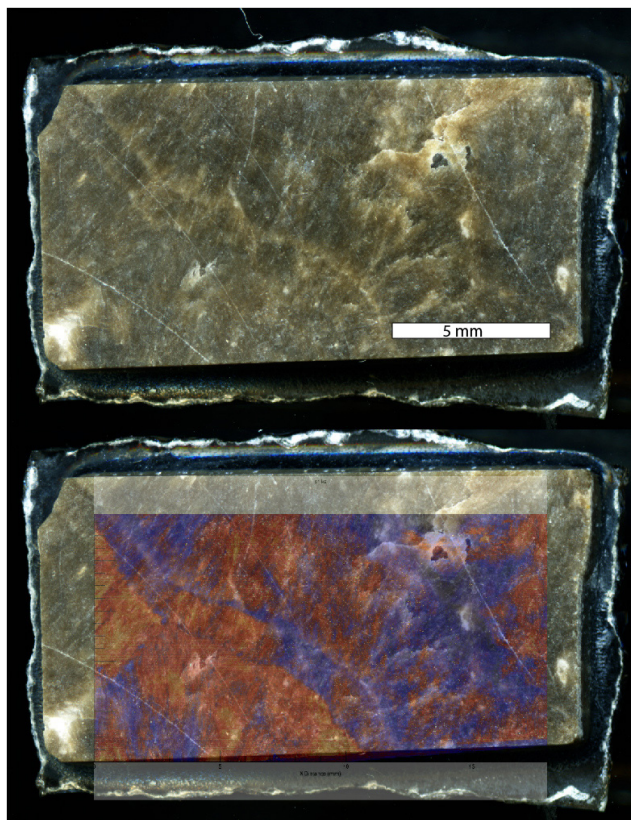


Figure 5. Synchrotron XRF Sr maps from beamline X26A NSLS Brookhaven National Lab overlain on the slab that was imaged. This XRF map was accomplished by on-the-fly scanning. To obtain U maps, we would have had to scan the same area above and below the binding energy for U and make a difference map because the $\text{SrK}\alpha$ peak is so large that the shoulder overlaps with the far less abundant UL_3 peak. However, based on the wealth of background information, we know that Sr is lost before U, and thus focusing on botryoids with elevated Sr should produce the best areas for LA-Carb reference material. This type of image can be registered for laser ablation so that only the most favorable areas are used as a reference material.

mostly been altered to calcite, though Chafetz et al. (2008) found original aragonite in similar cements from the same area. The calcite with the greatest alteration is light brown and has less favorable U/Pb (Jones et al., 1995). Petrographically, these cements preserve details of the original fibrous aragonite as inclusion trails. WC-1 (Walnut Canyon) comes from a Neptunian dike in the upper Capitan Formation of the Permian reef complex, equivalent to the Tansill Formation on the shelf. This Neptunian dike is exposed in Walnut Canyon just outside the Carlsbad Caverns National Park entrance. The botryoids that fill the Neptunian dike were made of radiating aragonite needles that bundle into centimeter-scale packages. The botryoids grow atop one another from both sides of the dike (Fig. 2). At the hand-specimen scale, cross-cutting white veins are obvious (Fig. 3). Other veins

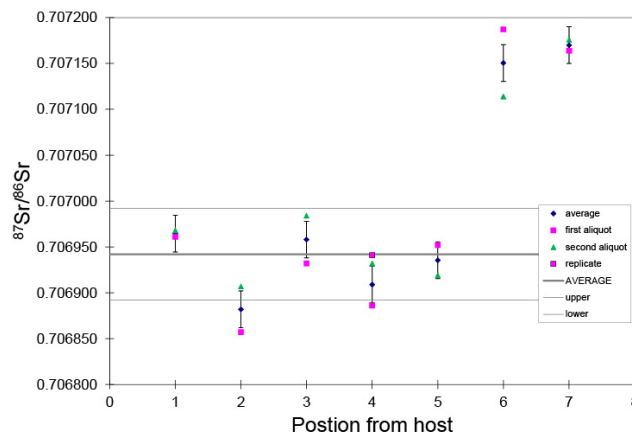


Figure 6. This graph shows Sr isotopes from the host to the center of the Neptunian dike. The aliquots were micro-sampled, dissolved and put through Sr spec resin, and run by thermal ionization mass spectrometry. The pink symbols represent two independent analyses from slabs that are at a quasi-equal distance from the host, and the blue diamond is the average of those analyses. While showing variability, the dark brown calcite has $^{87}\text{Sr}/^{86}\text{Sr}$ like Capitanian seawater with an average of aliquots 1–5 of 0.706930 (0.000069). The samples from positions 6 and 7 are a light brown color, and a boundary is clearly visible in 6. These may represent later fluid alteration or an extended marine cement history. This is presented because we suggest that this sample may also be a useful Sr isotope reference material. The slabs are about 0.5 cm across.

are smaller but can be detected with petrography and element mapping (Fig. 3). The Permian Reef Complex has seen many episodes of diagenetic fluids, including meteoric fluids accompanying the basin and range extension that exhumed the reef in the Neogene (Bishop et al., 2014; Loyd et al., 2013; Scholle et al., 1992; Budd et al., 2013).

Cathodoluminescence (CL) has been a go-to test for diagenesis, and when an activator such as Mn is present, this often gives phenomenal images that illuminate alteration, as well as veins and single crystals in fractures, which can track reactivation and changes in the chemistry and rate of fluid flow. However, it is also understood that Fe quenches luminescence; therefore, the Mn/Fe ratio is important in order to understand what luminescence or non-luminescence actually means (Barnaby and Rimstidt, 1989). In the case of Walnut Canyon, the well-preserved botryoids are non-luminescent and cements that line the botryoids are brightly luminescent (Fig. 3). Even through the botryoids are non-luminescent with excellent textural preservation, the wide range of Sr concentrations across the botryoids shows that they have been variably altered (Figs. 3–5). Element imaging is complementary to petrography, and while petrographic techniques like CL can provide qualitative information on Mn and Fe, XRF and LA imaging techniques give quantitative information on the Fe/Mn, Sr/Ca, and other ratios and element concentrations, providing far more insight into the carbonate diagenesis.

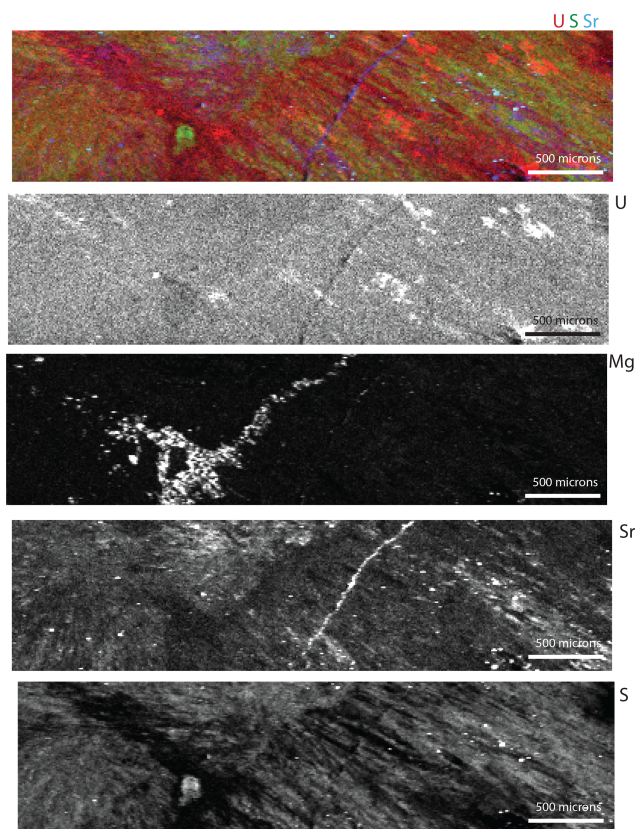


Figure 7. Tender energy range (TES) synchrotron XRF maps of the Walnut Canyon slab shown in Figs. 3–6. The panels are labeled with the elements they represent. The top map is a RGB map where red is U, green is S, and blue is Sr (note the scale bar on the bottom right of the RGB image is 100 μm). The brightest areas in the U map are artifacts from diffraction. The best preserved areas are an olive green.

sis. μXRF scanning is reasonably accessible, and we suggest that (depending on the original mineralogy) elements like Sr (Figs. 3, 4) could be mapped and registered so that only the best preserved parts of a rock slab could be targeted for a LAcarb reference material. This should greatly reduce the scatter that is currently seen in the WC-1 reference material.

While optical orientation is preserved and fluid inclusions and aragonite relict mineral inclusions delineate the original acicular growth habit, the carbonate is almost entirely replaced by cloudy brown calcite (Mazzullo, 1980). This neomorphic replacement may facilitate retention of U (Kelly et al., 2003), or perhaps the organic matter (that gives the sample its color and pungent smell when broken) complexed U and retained it in the calcite. Remarkably, Sr is lost well before U in this system, as evidenced by the rather homogeneous U concentration at about 4.5 ppm (which makes this a good U–Pb reference material) and the highly variable Sr (Fig. 3). Isotope dilution of this sample does not give much of a spread in U/Pb, and thus to maximize the spread a range of aliquots from dark brown to light brown were utilized

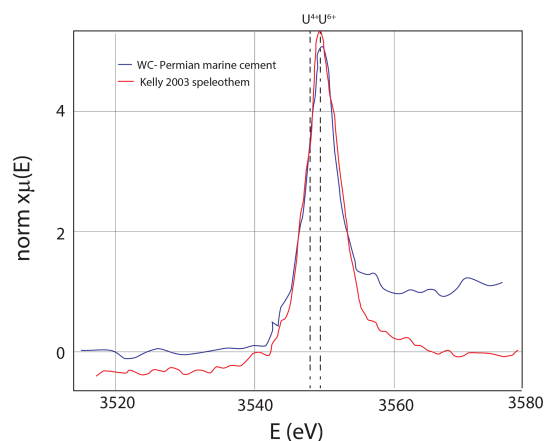


Figure 8. U M₅ edge X-ray absorption spectroscopy, with 20 scans (15 s each) showing that uranium is in the oxidized state. The TES beamline has a monochromator that is very stable, allowing for hours worth of scanning without drift. Speleothem from a cave in Austria (Kelly et al., 2003) that has U^{6+} for reference.



Figure 9. Hand specimen of a Barstow Formation tufa sample that is large enough to slab and share as a secondary LAcarb reference material.

(Roberts et al., 2017). Like the result reported in Jones et al. (1995), this produced an age that is nominally younger than the age of the reef based on dating of ash beds (Wu et al., 2020) (254.4 ± 6.4 instead of 260.8 ± 0.5 Ma) but not outside the uncertainty. The cements postdate reef cementation because they fill fractures but contain internal sediments

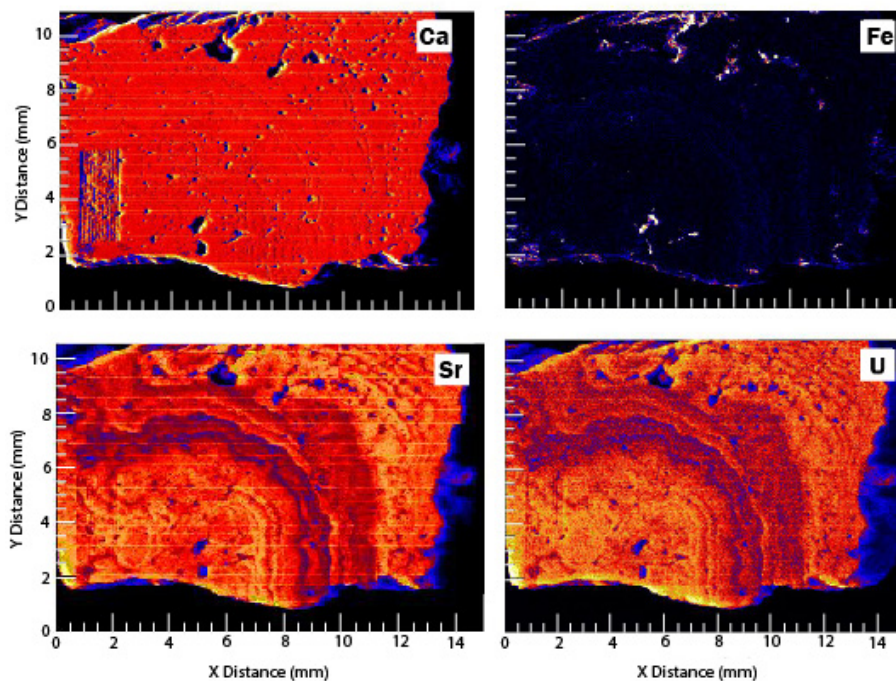


Figure 10. On the fly synchrotron XRF maps of Ca, Fe, Sr, and U for a slab of Barstow tufa. This is from the same suite of samples being characterized for a LAcab reference material, and it serves to show the relationships between U, Fe, and Sr in the Barstow tufa samples.

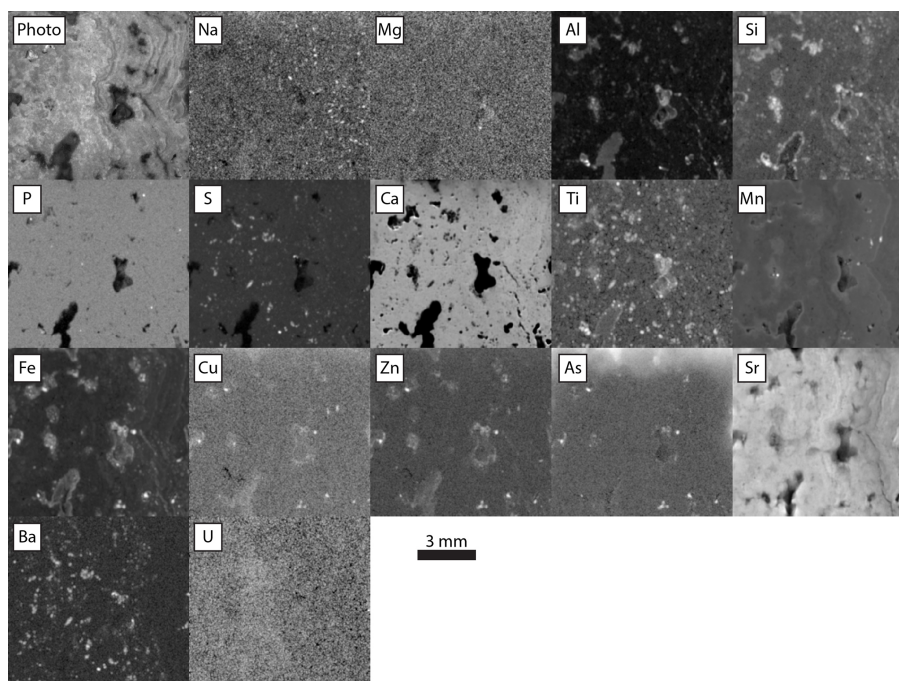


Figure 11. Relative intensities of emission regions for each element detected in Barstow tufa, imaged at 25 μm pixels with a 400 ms per pixel dwell time and 1.5 SD Gaussian blur. Each panel is adjusted in terms of gamma and contrast to emphasize gradients between texture. Na through Fe data collected with no incident radiation filter. Cu through U data collected with incident radiation filtered with 100 μm Al, 50 μm Ti, and 20 μm Cu foil.

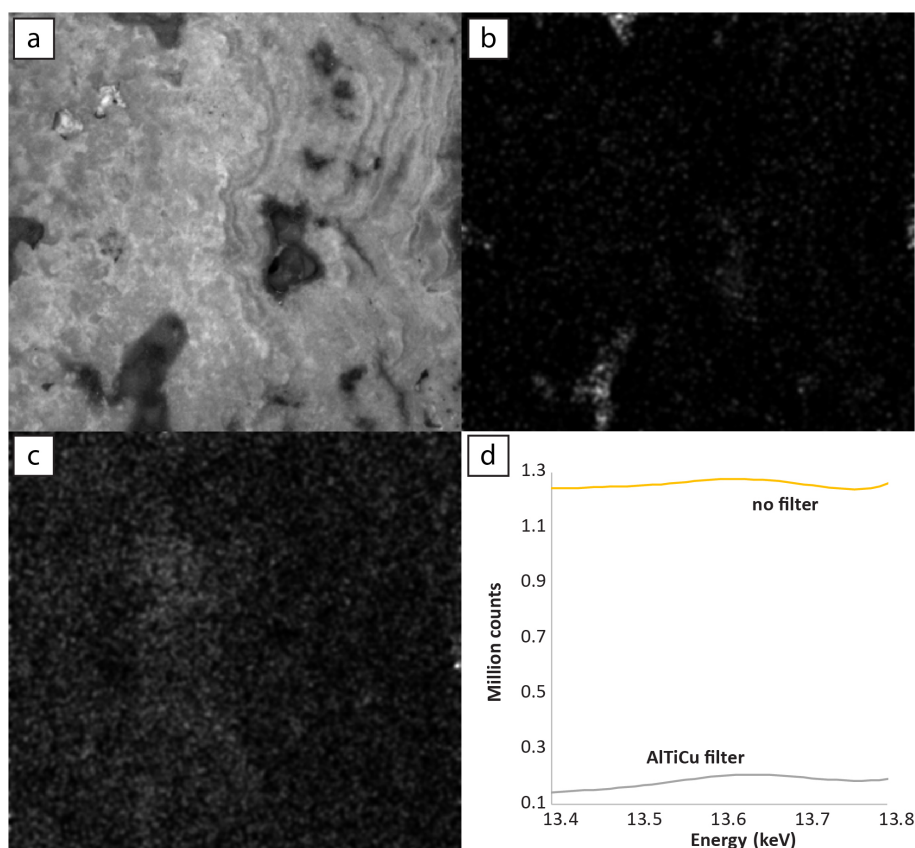


Figure 12. Comparison of U–L α maps of Barstow tufa, imaged at 25 μm pixels with a 400 ms per pixel dwell time and 1.5 SD Gaussian blur: (a) sample image; (b) no incident radiation filter; (c) incident radiation filtered with 100 μm Al, 50 μm Ti, and 20 μm Cu foil; (d) sum spectra of total counts in the U–L α line region.

and likely cemented penecontemporaneously with reef deposition. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.7069 to 0.7072 (Fig. 6), with an average of 0.706930 (.000069) for samples that make up the bulk of the dike. These values are similar to what Chafetz et al. (2008) reported from samples with primary aragonite from peritidal teepee structures in the correlative Tansill Formation of the Permian reef complex and are consistent with the Capitanian age of the Tansill reef. Samples at the center of the dike (youngest position) give $^{87}\text{Sr}/^{86}\text{Sr}$ near 0.7072 (Fig. 6). Without more work it is not possible to know whether the variation with position from the host is due to diagenesis or if it captures real changes in seawater through the growth of the cements. Rasbury et al. (2004) dated similar cements from the algal mounds of the Laborcita Formation in the Sacramento Mountains of New Mexico and obtained ages and $^{87}\text{Sr}/^{86}\text{Sr}$ that were also consistent with the biostratigraphically constrained age of deposition.

Laser ablation maps of WC-1 are presented in Roberts et al. (2017). Sr concentrations range up to 7000 ppm, and regions with high Sr have high U. Magnesium is elevated in veins along with V and Mn, as is also shown with μXRF (Fig. 4) and TES (Fig. 7). While LA and μXRF do not offer

the high resolution of synchrotron XRF, they do provide details at the scale that LA dating could be accomplished and few elements are inaccessible with quadrupole mass spectrometers.

High-resolution, on-the-fly (the sample is continually moving and the detector is accumulating counts over a prescribed distance) element mapping in the tender energy range (TES) allows us to examine U, Mg, Sr, and S in the Walnut Canyon sample. Comparing U, S, and Sr in an RGB map (Fig. 7) illustrates the spotty retention of Sr and S relative to U. As seen in the μXRF images (Fig. 4), Mg is elevated in veins and is thus introduced by later fluids. U M_5 XANES (X-ray adsorption near-edge spectroscopy) shows that the botryoidal cements have entirely oxidized U (Fig. 8). Uranium concentration in this sample is less than 5 ppm, and the ability to explore U oxidation states at this concentration is a major advance. An important factor to be considered for exploring for favorable U/Pb in carbonates is how U is incorporated. In the Walnut Canyon case we hypothesize the uranyl was brought to the site of precipitation by an oxidizing fluid (seawater) and structurally incorporated in aragonite which does not exclude U (Reeder et al., 2001; Kelly et al., 2003). Through neomorphism to calcite, U was left behind because

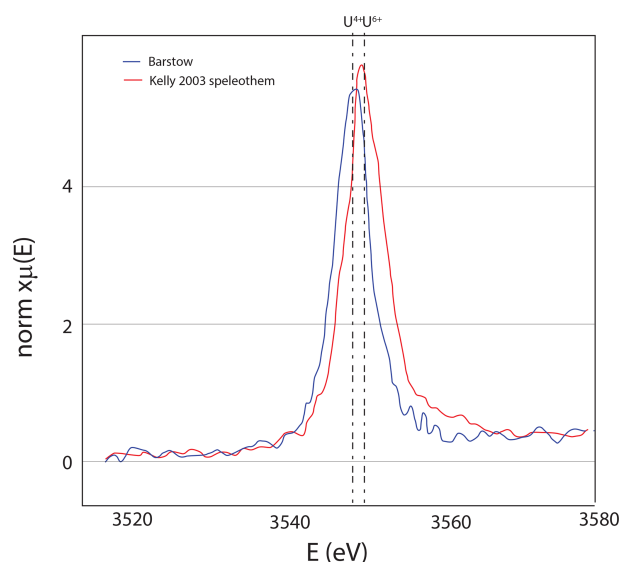


Figure 13. Uranium M_5 edge spectroscopy showing that uranium is in the reduced state; for reference, the U^{6+} speleothem of Kelly et al. (2003) is shown as well. Both datasets were measured at the TES beamline as described in Fig. 8.

active functional groups such as carboxyl have a high affinity for uranyl. Perhaps calcite grew around these complexed U ions preserving near original U concentrations. In contrast, Sr, which is also strongly partitioned into aragonite but has a lower affinity for calcite, was lost to the fluid because it does not have an affinity for organic matter.

2.2 Middle Miocene tufa – Barstow formation

The Middle Miocene Barstow Formation crops out in the Rainbow Basin near Barstow, California. Tufa mounds are found near the top of the Owl Conglomerate (Cole et al., 2004, 2005) and are assumed to have formed where springs entered a lake similar to the Mono Lake and Pyramid Lake tufa towers. These tufa deposits have more than 100 ppm U, several parts per million of Pb, and favorable U–Pb systematics (Cole et al., 2005). Here we build on the work of Cole et al. (2004, 2005) with additional synchrotron imaging, μ XRF imaging, and spectroscopy techniques. The sample that we are using to illustrate these tools for characterization is large enough to be suitable for distribution as a secondary reference material for LA carbonate dating (Fig. 9). Most of the samples used in the Cole et al. (2005) study were small to be distributed beyond our lab. Here, we are characterizing a new sample that is large enough to distribute widely. The previously studied tufa samples ranged in age from 14.8 ± 0.3 to 16.2 ± 0.2 Ma (Cole et al., 2005), so more work will be needed to determine the exact age of this sample.

Becker et al. (2001) showed that layers in the Barstow tufa deposits have a pattern of low (10 ppm) to high (sev-

Table 1. $^{87}\text{Sr}/^{86}\text{Sr}$ from aliquots of the Barstow tufa run by thermal ionization mass spectrometry.

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	2 SD
BT1	0.720423	0.000011
BT2	0.721038	0.000011
BT3	0.719877	0.000011

eral hundred parts per million) U concentrations across laminae revealed by fission track mapping. Uranium is lower at the base of laminae where larger crystals of calcite formed and is higher in the micritic calcite that forms the caps of laminae. Becker et al. (2001) reasoned that the laminae reflect seasonal increases in the freshwater supply that delivers Ca to a body of water with high alkalinity similar to the Great Basin Lakes. Phosphor imaging shows that in addition to the fine-scale trends observed with fission tracks, there are millimeter- to centimeter-scale layers of higher and lower U concentrations (Cole et al., 2004).

Synchrotron and μ XRF imaging of Sr and Mn faithfully matches the primary layering, demonstrating that later alteration has been minor (Figs. 10, 11). A comparison of U– $L\alpha$ maps with and without an incident radiation filter shows that the filter eliminates artifacts that result from scatter in pores and returns an accurate map of the U (Fig. 12). The filtered U μ XRF map shows that U is elevated in the micritic areas of the tufa. μ XRF maps of Al and Si show that large pores that are typical of the tufa deposits have clay minerals lining them (Fig. 11). Fe, Cu, and Zn are also elevated in the pores. A map of Ba closely matches the S map, suggesting that barite may be present. Strontianite is found in economic abundance in the Barstow Formation (Knopf, 1917). The extremely high Sr concentrations in the tufa calcite (tens of thousands of parts per million), suggests these fluids were contributing Sr during deposition. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of three aliquots ranged from 0.719877 to 0.721038 (Table 1). More work will be needed to determine if this sample can be a Sr isotope reference material as well as a secondary U/Pb carbonate reference material.

The U in these tufas is in the reduced state (U^{4+}), as shown by measurements at the U L_3 edge (Cole et al., 2004) and new data from the U M_5 edge (Fig. 13). With the high U concentration, the Barstow tufa could be a reference material for U XANES analyses. The Barstow tufa calcite is luminescent throughout (Fig. 14), consistent with the occurrence of reduced U in this sample. While it is easy to conceive of a stratified lake with reducing bottom waters, reduced U is insoluble in most solutions (Langmuir, 1978), begging the question of how it is available to go into the calcite. Elevated actinide concentrations are found in the Great Basin lakes, and it is thought that the carbonate alkalinity is responsible for this elevation (Anderson et al., 1982; Simpson et al., 1982). Similarly, Tullborg et al. (2017) demonstrates U^{6+} complexes in

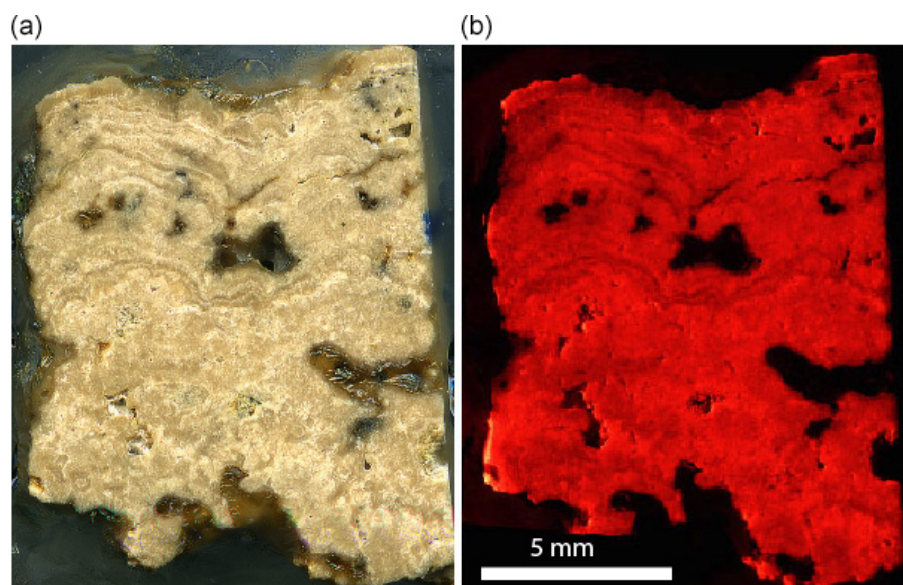


Figure 14. Slab from the Barstow Formation tufa sample that is being characterized for a possible secondary LAcarb standard. The fine laminae are like those described by Becker et al. (2001). The left image is a scan of the slab. The right image is a CL photomosaic from 360 images. Generally, the more micritic areas have a brighter luminescence, and the sparry layers have a duller luminescence.

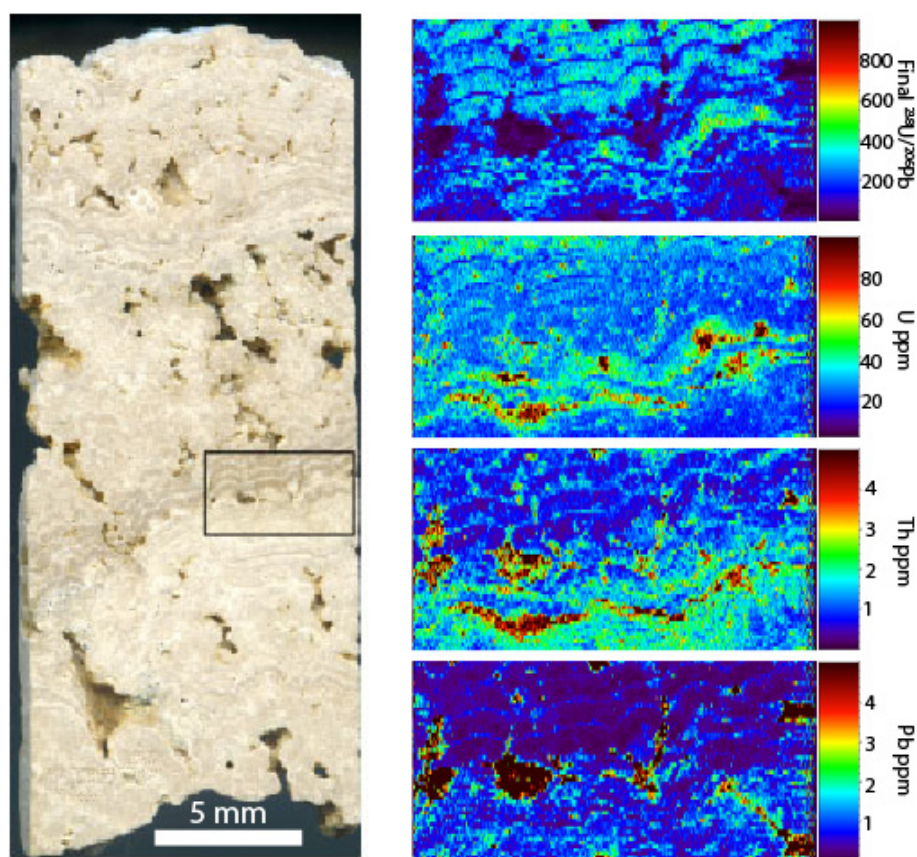


Figure 15. Slab of the Barstow tufa, approximately 1 cm wide. The box shows the location of the LA map, which is approximately 5 mm wide. Note that the pores have high U, Th, and Pb concentrations but unfavorable U/Pb. The laminae have the most favorable U/Pb because Pb is lower (mostly lower than 1 ppm).

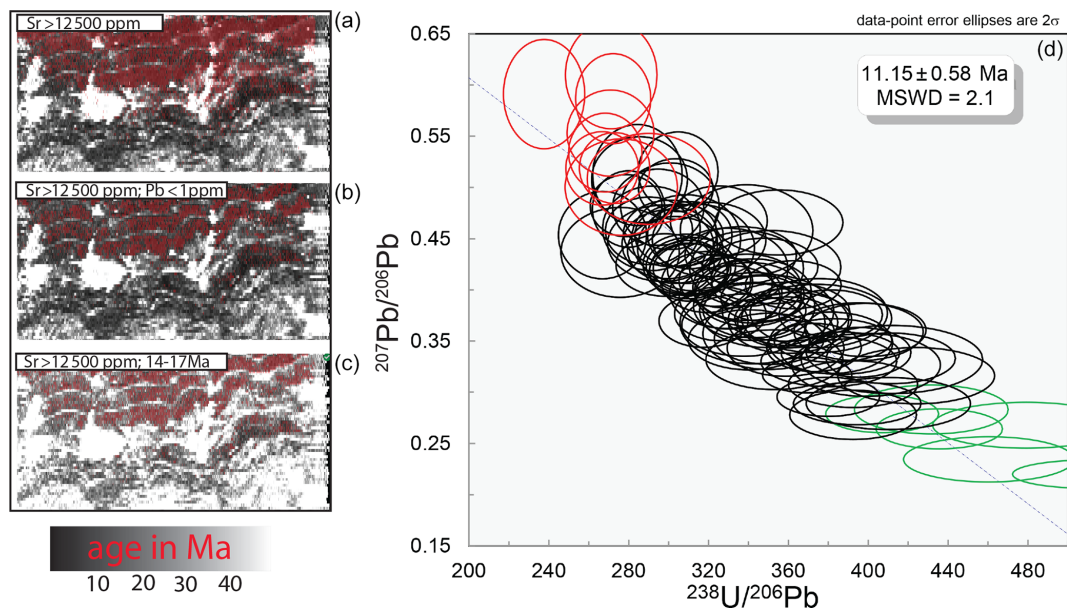


Figure 16. The base map for all ^{238}U – ^{206}Pb ages. This is the same map from Fig. 15 and is about 5 mm wide. In the top map, the red pixels are greater than 12 500 ppm Sr. Red pixels in the middle map are also greater than 12 500 ppm Sr, and the Pb concentration is less than 1 ppm. Red pixels in the lower map are greater than 12 500 ppm Sr and have an age range from 14 to 17 Ma with no correction for common Pb. The isochron plot is a binning of all of the red pixels from the second map (Sr concentrations greater than 12 500 ppm and Pb concentrations less than 1 ppm). Red and green data points represent the low and high tails, respectively.



Figure 17. Hand samples of the Turkana dolomite sample: both samples came from an area where carbonates were coating tree trunks. The big sample is taken from a very large cavity that was filled by calcite, then by the yellow dolomite that is peeking out, and finally by a coating of grey calcite. The smaller triangular-shaped sample has a bark texture on the outside and appears to have precipitated in the cavity between three logs. The thickness of the dolomite layer is about 2 cm and it coats every surface in this paleo-log pile. The small slabs come from the smaller of the two samples. The image on the left is the scanned slab used for XRF studies, and the one on the right is a CL photo mosaic with 459 photos.

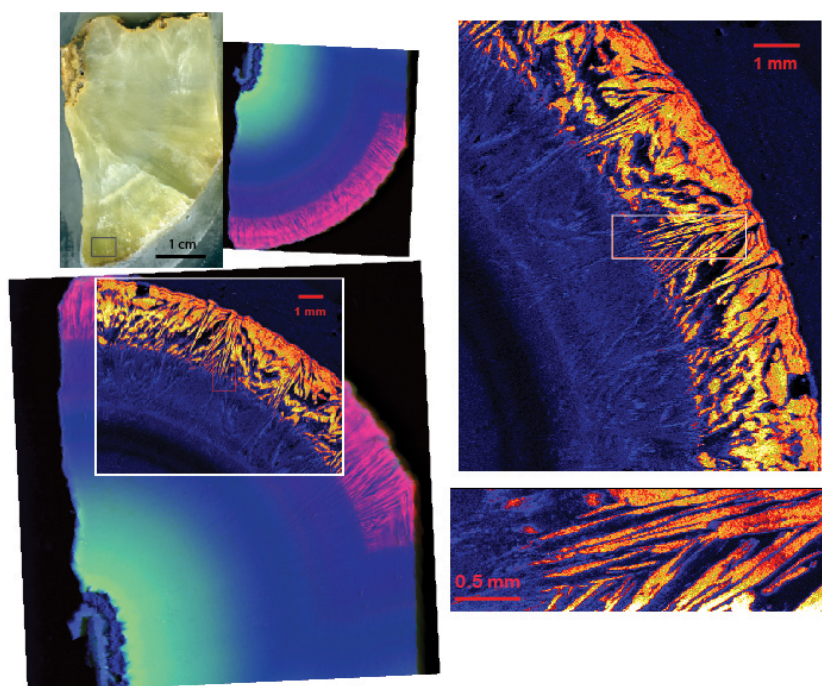


Figure 18. Slab of the dolomite with on-the-fly synchrotron XRF images. The rectangle at the bottom of the sample is the approximate location of the LA maps in Fig. 21. Directly to the right of the slab image is an RGB (U Sr Ca) map from beamline XFM at the NSLS II. The images on the right are maps of U from TES. On the lower left, the TES U map is overlain on the same area that was mapped at XFM. The XFM mapping was done at 17 keV with a 10 μm beam, a 10 μm step size, and a counting time of 0.1 s. The large TES map was made at 3550 eV with an 18 μm beam and 20 μm pixels, counting for 0.3 s. The detail map on the bottom right was also made at 3550 eV with a 4 μm beam and 3.75 μm pixels, counting for 0.3 s.

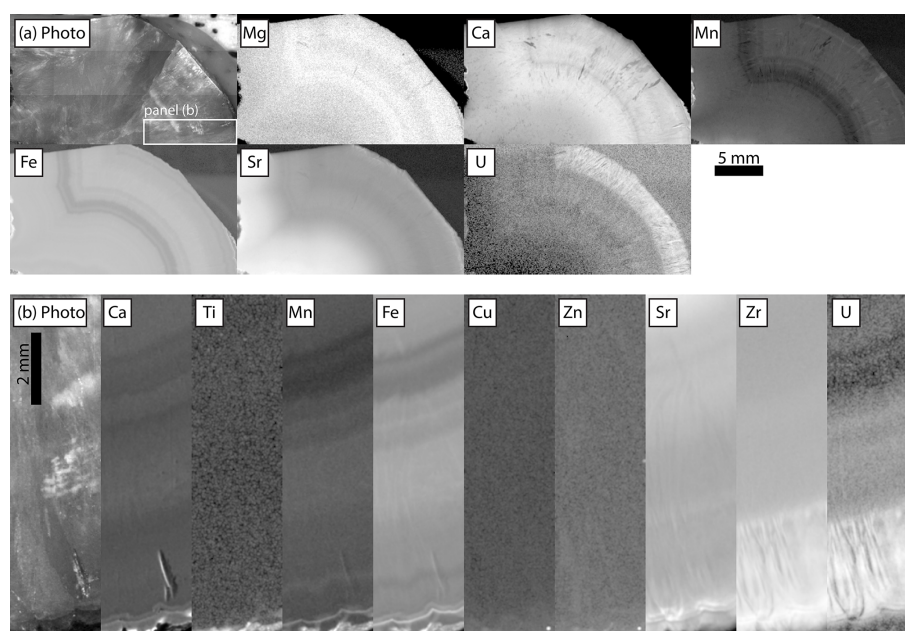


Figure 19. Relative intensities of emission regions for each element detected in Turkana dolomite. Each panel is adjusted in terms of gamma and contrast to emphasize gradients between texture: **(a)** no incident radiation filter, imaged at 25 μm pixels, with 120 ms per pixel dwell time and 1.5 SD Gaussian blur, and the box indicating the region that was re-mapped with the filter shown in **(b)**. **(b)** Incident radiation filtered using 100 μm Al, 50 μm Ti, 20 μm Cu foil, imaged at 20 μm pixels with 900 ms per pixel dwell time and 1.5 SD Gaussian blur.

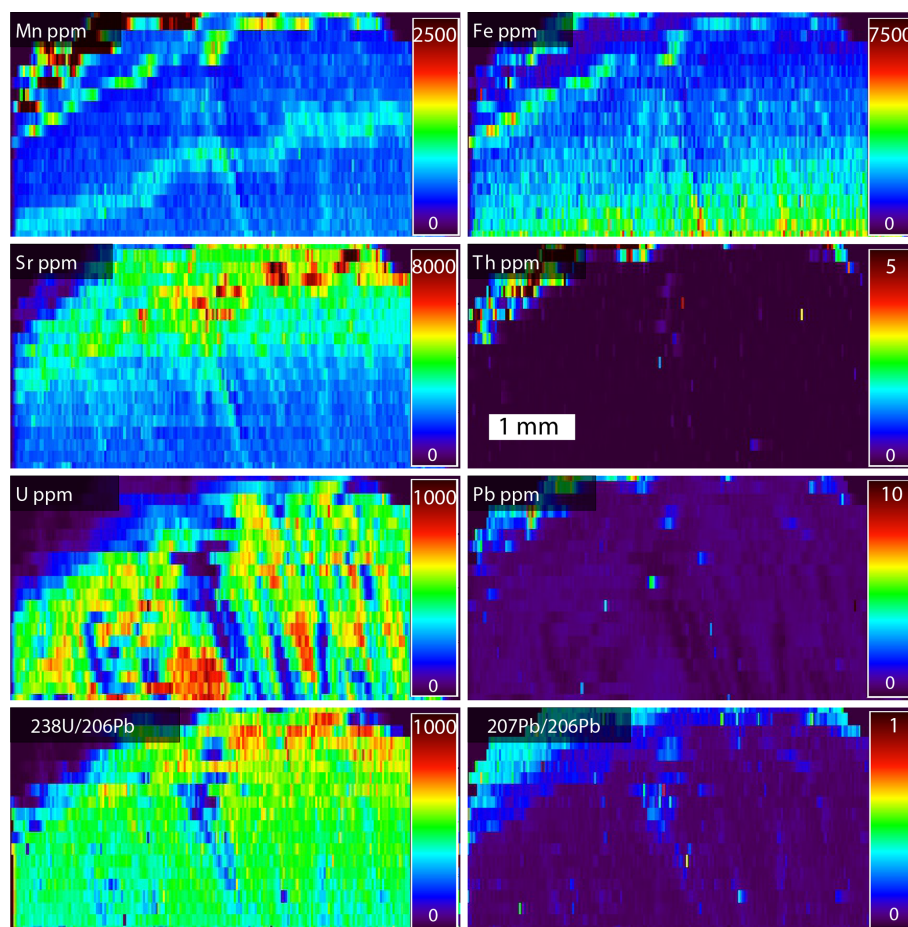


Figure 20. Laser ablation ICPMS map of the Turkana Basin Wood (TBW) dolomite. The mapped area is from near the box shown in the slab on Fig. 18. The area mapped is approximately 5 mm wide. U is high concentration, while Pb and Th are low concentration. The U/Pb ratio is very favorable.

extremely reducing fluids of deep groundwaters in Sweden. It seems clear that there is a kinetic barrier to U reduction even in the most reducing fluids, and yet some carbonates have entirely reduced U in their structures (Sturchio, 1998; Cole et al., 2004). More work is needed to understand the incorporation mechanism and use of synchrotron facilities to image the distribution of U with respect to other elements, and XAS measurements of U and other redox-sensitive elements are important tools for advancing this research. Additionally, lab-directed studies that can produce U^{4+} in carbonates would be a huge leap forward.

One of the biggest advances in LAcarb dating is a contribution by Drost et al. (2018) that used laser ablation imaging and inspection for concentrations or ratios that reflect something that could be considered to be related (like Sr concentrations). Pooling of pixels based on these criteria from across the mapped region and binning based on some additional criteria like $^{235}U/^{207}Pb$ gives isochron plots with a range of values that is typically greater (and certainly more filled in) than would be obtained by spot analyses. The ap-

proach is justified because it would not be possible to select pixels based on criteria other than the ratios being plotted that would have a meaningful isochron result if the assumption were invalid. This work built on a monocle approach introduced by Petrus et al. (2017), which provided a visual tool to easily compare maps, ratios, and patterns (such as Rare Earth Element, REE, patterns) that can be defined by the user. This package of tools is available in Iolite3 and Iolite4 and, beyond U–Pb dating, offers tremendous potential to better understand relationships between elements and how that relates to deposition and diagenesis. Inspired by the Drost et al. (2018) contribution, we performed 45 laser ablation lines on the Barstow tufa (Fig. 15). We used Iolite4 (Paton et al., 2011) for the data reduction. Note that the laminae are easily visible in Fig. 15. While the U concentration is not as high in the sparry calcite layers, the U/Th and $^{238}U/^{206}Pb$ ratios are much higher than the micritic calcite (Fig. 15). Similarly, the $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ are much lower, showing the radiogenic ingrowth of ^{206}Pb . Sr and Mg concentrations are elevated in the sparry calcite, and thus μ XRF maps of slabs

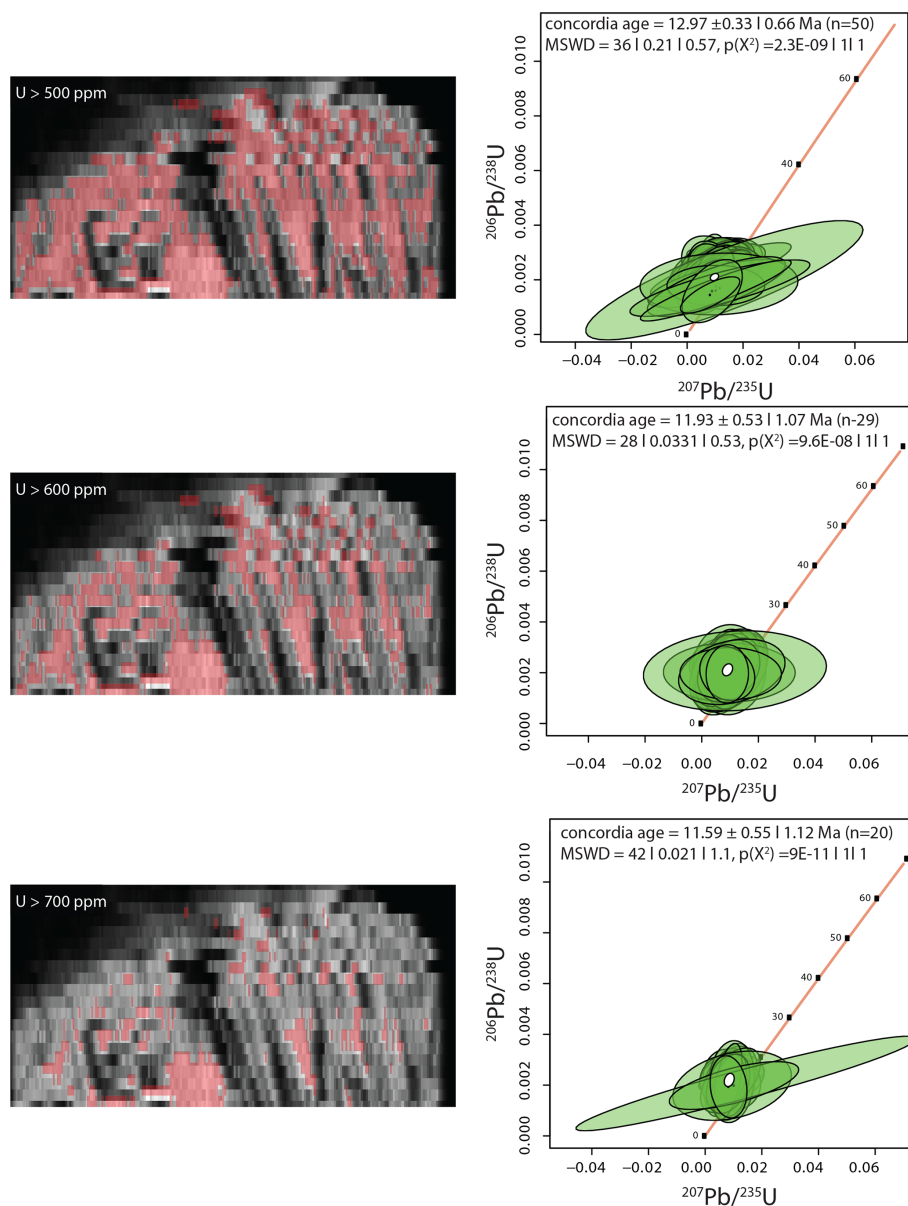


Figure 21. Map of U. Regions are selected based on U concentration as noted on the maps. Pooling pixels are based on U greater than 500, 600, and 700 ppm. The data are plotted in IsoplotR (Vermeesch, 2018). No corrections for Pb are made because we do not know if there is a bias between calcite and dolomite.

would provide a framework for selection of spots for LAcarb (Fig. 11). We extracted pixels based on the criteria that they were greater than 12 500 ppm Sr. We used this value based on the monocle feature in Iolite4, which allowed us to see that this would eliminate most of the pixels outside the sparry calcite (Fig. 16). Nearly 7000 pixels meet the criteria for being greater than 12 500 ppm Sr and less than 1 ppm ^{208}Pb . These were subdivided into 90 bins of 70–80 pixels each based on probability of the $^{207}\text{Pb}/^{235}\text{U}$ ratio (e.g., Drost et al., 2018). When all the bins are plotted on a Tera–Wasserburg concordia plot in Isoplot (Ludwig, 2003), there are tails on the low and high ends of the line. Removing 10 % on each end pro-

duces a much better line (Fig. 16). An age of 11 Ma is about 20 % too young. We did not make a correction because we do not know the age of this sample, but a correction could be made based on the secondary reference material and applied to unknowns. The purpose here is not to provide the age but to show that the sample is very well behaved. Pre-screening with μXRF to establish the best regions to use for LAcarb should produce a reproducible secondary reference material for quality assurance and quality control.

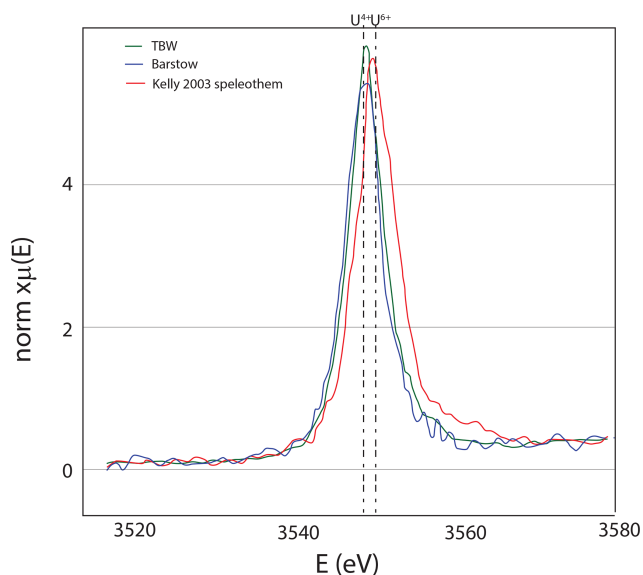


Figure 22. U M_5 edge spectroscopy of the TBW sample showing that uranium is in the reduced state; for reference, the U^{6+} speleothem of Kelly et al. (2003) is also shown. Both samples were measured at the TES beamline as described in Fig. 8.

2.3 Middle Miocene dolomite

A Miocene conglomerate horizon in the Napenagila fossil locality of the Turkana Basin in Kenya is extensively cemented by calcite and dolomite. The dolomite is unique in a number of ways. It forms an isopachous layer on surfaces of fossil trees, showing that it formed in the saturated zone. It has a bladed habit, and is a bright yellow color, becoming darker yellow in the growth direction (Fig. 17). While only an outer crust of the sample has typical bright orange luminescence, the sample glows in the luminescope (Fig. 17). The dolomite has variable trace element concentrations along the growth direction, and extreme U enrichment in the final phases of growth as shown by synchrotron XRF element mapping (Fig. 18), μ XRF (Fig. 19) and laser ablation (Fig. 20). The bladed morphology of the dolomite crystals is strongly emphasized by trace element patterns in the youngest part of the dolomite and is particularly striking in the very high-resolution maps from TES (Fig. 18). U M_5 XANES shows that the U in the dolomite is in the reduced state (Fig. 22). The stratigraphic context of this dolomite and other carbonates from the Turkana Basin is being studied by Kevin Hutton and will be presented in a more comprehensive way elsewhere. Meanwhile, the very well-behaved U–Pb systematics make this a possible dolomite reference material, and the XRF mapping and X-ray spectroscopy make it a good example for carbonate characterization. The $^{238}\text{U}/^{206}\text{Pb}$ ratios for the dolomite sample range from 250 to 550. Using a selection criteria of U concentrations greater than 500, 600, and 700 ppm and ^{208}Pb less than 0.3 ppm produces over 1683, 1043, and 452 pixels. Binning the pixels into 50, 30, 20 pixel

Table 2. $^{87}\text{Sr}/^{86}\text{Sr}$ from aliquots of the Turkana dolomite run by thermal ionization mass spectrometry.

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	2 SD
TBWi-1	0.703309	0.000011
TBWi-2	0.703299	0.000011
TBWo-1	0.703306	0.000011
TBWo-2	0.703312	0.000011

bins produces data that form a small cluster that does not lead itself to the isochron approach. Plotted on the Wetherill-type concordia plot, the data overlap with concordia and give a nominal age of an age of about 12 Ma (Fig. 21). Based on the Barstow results the age is likely slightly older. However, because this is a dolomite, more work is needed to understand how the different matrix will affect the U/Pb fractionation.

$^{87}\text{Sr}/^{86}\text{Sr}$ of three aliquots of the Turkana dolomite from the outside (oldest) to the inside (youngest) are indistinguishable from each other at 0.703306 (Table 2). With the well-behaved U–Pb systematics, high concentrations of reduced U and homogeneous $^{87}\text{Sr}/^{86}\text{Sr}$, and further work in collaboration with other labs, this sample could be a reference material for U–Pb dating, Sr isotopes, and synchrotron U spectroscopy.

3 Summary

Field relationships and petrography allow us to consider the relative timing of carbonate precipitation and alteration, and the tools for demonstrating these relationships are an important first step to any study. XRF mapping (both μ XRF and synchrotron XRF) and laser ablation mapping allows us to establish domains within rocks that are equivalent in time and to work out details of the fluids that were responsible for carbonate precipitation. Details such as the U concentration and its oxidation state compared to the concentrations of other elements helps to further constrain the geochemistry of the fluids that produced the final product. While the U oxidation state does not appear to matter for the reliability of U–Pb ages, a general pattern of elevated U is emerging for samples with reduced U. While elevated U is not necessary for U–Pb dating, samples that are amenable to LAcarb dating typically must have part-per-million-level amounts of U. The tools we have described here allow us to provide a spatial context that together with well-established petrography and field relationships are foundational for putting U–Pb ages into the overall geologic context.

Data availability. The data used in this paper are available on figshare: <https://doi.org/10.6084/m9.figshare.13604306> (last access: 18 January 2021, Rasbury et al., 2021).

Author contributions. ETR led the effort to review the literature on carbonate characterization. TMP did the μ XRF imaging of the carbonate standard materials. PN, RVT, and AL led the efforts for the synchrotron XRF and XANES measurements. KMW and KH led the laser ablation mapping efforts. KMW did the Sr isotope analyses. JMC did the work on the Barstow tufa. All of the authors contributed to writing the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

Special issue statement. This article is part of the special issue “In situ carbonate U–Pb geochronology”. It is a result of the Goldschmidt conference, Barcelona, Spain, 18–23 August 2019.

Acknowledgements. Portions of this work were performed at beamline X26A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. X26A was supported by the Department of Energy (DOE) – Geosciences (DE-FG02-92ER14244 to The University of Chicago – CARS). Use of the NSLS was supported by the DOE under contract no. DE-AC02-98CH10886. Portions of this research were also performed at the Tender Energy Spectroscopy (TES), X-ray Fluorescence Microprobe (XFM), and Submicron Resolution X-ray Spectroscopy (SRX) beamlines and used resources of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under contract no. DE-SC0012704. Construction of and work at the TES beamline was partly funded by the National Science Foundation, Earth Sciences (EAR-1128957); NASA (NNX13AD12G); and the Department of Energy, Geosciences (DE-FG02-12ER16342). μ XRF data were acquired in the Caltech GPS Division Analytical Facility with the support of Chi Ma, John Grotzinger, and the Simons Foundation. We thank Stephen Cox, Frank Sousa, Elena Steponaitis, and Sidney Hemming for the discovery of the dolomite in the Turkana Basin and acknowledge funding from the Columbia University Global Center for field work. Numerous discussions with Bruce Ward have greatly improved our understanding of carbonates. Journal reviewers Don Davis and an anonymous reviewer and associate editors Nick Roberts and Klaus Mezger are thanked for their thoughtful comments which help improve the clarity of the manuscript.

Financial support. Some instrumentation that was used in this study was funded by the DOE (grant nos. DE-FG02-92ER14244, DE-AC02-98CH10886, DE-SC0012704, DE-FG02-12ER16342), NSF (grant no. EAR-1128957), and NASA (grant no. NNX13AD12G). However, this work was not funded by any agency.

Review statement. This paper was edited by Nick Roberts and reviewed by Donald Davis and one anonymous referee.

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