Timescales of faulting through calcite geochronology: A review

Nick M.W. Roberts [a,*], Robert E. Holdsworth [b]

[a] Geochronology and Tracers Facility, British Geological Survey, Nottingham, NG12 5GG, UK
[b] Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK

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ABSTRACT

Calcite is a common mineral precipitated within upper crustal fault zones and associated fractures, forming veins, mineral cements and fault coatings. It has the potential to be dated using several radioisotopic systems if parent/daughter isotope abundances are suitable for the currently available analytical techniques. U-Pb dating can be most readily achieved using the *in-situ* laser ablation technique, which has led to a rapid growth area in the U-Pb dating of calcite. The ability to constrain the timing of fault slip hinges critically on the ability to confidently link calcite precipitation to fault movement and/or spatially and temporally associated fracture opening which requires careful microstructural and petrographic documentation. We discuss the varying reliability of different fracture fill types to make these links, and demonstrate that crack-seal-slip fills associated with faults are the most suitable for unambiguously linking calcite growth to phases of fault slip. Previous applications of the U-Pb and U-Th methods to natural examples at a range of temporal and spatial scales are reviewed, in particular their implications for the timescales of faulting and for the rates of fracture-filling. We then highlight the main limitations of the method, and provide a brief commentary on future directions.

1. Introduction

It is important to understand faulting and fracturing in the upper crust to make best use of the subsurface for the extraction and storage of natural and anthropogenic materials, and to understand the hazards posed by active crustal faults. The development of crustal faults also provides insights into plate boundary interaction and crustal deformation processes past and present. Although faults and associated fracture zones have been studied for several decades, the absolute timing of fault slip and fracture formation has in general remained a poorly constrained parameter. Indirect dating methods include using the timing of uplift using thermochronology (e.g. Brichau et al., 2006), exposure dating of geomorphological features (e.g. Brown et al., 2002), and dating of structures offset by displacement (e.g. Searle et al., 2010). Direct dating of ductile deformation (shear) zones is potentially more straightforward as it can utilise the growth/overgrowth or isotopic resetting of moderate to high temperature minerals (>400 °C) such as mica, zircon, monazite and titanite, to infer when shearing was active (e.g. Mottram et al., 2015; Viola et al., 2016). Beyond the timescales of surface exposure dating, the direct dating of faults in the brittle regime requires the presence of mineralization formed during or shortly after slip, either in gouge, veins or along fault surfaces (e.g. Eyal et al., 1992; van der Pluijm et al., 2001;

Ault et al., 2015; Dichiarante et al., 2016). One of the most widespread syn-tectonic upper crustal mineral precipitates is calcite, commonly occurring along shear fractures or faults as slickenfibres and in fault-related opening-mode fractures as veins. If calcite can be reliably dated, and can be shown to have grown at the time of fault-slip and/or regional deformation events, then it offers a method that has wide applicability across many upper crustal deformation zones.

Here, we present a summary of recent progress in calcite geochronology applied to upper crustal faults that has seen a rapid adoption of this method, and show that this is opening new avenues of investigation in structural geology. We focus our attention here on fault-related structures, rather than opening-mode fractures (or veins) in general. Although not specifically covering geochronology, the review of Laubach et al. (2019) provides an excellent synopsis of opening-mode fracture cements and fills which should also be used as a reference source for calcite cement dating studies in general. With regard to fold-related structures, Lacombe et al. (2021) also provide detail on several associated mineralization structure types than can potentially be dated using calcite fills. Here, we discuss the importance of linking the dating of mineralization to fault movement and fracture opening, which represents a critical, but currently somewhat underdeveloped keystone of this geochronological application.

* Corresponding author.
  E-mail address: nirob@bgs.ac.uk (N.M.W. Roberts).

2. The calcite chronometer

Calcite ($CaCO_3$), a trigonal mineral, and the most stable form of calcium carbonate, is commonly found precipitated within opening mode fractures and along fault planes in a wide variety of host lithologies and tectonic settings. These are commonly termed 'veins', but as Gale et al. (2014) point out, the term is used somewhat inconsistently. Calcite incorporates various metals at the trace level which can act as potential radioisotopic chronometers (Jahn and Cuvellier, 1994; Rasbury et al., 2009). Most commonly utilised is uranium, which can be dated through decay to its final daughter product, lead (U-Pb geochronology) or via decay to its intermediate daughter products ^{234}U and ^{230}Th (U-Th geochronology). U-Th geochronology is applicable over timeframes ranging from several years to around 600,000 ka (Edwards et al., 1987; Williams et al., 2017), although it requires very high analytical precision at the older end of this age range. U-Pb geochronology is theoretically applicable across the entire geological timescale, but is most commonly used beyond the realm of U-Th dating at > 1 Ma, and within the Phanerozoic eon (Roberts et al., 2020). The Sm-Nd isotopic system has been utilised in several past studies, mostly for hydrothermal carbonates in economic mineral deposits (e.g. Peng et al., 2003; Uysal et al., 2007; Barker et al., 2009; Sun et al., 2020). Other possible systems in carbonate minerals include Rb-Sr and Lu-Hf (Maas et al., 2021); we will return to these in a later section.

Each radioisotopic system has benefits and limitations. With the exception of U-Pb, all other methods are traditionally achieved through micro-drilling aliquots of the sample, followed by chemical dissolution and chromatography to separate parent and daughter isotopes. This is than followed by analysis with either Thermal Ionisation Mass Spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The spatial resolution of the micro-drilling sampling can be as fine as <100 μm; however, depending on the technique used for measurement and concentration of the isotopes, the volume needed can be considerable (>5 mm^3). Given that hydrothermal calcite is commonly zoned at a very fine scale (e.g. Roberts et al., 2020a), these methods can potentially average out several generations of calcite growth. More recently, the *in-situ* technique, laser ablation ICP-MS (LA-ICP-MS) has been developed for U-Pb in calcite (Li et al., 2014; Ring and Gerdes, 2016; Roberts et al., 2017). Although LA-ICP-MS can also be applied to U-Th dating (Eggins et al., 2005), the method has large uncertainties and requires relatively high U contents compared to that of U-Pb. Use of the LA-ICP-MS technique means that ablation spots on the order of 50–200 μm can be accurately placed within single growth phases and combined to calculate a single date. The benefits and applications of LA-ICP-MS to U-Pb dating of carbonate phases have been extensively reviewed in recent publications (e.g. Woodhead and Petrus, 2019; Roberts et al., 2020a; Kylander-Clark et al., 2020; Guillong et al., 2020; Elisha et al., 2021).

3. Calcite as a syn-kinematic mineral associated with faults

Calcite precipitates within fault zones along individual fault and fracture planes, forming mineral fills and cements that can be discrete or continuous at the outcrop scale. The types and origin of fault-related calcite fills have been reviewed extensively in the literature, e.g. Bons et al. (2012), Gale et al. (2014), Ukar and Laubach (2016) and Laubach et al. (2019) for recent summaries, along with Ramsay et al. (1983), Passchier and Trouw (2005) and Fossen (2016) for relevant book chapters. A key premise of using calcite fill to date the timing of fault slip, is that the dated mineral growth occurred either during fault slip or associated fracture opening, or, shortly thereafter. The notion of 'shortly thereafter' in this context, being that the duration between fault slip and calcite precipitation is smaller than the uncertainties of the dating method. This premise is complicated by the fact that: (1) faults will often be composed of many incremental phases of slip over hundreds to millions of years (e.g. Fossen 2016); and (2) some cements and fills may potentially result from localised chemical diffusional processes that are unrelated to faulting (e.g. Wiltschko and Morse, 2001). A second premise, is that the calcite fill, and in particular, the dated isotopic system, has remained undisturbed by later structural or fluid-related activity (Roberts et al., 2021).

Fig. 1 highlights several common field occurrences of calcite precipitated as a consequence of fracture opening associated with faulting, i.e. the fractures either lie along a fault zone or occur in its associated damage zone. These include: slickenfibres grown along a fault plane with a clear lineation azimuth (Fig. 1a); calcite fills occurring in extensional jogs along a fault plane that exhibits a lineation (Fig. 1b) and multiple phases of deformation (Fig. 1c); calcite fill in a planar opening-mode fracture with no shear displacement (Fig. 1d); a swarm of sub-parallel contemporaneous calcite fills in opening-mode fractures (Fig. 1e); fracture-fill cements that have hosted open fluid-filled space leading to vuggy crystal growth (Fig. 1f); en-echelon fractures filled with calcite formed in association with a fault plane with a sense of shear (e.g. 'wing cracks' Fig. 1g); a cemented fault breccia (Fig. 1h); and an example of a cone-in-cone structure in calcite that is spatially associated with a fault plane (Fig. 1i).

The ability to link calcite mineralization to fault kinematics and associated fracturing processes is dependent on its origin and morphology; critically, this requires an understanding of the microstructure and textures of calcite fills, and can be assisted with the addition of geochemical and compositional information. Fig. 2 schematically shows several types of fracture morphologies that can be cemented with calcite, whilst Fig. 3 shows a range of natural examples viewed in thin section. The fill types and textures shown here are not exhaustive, but include some of those commonly used to directly infer the timing of fault slip and associated fracture opening relative to calcite precipitation (e.g. Roberts and Walker, 2016; Nuriel et al., 2012a, 2017, 2019; Oren et al., 2020; Roberts et al., 2020b; Miranda et al., 2020; Cruset et al., 2020). The purpose here is not to discriminate the only fill morphologies that can be used for geochronology, but to demonstrate that some examples of calcite mineralization can be more confidently linked to fault slip and associated fracturing than others. The cemented fractures shown in Fig. 2 have varying ability to be confidently linked to both the timing and kinematics of fault slip, and are drawn so that those on the left are easiest to unequivocally link to fault slip, whilst those on the right are less reliable. We also highlight common growth morphologies in calcite associated with these vein types. The terminology is purposely restricted to syntaxial and antitaxial to describe growth from the host rock towards the centre of the open void (syntaxial), and from a nucleation point within the void or vein towards the host rock (antitaxial); stretching fibres may exist with both of these opposing growth structures, and various other terms are in use in the literature (see Bons et al., 2012).

Slickenfibres (Type I in Figs. 2 and 3a and b), although a sometimes-misplaced term (in terms of being used more broadly for calcite fault plane precipitation), are generally one of the most desirable forms of fault precipitates in that it provides clear kinematic information such as the azimuth of slip and in many cases the sense of shear. Slickenfibre calcite is a form of fracture-filling cement that fills an extensional jog space that is created in incremental steps (Bons et al., 2012); these are often on a scale that is not discernible to the naked eye, but are clearly seen in thin section. The example of Type II (Figs. 2 and 3a) is a larger pull-apart void space – or jog - that is mineralized during each phase of fault slip, i.e. precipitation is occurring synchronous with movement along the slip plane, as with slickenfibres. Opening mode tensile and hybrid (shear) veins (Type III) may form adjacent to major fault planes, or along minor fractures within fault damage zones. In such cases, it is important to establish the relative timing and kinematic links between fracture-sets and fault displacements where the relationships are evident. For example, it can be demonstrated that vein geometries and opening directions are consistent with the sense of displacement along nearby faults (e.g. Fig. 3a, b, d).
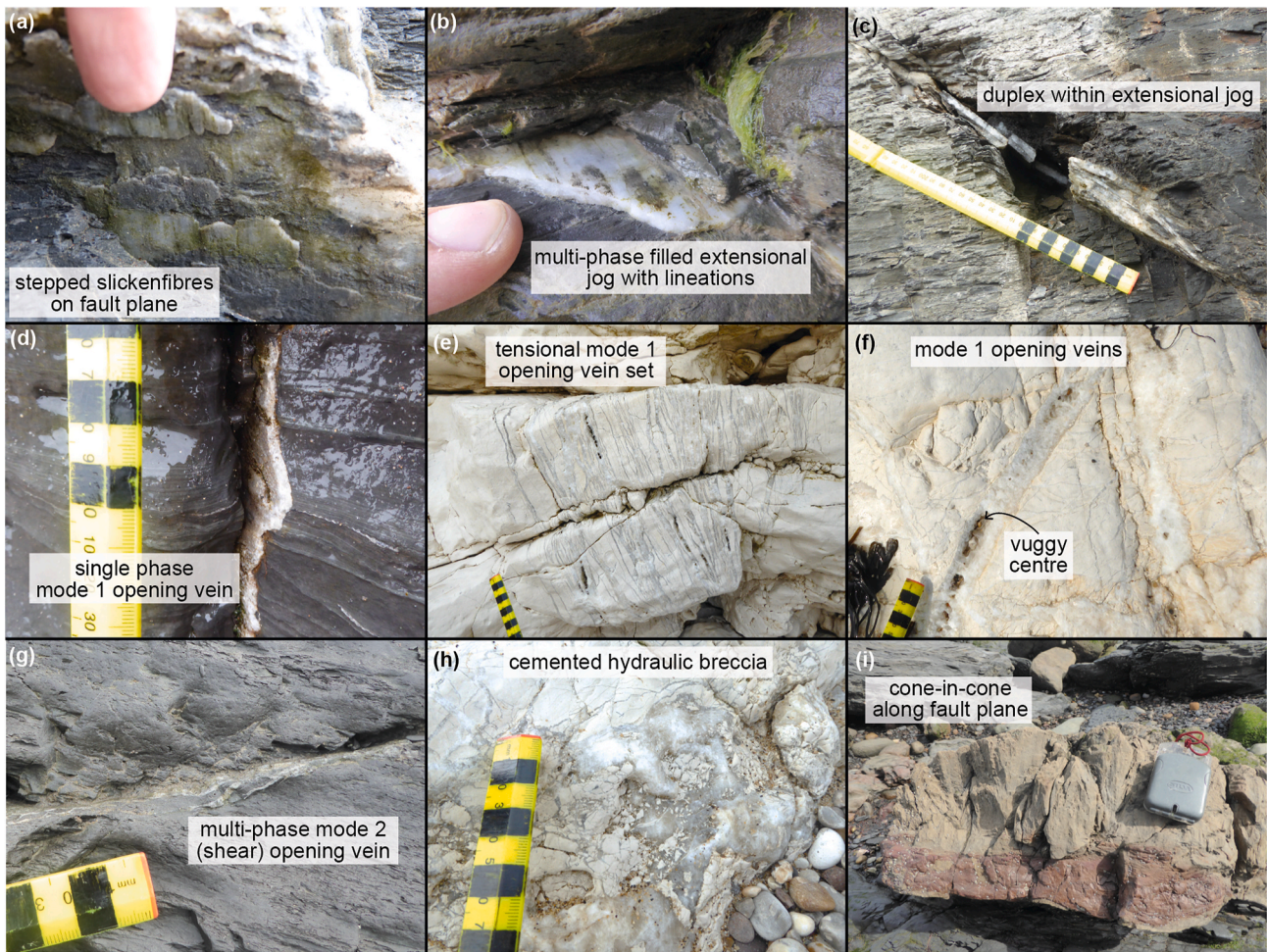
Fig. 1. Field examples of calcite fracture-fills related to faulting. See text for description.
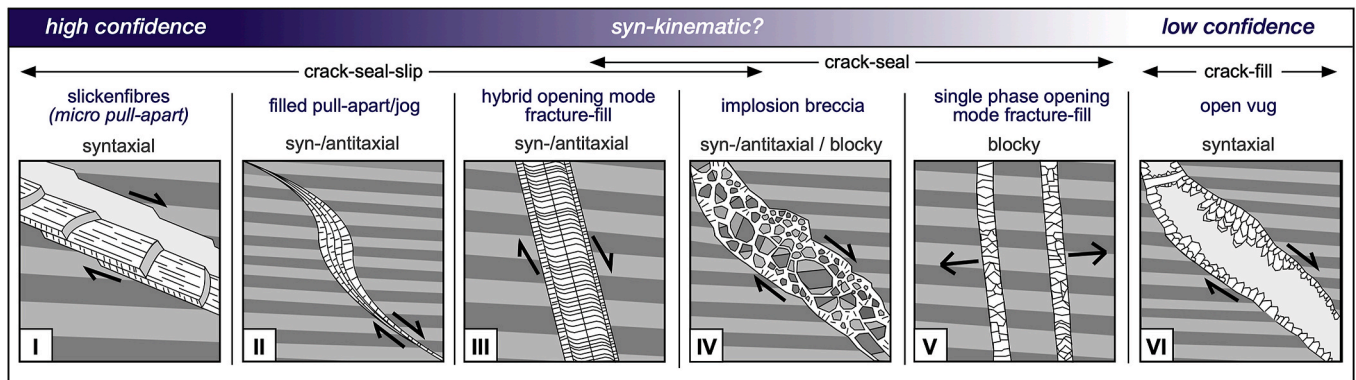

Fig. 2. Types of fault-related calcite fracture-fills (veins); type I modified from Bons et al. (2012). Structures are drawn such that those on the left can be more reliably linked to fault slip kinematics, whereas those on the right are less reliably linked to fault slip and provide poorer fracture kinematic information. Natural examples occur on a range of scales, hence no explicit scale is drawn; however, the change in scale is indicated by the banding of the host rock. Note the bridge and rind structure in Type VI.

The aforementioned varieties all commonly exhibit crack-seal inclusion trails (e.g. Fig. 3b and c) left behind when a fracture opens due to displacement, and is then subsequently sealed by mineralization (Ramsay 1980). Petit et al. (1999) introduced the term 'crack-seal-slip', which is appropriate here, because there is commonly a cyclicity of fault slip along individual fault planes that leads to multiple phases of cracking and sealing. The crack-seal concept has been addressed in a number of studies investigating the role of stress release, dilation rate, fluid pressure and host rock strength, amongst other factors, on the formation of these cement types (Gaviglio, 1986; Lee and Wiltschko, 2000; Hilgers & Urai, 2005; Renard et al., 2005; and Holland & Urai, 2010). Crack-seal-slip cemented fractures along faults commonly display curved or inclined fibrous/elongate mineral growth leading to the development of 'slickenfibre steps', which can be used to infer the sense of shear (e.g. Passchier and Trouw 2005). Because such mineral growth forms synchronously with displacement along shear fractures,
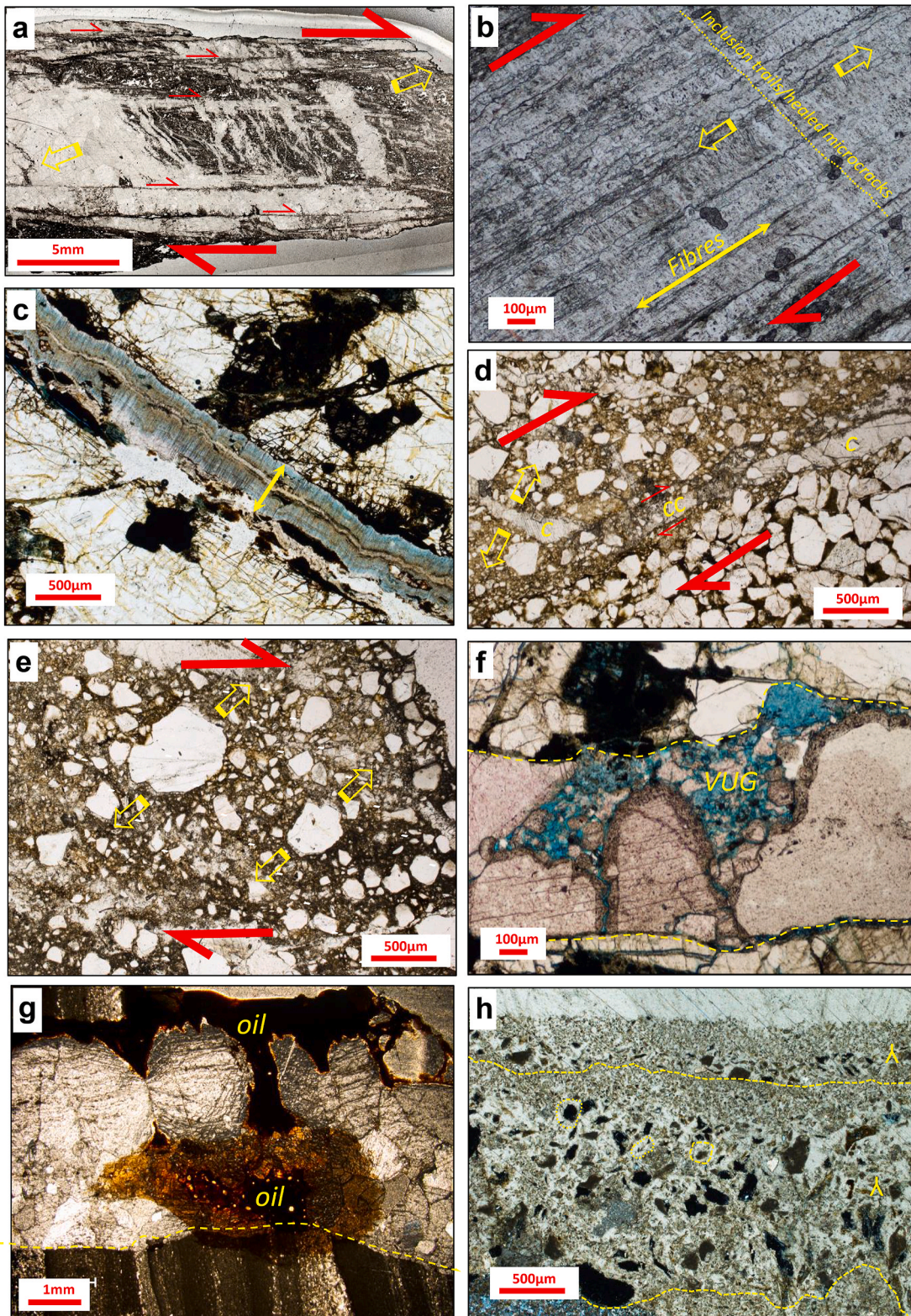
(caption on next page)

Fig. 3. Examples of textures and microstructures that can be used to directly link fault or vein-related displacements to calcite mineralization. All sections cut parallel to local slickenline/fibre lineations in the samples (if present) and are in plane polarized light. Red arrows show senses of shear, whilst yellow arrows show local opening and fibre directions. (a) Stacked dextrally shear and dilational veins in Devonian strata (Inner Moray Firth Basin, New Aberdour, Scotland (from Tamas et al., 2021). (b) High power view of fibres from the same sample as (a) with aligned crack-seal inclusion trails and healed microfractures – note obliquity consistent with dextral shear. (c) Crack-seal fibrous fill of ferroan calcite (stained blue) in tensile vein with oil stains from the Lancaster field basement reservoir (see Holdsworth et al., 2020). (d, e) Calcite cemented and veined cataclasite-gouges from a fault splay of the Great Glen Fault, cutting Jurassic sandstones at Shandwick, Inner Moray Firth Basin, Scotland. Samples collected by Alex Tamas. (d) Calcite veins both cross cut – those labelled 'c' – and are cataclastically deformed – vein labelled 'cc' – by likely recurrent movements along the same dextral fault zone; thus mineralization and faulting are likely broadly contemporaneous. (e) shows gouge from the same fault system with fibrous overgrowths of calcite oriented in a direction consistent with dextral shear. (f) Zoned calcite (pale pink stain) associated with an open vug (filled with blue resin to highlight porosity) from the offshore Lancaster fractured basement reservoir (see Holdsworth et al., 2020). (g) Vuggy calcite vein cutting Devonian laminated siltstone from the Orcadian Basin, N Scotland. Here the vugs are filled with locally derived oil which is contemporaneous with calcite and base metal sulphide mineralization of Permian age (see Dichiarante et al., 2016). (h) Graded sediment suspensions from a calcite mineralized vug, with micro-cockade rims around clasts (examples highlighted). At least two sets of graded infills are seen indicating local way up (younging arrows). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

these types are desirable for confidently linking dated mineral growth to fault slip.

Calcite precipitate Types IV and V may also form from a process akin to 'cracking' and 'sealing', but are single phase, i.e. crack-seal but not crack-seal-slip. This does not mean that the associated host fault only had one phase of slip however, as subsequent slip may have been accommodated along adjacent or nearby fractures (i.e. crack-jump; Caputo and Hancock, 1998). Wall rock clasts in fault-related breccias and gouges (e.g. Type IV) may display overgrowths of calcite – so called strain shadows (see Passchier and Trouw 2005 for a review) – that are also arranged in an orientation consistent with the sense of fault slip (e. g. Fig. 3e).

The last precipitate (Type VI), is associated with the development of vuggy textures (e.g. Fig. 3f and g) and is potentially the least reliable in terms of providing robust timing constraints on fault slip. This is because the time gap between fault slip and precipitation into an open fracture void may be prolonged and could be much greater than the uncertainty of the dating method (Becker et al., 2010; Fall et al., 2012; Nuriel et al., 2012b). The vugs may remain open to the present day or become occluded by later calcite or other minerals. In many examples the calcite may display complex zoning, rind development, bridging structures (single bridge shown in Fig. 2) and even cockade textures consistent with repeated episodes of mineral precipitation and fluid flow (e.g. Fig. 3f; Laubach 2003, Frenzel and Woodcock 2014; Lander and Laubach, 2015). Dates of Type VI can provide minimum dates of fault slip (e. g. Roberts et al., 2020b), but they may also be used to determine the timing of other processes such as the timing of hydrocarbon generation, migration and accumulation (e.g. Fig. 3g; Drake et al., 2019; Holdsworth et al., 2019, 2020). Fault-related open fracture systems of this kind commonly contain sediment fills when formed close to the surface (e.g. Wright et al., 2009; Walker et al., 2011; Holdsworth et al., 2019) and dating of calcite precipitates in such cases may help to constrain the timing of both faulting and regional exhumation (Fig. 3h; Roberts et al., 2020b).

It is clear therefore that, despite the many complexities of natural fault-associated fracture fills, one can usually distinguish pre-, syn- and post-kinematic calcite and other mineralization using careful field observation and petrographic analysis. It is also notable that calcite mineralization shows a remarkably high survival rate following brittle deformation and cataclasis and that even post-kinematic fills are useful as they provide a minimum age for fracture opening. We suggest that fault hosted crack-seal-slip mineral fills are the most desirable for direct dating methods, and are the most reliably identifiable as syn-kinematic; we provide three reasons for our suggestion: (1) they record the direction of slip via mineral growth; (2) individual slip phases can be identified and dated; and (3) they preserve evidence of incremental growth that is unlikely to be preserved should phases of post-faulting fluid-flow and calcite reprecipitation occur. In addition, crack-seal-slip veins often host fluid inclusions which are useful for determining the composition and temperature of fluids at the time of faulting (e.g. Bons et al., 2012). This then allows linking of fracture fill temperatures to burial history

curves (e.g. Becker et al., 2010; Fall et al., 2012, 2016; Laubach et al., 2016). In contrast, it is theoretically possible to overprint simple single-stage veins, breccia cements or crack-fill veins during later phases of fluid-flow, therefore these may be harder to unambiguously link to fault slip. Regarding crystal morphology, although blocky calcite may form as a response to precipitation during fracture opening (Ankit et al., 2013; Spruženiece et al., 2021), it is potentially harder to distinguish from later phases of fluid-flow and vein overprinting than fibrous or elongate growth types.

The above discussion focuses on fault plane precipitation; however, there are other means to use calcite to date fault activity. Notably, through the use of calcite precipitation that occurs due to enhanced fluid-flow during episodes of crustal deformation and hydrothermal mineralization in near surface settings. These most commonly occur in certain regions where geological conditions are ideal, i.e. areas with carbonate-rich lithologies, and hydrothermal fluid circulation. The various forms of these carbonate precipitates, most commonly referred to as travertines, have been used extensively in areas such as Turkey to understand neotectonics (e.g. Temiz et al., 2009, 2013). Brogi et al. (2021) recently reviewed this field of travitonics. Some of the dated structures can be classed as opening-mode (tensile) veins (e.g. Uysal et al., 2011), and can be linked to local fault displacements. Other features are linked to underlying faults through their morphology, such as fissure ridges. In the latter case, the kinematic link is somewhat limited since it is difficult to link calcite precipitation to exact episodes of fault displacement. Also noteworthy is that the same premise has been used for dating of neotectonic activity offshore within continental margins, where carbonate precipitating at methane seeps has been linked to fault reactivation driven by glacial tectonics (e.g. Himmler et al., 2019).

4. Chronology within context

Following the arguments outlined above, detailed structural characterisation of dated material is necessary to make the links between timing of crystal growth and fault slip/fracture opening (Nuriel et al., 2012a, 2012b; Craddock et al., 2021). It is also necessary to elucidate whether primary crystal growth has been preserved, or obliterated by secondary reprecipitation and/or alteration due to later fluid activity; a process that is entirely permissible, even for calcite slickenfibres (Roberts et al., 2021). There are a range of imaging techniques available for micro-structural and compositional characterisation of calcite. Collectively, Rasbury et al. (2021) and Roberts et al. (2020a) provide a synopsis of these with examples for different carbonate occurrences. Although advanced analytical techniques can provide intricate detail on elemental composition, such as U zonation using X-ray fluorescence (XRF) mapping, some of the more readily available methods are the most useful for structural characterisation at the sample scale. Standard microscopy using transmitted and reflected light on well-polished surfaces can provide excellent detail of crystal morphology and the structural relations between growth phases (e.g. see Fig. 3), as well as detail on inclusions. Using microscopy on orientated samples, the twinning of

calcite within and across a sample can be described; calcite twinning can be used an indicator of strain direction, intensity and temperature of deformation (e.g. Rowe and Rutter, 1990; Ferrill et al., 2004; Van der Pluijm et al., 1997). Cathodoluminescence (CL) provides some of the highest resolution levels of elemental zonation, and can be conducted using an SEM, or desktop microscope fitted with a CL detector and vacuum stage. CL remains one of the most common methods for carbonate petrography and microstructure. Elemental mapping using LA-ICP-MS provides compositional information at a useful scale for in-situ geochronology, and reveals detailed compositional variation of elements beyond the detection limits of SEM-based techniques. Information from elemental maps can also be easily correlated with isotopic age information, improving the ability to objectively interpret the resulting data (Drost et al., 2018; Roberts et al., 2020a; Simpson et al., 2021b). Electron back-scatter detection (EBSD) is a less common technique currently for calcite, but can be used to assist with characterisation of calcite growth and deformation structures (Elisha et al., 2021).

The scale of *in-situ* analyses (typically 50–200 μm spots), means that precise location of sample analyses can be achieved with respect to structural and compositional domains. The scale of complexity within calcite fills should not be underestimated however. To demonstrate this, Fig. 4 shows an example of a complex calcite vein with structural domains narrower than 100 μm. The sample comes from a bedding-parallel fracture fill hosted in the Jurassic Whitby Mudstone Formation at Staithes in N England. Minor truncation of bedding laminations is seen in the field images, but the vein extends for over 400 m broadly parallel to the bedding. The CL image shows that at least three different gross structures can be discerned, with syntaxial growth zoning at the upper level, and repeated bands of bladed and fibrous calcite. The latter are inclined, indicating the direction of oblique opening and therefore a component of shear displacement across the fracture. A stylolite indicates dissolution due to vertical/sub-vertical shortening. This example demonstrates that precise placement of ablation spots, or micro-drilled domains, is required to sample individual structural domains and potentially date different stages in the filling and associated fault movement history.

5. Faulting and calcite precipitation timescales

An important concern in the application of calcite geochronology to fault timescales is the duration of time between fault slip (and associated fracture opening) and calcite precipitation. The rates of calcite precipitation and of fracture sealing are also an important consideration in understanding rock strength and permeability in the sub-surface; e.g. because sealed mineral fills can be stronger than the host rock (Caputo and Hancock, 1998). To date, Williams et al. (2019) is the only study which has been carried out with the sole intention of providing accurate constraints on calcite growth rates using absolute geochronology. U-Th dates from the centre and edge of several vein samples provided rates between ca. 0.05–0.8 mm/ka. Several other previous studies exist where multiple dates across single fracture fills have been measured, which can be used to estimate growth rates. Based on continuous precipitation of a coseismic travertine sample 20 cm wide that yields a span of ages over 400 ka, a 0.5 mm/year growth rate can be inferred (Uysal et al., 2007; Karabacak et al., 2019). Karaback et al. (2019) dated the centre and rim of several travertine-type deposits with U-Th, yielding growth rates between 0.1 and 0.11 mm/yrs. Observations of calcite precipitation in modern environments reveal even shorter time-frames. For example, Tulloch (1982) observed growth of platy calcite crystals in a geothermal well of 0.1 mm/day. Such platy (or bladed) crystals occur typically in natural geothermal fractures with high fluid temperatures (McNamara et al., 2016).

Estimates of fracture fill sealing rates can be determined empirically, using the premise that where resolvable ages of fault recurrence can be demonstrated, the sealing rate is likely to be much faster than the measured recurrence rate. At the coarser end of the scale, Craddock et al.
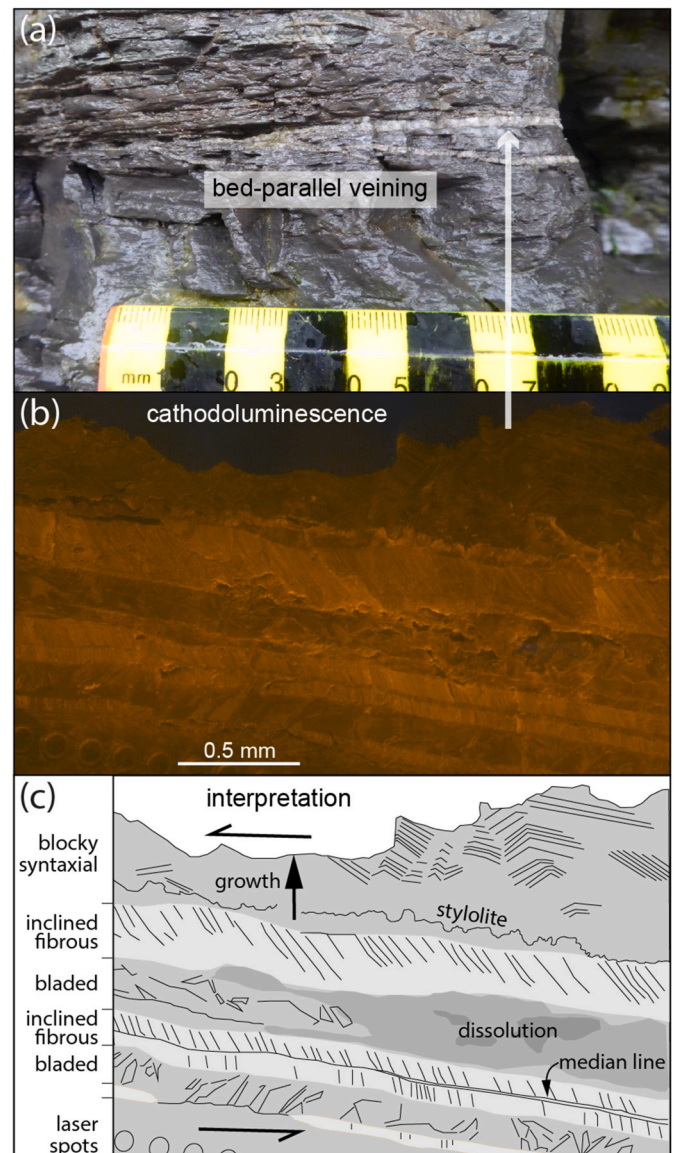
Fig. 4. Example of the complexity within a single narrow calcite fracture-fill (vein). (a) field photograph of a mudstone-hosted bedding parallel calcite fracture-fill; (b) CL image of part of the fill; (c) an interpretation of the different growth structures.

(2021) resolved several distinct phases of faulting within a single fracture fill sample from the Gishron Fault, part of the Dead Sea fault zone. Based on the ability to resolve different generations of faulting using multiple ages, it can be inferred that the sealing time of each crack-seal phase was less than the recurrence time of ca. 2 million years. The ages of this single fracture fill overlap those from across the region (Nuriel et al., 2017), indicating that detailed chronologies of single fills can record protracted regional deformation. At a finer scale, Williams et al. (2017) demonstrated a recurrence interval of the Loma Blanca fault using U-Th geochronology of 40–50 ka.

Growth rates of calcite fracture fills and veins have also been modelled both experimentally and numerically. Experimental models suggest that solute (i.e. Ca) saturation and volume of the fluid control the rate of precipitation, and that filling of natural fracture fills may take thousands to millions of years (e.g. Lee et al., 1996; Lee and Morse, 1999); however, these types of growth models may be overly simplistic compared to nature, and thus the rates may not be directly applicable (Hilgers and Urai, 2002). Numerical modelling of fracture-fill

mechanisms have become more complex over time (e.g. Hilgers et al., 2001, 2004; Nollet et al., 2005; Ankit et al., 2015; Prajapati et al., 2018; Späth et al., 2021; Spruženiece et al., 2021), but the scaling of these experimental rates to natural examples is uncertain. It is clear from the previous studies utilising absolute chronology summarized above that rates of crystal growth and vein sealing probably have a high variability in relation to availability, composition and temperature of fluids (e.g. Williams et al., 2019), and this will vary, potentially by orders of magnitude, across individual fault strands, damage zones and fault systems. With regard to the application of directly dating faulting, the key issue is knowing what the rates are likely to be within 'normal' upper crustal fault systems. Importantly it seems that the precipitation and sealing rates observed in these empirical studies, indicate that fracture fill/vein sealing generally occurs on much shorter timescales than those of the current dating methods. This validates the use of these methods for constraining fault slip chronologies.

5.1. Case studies – individual fault histories

Several studies have used calcite geochronology to investigate the timescales of individual fault strands (Fig. 5). Craddock et al. (2021) document a single mineralized fill sample from a strand of the Gishron Fault that exhibits normal and sinistral strike-slip offsets within the Dead Sea region. They obtained nine reliable ages, which clustered into five periods of faulting spanning ca. 20 to 13 Ma, each of which is associated with a change in the recorded direction of strain across the fault as determined through calcite twinning analysis. Williams et al. (2017) presented twenty reliable U-Th dates from the Loma Blanca normal fault in the Rio Grande rift, spanning several individual fracture fill samples. Their dates range from ca. 575 to 150 ka and, as highlighted above, can be used to demonstrate a recurrence interval of some 40 to 50 ka. The Dead Sea Fault Zone has been dated in several studies using both U-Th and U-Pb. Nuriel et al. (2012a and 2012b) dated several samples from a single quarry, close to the Hula Western Border Fault, which exposes several sinistral strike-slip fault planes. One sample has U-Th dates ranging from 237 to 28 ka, with another ranging from 159 to 61 ka. Uysal et al. (2011) dated a 3 cm wide banded calcite opening-mode vein taken from a normal fault in a tectonically active area of SW Turkey. Twenty dates across this single vein range from 23.9 to 11.8 ka. These studies indicate prolonged activity across individual fault strands on the order of thousands of years to 10s of ka.

5.2. Case studies - regional fault histories

Analysing regional fault histories with U-Pb has become the most common use of absolute chronology to faulting timescales, and has been applied to a wide variety of geodynamic settings (Fig. 6). Roberts and

Walker (2016) dated several conjugate normal, strike-slip and oblique-slip fault strands that dissect the Faroe Islands using calcite precipitates occurring as filled extensional jogs and implosion breccias. The structures themselves were previously linked into a multi-phase kinematic framework of deformation that occurred as the North Atlantic Ocean opened (Walker et al., 2012). The dates (45–11 Ma) are younger than the widely accepted age for the onset of rifting (ca. 55 Ma), demonstrating that deformation associated with this rifted continental margin was protracted and outlasted the propagation of the oceanic spreading centre.

Far-field and intraplate deformation has been dated in several studies. Goodfellow et al. (2017) dated slickenfibres precipitated on brittle strike-slip fault planes exposed in SE Sweden. Although complex age systematics were obtained, the authors unpicked ages of movement of 65 and 55 Ma, which they loosely tied to the far-field effects of Alpine convergence to the south. Roberts et al. (2020b) dated calcite fills associated with the final phase of normal fault movements along the Flamborough Head fault zone in NE England in an area where previous structural work had proposed a complex kinematic evolution with multiple reactivation events due to Alpine and other inversion events (e. g. Starmer, 1995). A cluster of dates ca. 65-56 Ma from a normal fault breccia cement and adjacent opening-mode veins, indicate that the normal faulting and earlier deformation occurred in the late Cretaceous. This means that all of the Flamborough Head fault zone movements onshore were unlikely to be related to Alpine or Pyrenean inversion. The dated deformation and associated calcite mineralization does, however, overlap the North Atlantic hotspot uplift and regional tilting of Britain.

As far as collisional orogens go, the timing of deformation within the European Alps is receiving considerable attention using calcite geochronology. Sinistral transtensional deformation, accommodated by both normal and dip-slip movement along faults bounding the Alpenrhein Graben in the Central Alps, was dated using slickenfibre calcite at 25 to 22 Ma by Ring and Gerdes (2016). The authors interpret this deformation as forming due to E-W extension in the Oligocene related to localised tangential stretching induced by subduction and convergence geodynamics along the Alpine belt. The Jura mountains represent a foreland fold and thrust belt in the northwest of the Alpine orogen, that exhibits detachment faulting along evaporite layers (e.g. Sommaruga, 1999). Looser et al. (2021) dated thrust faults within the Jura that were active during the foreland propagation of this belt, with one thrust being active at ca. 15 to 9 Ma, and another as young as 4.5 Ma. The Penninic Frontal Thrust represents a boundary in which 'internal' high-grade metamorphic units were thrust over less metamorphosed 'external' units of the Alpine belt; this thrust zone was then reactivated as an extensional fault during the late stages of the orogen (e.g. Sue and Tricart, 2003). Bilau et al. (2020) date the onset of this extensional reactivation through calcite veining and cementation of cataclasite to at least
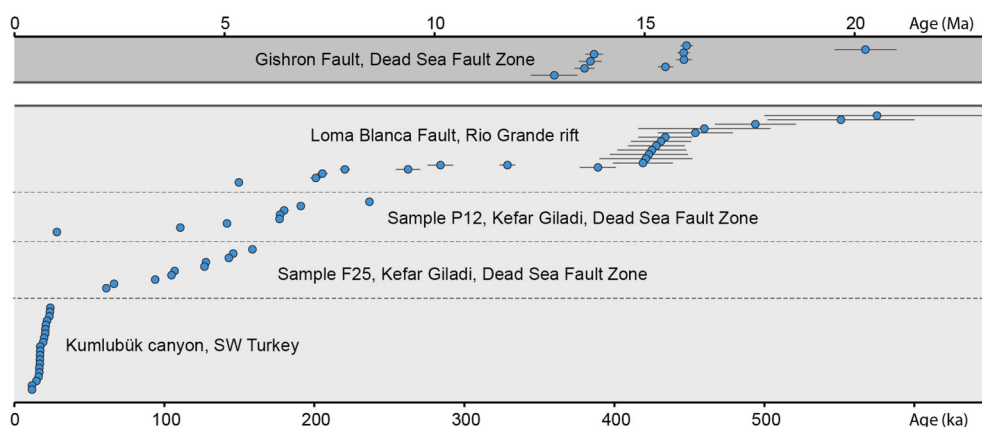

Fig. 5. Examples of extended fault histories from single faults (Loma Blanca Fault), and single vein samples (all others). Note the change in scale from Ma to ka. Error bars are 2σ age uncertainties. Data taken from Craddock et al. (2021), Williams et al. (2017), Nuriel et al. (2012a and 2012b) and Uysal et al. (2011).
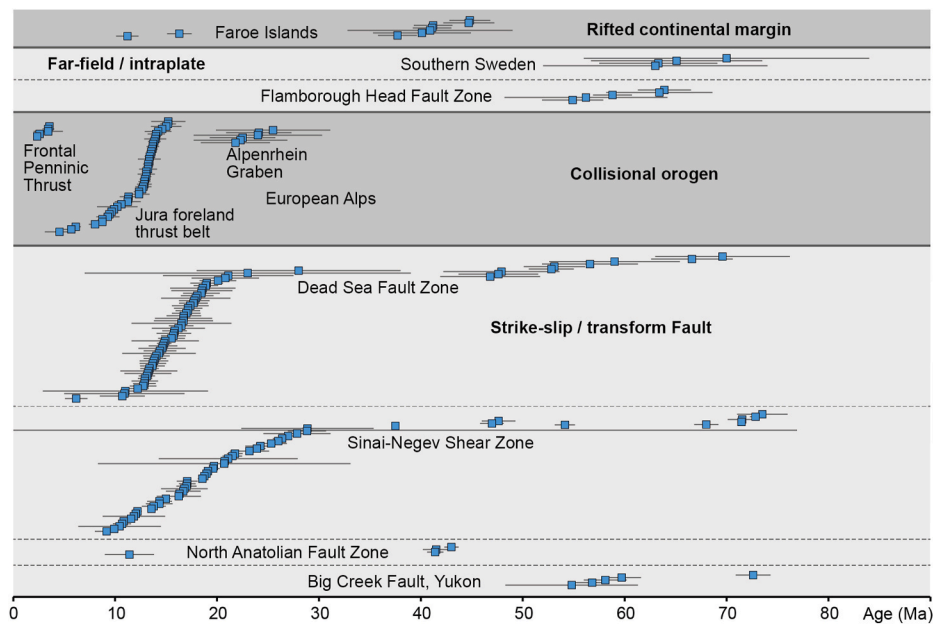
Fig. 6. Examples of regional fault histories from calcite U-Pb geochronology, grouped by tectonic setting. Error bars are 2σ age uncertainties. Data taken from Roberts and Walker (2016), Goodfellow et al. (2017), Roberts et al. (2020b), Ring and Gerdes (2016), Looser et al. (2020), Bilau et al. (2020), Nuriel et al. (2019), Oren et al. (2020), Weinberger et al. (2020), and Mottram et al. (2020).

ca. 3.5 Ma, with a separate phase of reactivation occurring at ca. 2.5 Ma.

Various strike-slip and transform fault systems have been dated, some with large sampling campaigns. The Big Creek Fault is a large (>150 km) strike-slip fault within the Canadian Cordillera. Mottram et al. (2020) dated calcite that yielded two ages of fault movement, at ca. 73 and 60-57 Ma. Notably, they also utilised K-Ar illite dating to compare with the calcite chronology, and both methods yielded overlapping age constraints for fault activity. The Dead Sea Fault Zone is an active transform plate boundary between the Arabian and Sinai tectonic plates. Nuriel et al. (2017) dated onset of strike-slip fault activity through calcite fault precipitates to ca. 21 Ma in the southern Elat region, and ca. 17 Ma in the northern Hermon region. Oren et al. (2020) expanded upon this study, providing strike-slip fault activity constraints of 18 to 10 Ma, peaking at 14 Ma, indicating that faulting likely propagated from south to north. The Sinai-Negev Shear Zone is an E-W trending strike-slip fault slip that interacts with the Dead Sea Fault Zone at its eastern boundary. Weinberger et al. (2020) demonstrated that faulting here was initiated as early as ca. 73 Ma, with the main phase beginning at 27 to 22 Ma, and activity continued until at least 10 Ma, as constrained by the youngest U-Pb calcite date obtained. The North Anatolian Fault Zone is another seismically active strike-slip dominated region within the eastern Eurasian margin. Nuriel et al. (2019) dated part of the fault zone that was active as an extensional normal fault at 42 Ma, and showed that reactivation as a dextral fault zone occurred at ca. 11 Ma. Calcite sampling and dating campaigns of this nature are throwing additional insight to the interaction of plate boundaries and the resultant duration of activity along individual fault strands.

6. Limitations

There are several important limitations to the application of absolute geochronology methods to fault timescales, some that are general, and some specific to the isotope system. A general limitation is the ability to confidently link measured calcite dates with specific fault activity, and to provide robust evidence that the dated material represents primary calcite growth, and not later thermal or fluid-related activity. As discussed above, alleviating this limitation requires a combination of geochemical, compositional and microstructural characterisation (e.g. Figs. 1–4).

The usefulness of a date depends in part upon its age precision. For U-Pb dating, the individual uncertainties are often large spanning several million years or more. However, applying the method to areas where the timing of faulting is inferred based on cross-cutting relations, and often limited to periods of time such as 'Alpine' or 'Laramide', means that any new absolute age constraints still represent significant advances in our knowledge of regional timings (e.g. Parrish et al., 2018; Holdsworth et al., 2019; Roberts et al., 2020b).

In order to improve the precision of the in situ U-Pb carbonate method, more homogeneous reference materials will be required (in terms of their measured age), as the commonly used reference material (WC1; Roberts et al., 2017) imparts a >2.5% limit with which we can interpret any one age. The recently characterised material ASH15D presents a suitable candidate with an age uncertainty of only 0.4% (Nuriel et al., 2021), although its low concentration of radiogenic lead make it really only suitable for multi-collector instrumentation.

An important limitation to all radioisotopic methods, is having measurable quantities of the parent and daughter isotopes. For U-Pb, low uranium is a common and unpredictable issue in particular for fracture-filling calcite, as is a high abundance of common lead, which can swamp any measurement of radiogenic lead (Roberts et al., 2020a). At present, there are no known ways to easily screen samples to pick those most suitable for U-Pb dating, as U and Pb incorporation are compounded by a multitude of factors during calcite precipitation (Rasbury et al., 2009; Roberts et al., 2020). Widespread interest in this method hopefully means this will not always be the case. A further limitation of U-Pb dating, is the potential disequilibrium of intermediate daughter products, which can significantly impact the accuracy of very young (<5 Ma) samples (see Roberts et al., 2020a).

For the U-Th method, similar problems of low U and high Th compound the measurement and obtainable precision. For isochron methods, such as Sm-Nd, Rb-Sr and Lu-Hf, age precision will in part be limited by the spread in initial parent-daughter isotope compositions, with a low spread in parent isotope abundance across the measured sample region leading to a lower precision isochron. The literature data on incorporation of these elements into calcite is sparse, but over time it is hoped that selection of suitable materials for each of these isotopic systems will become feasible. As all of these techniques develop over the next few years, it is likely that 'best practise' and knowledge about the

most efficient means of screening, documenting and analysing samples will also improve.

7. Beyond faulting

Faults are one of the major manifestations of crustal deformation; folds are another, and the two are often intimately linked. As with faulting, the timing of folding can be dated using associated calcite mineralization, as certain fracture fill (or 'vein') occurrences can be kinematically linked to fold development. Lacombe et al. (2021) provide a recent review of this application and the types of structures that can be utilised. To date, a number of studies have used U-Pb dating of fold-related structures to establish the absolute timing of deformation within various orogenic settings. These include basin inversion resulting from far-field tectonic stress in southern England (Parrish et al., 2018); Laramide and Sevier foreland shortening in the western USA (Beaudoin et al., 2018); shortening and extension due to ophiolite obduction in Oman (Hansman et al., 2018); and nappe stacking in the Pyrenees (Cruset et al., 2020; Hoareau et al., 2021).

Opening-mode calcite veins in the upper crust can also form due to changes in lithostatic and hydrostatic pressure during burial and exhumation, typically through 'overpressure' relating to trapped fluids in the subsurface. The timing of such vein formation can potentially give information about the burial history of a sedimentary basin and the potential timing and processes of hydrocarbon formation and migration (e. g. Cruset et al., 2021). Overpressure related veins are just one example of opening-mode fractures that are not fault-related. The reviews of Bons et al. (2012), Gale et al. (2014) and Laubach et al. (2019) cover the formation of fracture fills in the various different settings that lie beyond the realm of those directly related to faulting.

The dating of calcite related to faulting has to date been restricted to brittle deformation. However, carbonate-bearing rocks can also be found in ductile shear zones. Such rocks, typically occurring as calc-silicates or marbles, could potentially yield information about the timescales of ductile shearing. How conclusive the data acquired would be, requires knowledge about the mineral growth and isotopic resetting – topics that are currently underexplored. For example, do dissolution-precipitation creep processes, as found in many mylonites and other foliated fault rocks, lead to isotopic resetting of calcite? At what temperature, on geological plausible timescales of heating, does isotopic resetting occur within calcite? At present, the empirical and experimental data on U and Pb diffusion within calcite are sparse, with the experimentally derived estimate of Cherniak (1997) indicating that temperatures above >350 °C are needed to induce diffusion on relevant length scales. Meinhold et al. (2020) dated a calcite concretion exhibiting cone-in-cone texture that has been deformed. A younger date for a deformed region compared to the undeformed region, led the authors to speculate that the U-Pb had been reset during low-grade regional metamorphism. Calcite within deformed calc-silicate rocks formed under semi-brittle to ductile deformation has been dated from a detachment fault in Turkey (Gürer, pers comm. 2019; Gürer et al., 2019), implying that there is potential for the dating of ductile shear-zone activity using this method.

8. Future directions

The future directions for using calcite geochronology fall under two areas. The first lies within the development and improvements to the analytical techniques themselves. At present, LA-ICP-MS U-Pb is being rapidly adopted by many groups as it is requires instrumentation that is commonly available in many institutions and research centres. Other isotope systems that require clean suites for chemical procedures are likely to remain less popular. A new generation of instrumentation, whereby collision cell technology is employed in ICP-MS instrumentation, both of the quadrupole and multi-collector types, is opening up new frontiers in other isotope systems. For example, Rb-Sr, a method

that was popular in the late 20th century but declined in popularity in the last couple of decades, is undergoing a renaissance, as Rb-Sr dating is now in the reach of LA-ICP-MS instrumentation (e.g. Zack and Hogmalm, 2016; Li et al., 2020; Bevan et al., 2021; Subarkah et al., 2021). Tillberg et al. (2020, 2021) have demonstrated the application of Rb-Sr dating to cogenetic adularia and calcite formed in various fault and fracture-fill mineralization occurrences within the Fennoscandian Shield. Sm-Nd and Lu-Hf are both permissible methods that are achievable using LA-ICP-MS, but require significant ingrowth of the daughter isotopes to reach useful levels of precision; this means a combination of high concentrations of parent Sm and Lu, and samples that are old enough. How old depends on the instrumentation and concentration, but Simpson et al., (2021a, 2022) have used a quadrupole instrument to demonstrate the ability to date Proterozoic apatite, garnet and calcite using Lu-Hf in situ. Dating young samples (<500 ka) with the U-Th method is not a common method, and developments of laser ablation U-Th dating have been slow to progress. In general, the U contents of vein-related calcite seem too low for the current generation of instrumentation for in situ (laser ablation) measurement, meaning that the method is confined to a micro-drilling and sample dissolution approach (e.g. Uysal et al., 2011; Prouty et al., 2016).

The other direction lies in the application of the method to ever more detailed levels of fault and fracture-fill timescales and processes. For example, at the largest scale this may involve campaign-style dating of transform fault systems to learn the complete history of plate boundary evolution. At the finer scale, it can encompass a better understanding of fault recurrence intervals through detailed and precise chronologies of young and active fault systems, potentially impacting our knowledge and prediction of hazardous (seismically active) faults. The method also has significant application to several applied research areas. These include dating faulting in relation to hydrocarbon migration (e.g. Holdsworth et al., 2019) and mineral systems (e.g. Jin et al., 2021), particularly since many economic deposits host calcite as a cogenetic hydrothermal mineral. In general, the information we require about the terrestrial subsurface is changing, with geothermal energy, underground carbon and hydrogen storage, and building of offshore wind farms and onshore nuclear facilities, all being examples where greater knowledge of the timing of fault and fracture-controlled deformation, strength, fluid-flow and permeability of rock volumes are required. Furthermore, the ability to directly link dated calcite to the composition and temperature of the source fluid, through fluid inclusions, stable isotopes (carbon and oxygen), radiogenic isotopes (Sr) and clumped isotopes ($\Delta47$), and the possibility of doing this within or across individual crystal domains (e.g. MacDonald et al., 2019; Drake et al., 2021), means that calcite provides a powerful repository of past fault and fracture-hosted fluid-flow and fluid-rock interaction.

9. Summary

As initiated through the pioneering work of Ramsay (1980) on crack-seal processes, calcite mineralization associated with faulting can provide robust constraints on the timing of fault slip and associated fracturing. A key requirement for geochronology, is that detailed field observations and petrographic information of the analysed domains need to be carried out in order to unambiguously link the calcite growth history to fault activity. Crack-seal-slip calcite mineralization typically gives the best opportunity to link dated calcite to specific episodes of fault slip recognized in the field. Various isotope systems (U-Th, U-Pb, Sm-Nd and Lu-Hf) make the technique potentially applicable to fault histories across a wide range of geological timescales. The spatial resolution of the laser ablation technique lends itself to dating of fine-scale, complex-zoned, fault-related calcite.

Author statement

Nick Roberts: Conceptualization, Writing – Original Draft,

Visualization. Roberts Holdsworth: Visualization, Writing – Review & Editing.

Declaration of competing interest

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