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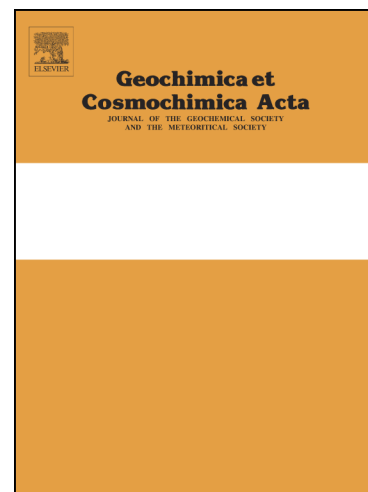
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# Reliability of micritic carbonates in recording well-preserved isotopic composition and implications for paleoelevation estimates in central Tibet

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## Abstract

Paleoelevation and paleoclimate reconstructions based on carbonate proxies rely on the preservation of syndepositional surface water isotopic signatures. This study investigates the reliability of fine-grained carbonates (micrites) in recording well-preserved isotopic composition. Utilizing a suite of research tools, including petrography, X-ray diffraction mineralogy, stable isotopes, clumped isotope temperatures, isotope mixing, solid-state bond reordering modeling, and trace element concentrations, we examine the diagenetic history of late Oligocene micritic carbonates from the Nima Basin in central Tibet. Our findings reveal that the lacustrine carbonates at deposition were micritic and calcite-dominated. However, they underwent partial dolomitization through cryptic recrystallization during shallow burial at temperatures of ~34–40 °C, likely influenced by groundwaters with abundant Mg<sup>2+</sup> and trace elements distinct from surface waters. Subsequently, during the further burial at temperatures of ~120–130 °C, vein calcites precipitated from thermal fluids. Concurrently, the calcite component of fluid-adjacent micrites underwent open-system recrystallization, recording temperatures of 100–130 °C, while the associated dolomite component remained minimally altered due to its higher resistance to dissolution. In contrast, micritic calcites unaffected by thermal fluids experienced partial solid-state bond reordering that elevated clumped isotope temperatures to 50–60 °C. This study underscores the complex diagenetic histories that micrites can undergo, emphasizing the need for caution when interpreting carbonate stable oxygen isotopes in paleoclimate and paleoelevation studies, especially in tectonically active regions. Finally, our analysis infers that the stable oxygen isotopic values of the calcitic soil carbonates in the Nima Basin are well-preserved and reflect moderately high paleoelevations of ~3.3 km at 26–25 Ma. This suggests a >1 km elevation gain during the Neogene, highlighting subsurface geodynamic processes as additional drivers of surface uplift in central Tibet.

## Keywords:

Micrite, diagenesis, clumped isotopes, dolomitization, solid-state bond reordering, paleoelevation

36

37 **1. Introduction**

38 Quantitative stable isotope-based paleoaltimetry has received considerable attention during  
 39 the last two decades, because of its significance to geodynamic history, to regional and global  
 40 climate changes, and to biodiversity (An et al., 2001; Ding et al., 2022; Garzzone et al., 2017;  
 41 Raymo and Ruddiman, 1992; Spicer et al., 2020). For example, reconstructed surface uplift  
 42 histories have been used to infer that both upper-crustal shortening and sub-surface geodynamic  
 43 processes (crustal flow and sinking of lower lithosphere) contributed to the topographic growth of  
 44 the South American Andes and Tibetan Plateau (Ding et al., 2022; Garzzone et al., 2017; Li and  
 45 Garzzone, 2023). Surface uplift of the Tibetan Plateau has also been widely considered a major  
 46 player in shaping the Cenozoic climate system of Asia, including the initiation and intensification  
 47 of summer monsoon systems in South and East Asia as well as aridification of central Asia (An et  
 48 al., 2001; Kutzbach et al., 1993; Molnar et al., 2010; Wu et al., 2022).

49 Among the many proxies used to reconstruct paleoelevations, such as organic lipids, fossils,  
 50 and hydrothermal silicates, authigenic carbonates (e.g., lacustrine and paleosol carbonates) have  
 51 been the most widely used, as both their stable oxygen isotopes ( $\delta^{18}\text{O}_{\text{carb}}$ ) and clumped isotope  
 52 temperatures can be used for paleoelevation estimates (Huntington and Lechler, 2015; Rowley and  
 53 Garzzone, 2007). To derive reliable paleoelevations, carbonate rocks need to retain syndepositional  
 54 Earth-surface isotope signatures, although it is widely known that carbonate minerals and rocks  
 55 are prone to diagenesis (Armenteros, 2010; Garzzone et al., 2004; Immenhauser, 2022; Longman,  
 56 1980; Quade et al., 2020; Swart, 2015; Tucker, 1990).

57 Depending on the timing and environment, diagenesis can occur in three broad stages  
 58 (Armenteros, 2010; Choquette and Pray, 1970): 1) eogenesis occurs shortly after deposition when  
 59 the carbonates are still shallowly buried and in the presence of surface waters; 2) mesogenesis  
 60 indicates alteration during moderate to deep burial with elevated temperatures and with or without  
 61 the presence of fluids that are probably different from surface waters; and 3) telogenesis is the  
 62 alteration during or after exhumation to the Earth-surface. It is essential to identify whether  
 63 carbonates experienced diagenesis after deposition, and the stages of diagenesis, as this will  
 64 determine the evolution of stable and clumped isotopic values. For example, although mesogenesis  
 65 usually indicates alteration of precursor isotope signatures, if it occurred in a closed system or the  
 66 carbonates only experienced solid-state bond reordering, the stable isotopes wouldn't be changed,  
 67 but still reflect syndepositional Earth-surface water signatures (Huntington and Lechler, 2015).

68 Numerous quantitative paleoelevation studies based on either the stable or clumped isotopes  
 69 of carbonates have been conducted in the Tibetan Plateau (see reviews in Ding et al., 2022; Li et  
 70 al., 2022). With few exceptions, most of the studies inferred well-preserved carbonate stable  
 71 isotope signals based on the preservation of micritic textures using a petrographic microscope  
 72 and/or cathodoluminescence imaging. However, the preservation of micritic textures alone is not  
 73 sufficient to determine whether isotopic signals are well-preserved (Leier et al., 2009; Winkelstern  
 74 and Lohmann, 2016). In recent years, the integrated analyses of stable and clumped isotopes have  
 75 increased our ability to identify diagenetic alteration (Bergman et al., 2013; Dale et al., 2014;  
 76 Ingalls et al., 2020; Lacroix and Niemi, 2019; Ryb et al., 2021; Shenton et al., 2015; Veillard et  
 77 al., 2019; Winkelstern and Lohmann, 2016). Additionally, research tools such as carbonate U-Pb

dating (Cong et al., 2021; Hagen-Peter et al., 2021; Lawson et al., 2018; Mangenot et al., 2018) and electron microscope techniques (Ingalls and Snell, 2021; Li et al., 2019) provide new opportunities to identify different diagenetic stages, as well as to observe diagenetic features at much finer scales, i.e., micritic textures.

A major purpose of this study is to explore the reliability of fine-grained micritic carbonates (micrites) in recording well-preserved isotopic composition. We choose the Nima Basin in central Tibet (Fig. 1A) as a case study. Previously, DeCelles et al. (2007b) reported  $\delta^{18}\text{O}_{\text{carb}}$  values of pedogenic carbonates as low as -18‰ (VPDB) from the 4DC section (Fig. 1B), which was used to infer the attainment of similar-to-present high elevations of central Tibet since ~25 Ma. Later, Huntington et al. (2014) reported clumped isotope temperatures from lacustrine carbonates of the same 4DC section, which exhibited higher than Earth-surface temperatures of 40–60 °C and were interpreted to indicate closed-system cryptic recrystallization. This study aims to explore further the diagenetic history of the 4DC section for three reasons. First, in the 4DC section of the Nima Basin, vein calcites exist in many stratigraphic levels and exhibit very negative  $\delta^{18}\text{O}_{\text{carb}}$  values, i.e., -19‰ (DeCelles et al., 2007b). The potential influence of the vein calcite-associated diagenesis on surrounding micrites has not been explored. Second, recent studies in southern Tibet, especially along the Indus-Yarlung suture zone, emphasize extensive late-stage carbonate diagenesis due to deformation and magmatism, which casts doubt on previous paleoelevation reconstructions in that region (Huang et al., 2022; Ingalls, 2019; Leier et al., 2009; Quade et al., 2020). Third, the paleoelevation history of central Tibet is still widely debated despite considerable recent efforts (see reviews in Li et al., 2022), which hinders our understanding of the mechanisms of the Tibetan Plateau growth (Ding et al., 2022; Li et al., 2022).

In this study, we report additional clumped isotope temperatures from both lacustrine micrites and vein calcites, as well as one paleosol nodular carbonate, from the 4DC section, Nima Basin, using laser-based spectroscopy developed at the University of Arizona (Wang et al., 2020; Yanay et al., 2022). We aim to explore the diagenetic history of micritic carbonates and their implications for previous paleoelevation estimates. In combination with X-ray diffraction (XRD) mineralogy, petrographic observation, scanning electron microscope (SEM), electron probe microanalysis (EPMA), stable isotopes, isotope mixing, solid-state bond reordering modeling, and carbonate LA-ICP-MS trace element analyses, we illuminate a more complete and complex carbonate diagenetic history that includes at least two distinct burial diagenesis stages: shallow burial partial dolomitization and moderately burial open-system recrystallization and solid-state bond reordering. We further discuss potential variations of both stable isotopes and clumped isotopes during these different stages of diagenesis. Finally, with this new understanding, we reinterpret previous paleoelevation data and obtained a ~3.3 km paleoelevation at 26–25 Ma, which requires a >1 km elevation gain during the Neogene and subsurface geodynamic processes as additional drivers of surface uplift in central Tibet.

## 2. Geologic setting

The Nima Basin is located in central Tibet along the Bangong suture zone (Fig. 1A), which marks the Late Jurassic–Early Cretaceous westward, diachronous collision between the Lhasa and Qiangtang terranes (Kapp and DeCelles, 2019; Yin and Harrison, 2000). The modern basin is ~150



km long from east to west, and ~50 km wide from north to south. Restored balanced-cross sections indicate that the basin was originally >110 km wide during the mid-Cretaceous, in response to the flexural loading of the north-dipping Muggar thrust (a section of the Shiquanhe-Gerze-Amdo thrust system) on the north and the south-dipping Gerze-Seling Co backthrust on the south (Kapp et al., 2007; Kapp et al., 2005). The basin was partitioned into the northern and southern sub-basins by internal shortening since Late Cretaceous time (DeCelles et al., 2007a; Kapp et al., 2007). Contractional deformation and concomitant sedimentary deposition lasted until the Miocene. Paleocurrent and provenance studies indicate that the southern and northern Nima basins received detritus dominantly from the south and north of the basin, respectively (DeCelles et al., 2007a).

In the southern Nima Basin, Oligocene–Miocene strata of the Nima Redbed Unit vary along strikes (DeCelles et al., 2007a). Strata to the west and south of Nima town are dominated by sandstone and siltstone that are interpreted to represent fluvial sedimentary systems, with channel, overbank floodplain, and crevasse-splay deposits. East of Nima town, the 1DC and 4DC sections are dominated by fan-delta and fine-grained lacustrine deposits (DeCelles et al., 2007a). In the 4DC section, thin yellowish gray-colored lacustrine marl beds are interbedded with massive brick red-colored siltstones (Fig. 2A) and well-developed calcisols with pedogenic carbonate nodules (DeCelles et al., 2007b). This study focuses on the lacustrine marls (micritic carbonate) of the 4DC section. Secondary vein calcites are observed in many stratigraphic levels and can be abundant in certain layers (Fig. 2B).

No absolute age constraints are available for the 4DC section. However, tuffs from the adjacent 1DC section (Fig. 1B) that are at similar stratigraphic levels as the 4DC section yield biotite  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of  $25.8 \pm 0.2$  Ma and  $24.9 \pm 0.1$  Ma (DeCelles et al., 2007b). The depositional ages of the 4DC section are thus inferred to be late Oligocene. Carbonate U-Pb analyses were conducted on three lacustrine micrite samples from the 4DC section, but they yielded ages with large uncertainties (see section 4.7 for details).

### 3. Methods

#### 3.1 Petrographic, CL, SEM, and mineralogical analysis

Polished thin sections were made from five selected carbonate samples and were observed under a petrographic microscope using both plain- and cross-polarized light at the University of Arizona. A Reliotron cold cathodoluminescope operated at an acceleration voltage of 7–9 kV and a beam current intensity of 0.3–0.5 mA was used to examine the luminescence of the same thin sections at the University of Texas at Arlington. Scanning electron microscopy (SEM) was conducted using an FEI Helios NanoLab 660, housed in the Kuiper Imaging Facility at the University of Arizona, under a voltage of 5 kV and a current of 0.2 nA.

Eight carbonate samples were powdered for XRD analysis to determine mineralogy. The experiments were conducted using a Philips PANalytical X'Pert PRO MPD instrument in the Department of Chemistry and Biochemistry at the University of Arizona. The X-ray radiation wavelength was about 1.54 Angstroms (Å) (copper Ka radiation generated by a sealed X-ray tube with copper anode), and the Bragg-Brentano theta-theta geometry was used in the measurements.

Semiquantitative estimates of the weight percentage (wt%) of each mineral present were estimated using the reference intensity ratio (RIR) available in the XRD database. The wt% is proportional to the (XRD intensity)/RIR. All wt% values were normalized in such a way that the sum of all entries equals 100%.

### 3.2 EPMA element mapping

Two carbonate samples were selected for element mapping using an Electron Probe Micro-Analyzer (EPMA). Rock slabs were polished, carbon coated, and then analyzed at the Kuiper Imaging Facility at the University of Arizona using a Cameca SX-100 Ultra instrument. For all element maps, the instrument was configured to 15 kilovolts (kV) and 40 nanoamperes (nA). The magnesium (Mg), calcium (Ca), manganese (Mn), strontium (Sr), and iron (Fe) elements were collected using wavelength-dispersive spectrometers; while the silicon (Si), chromium (Cr), barium (Ba), and sometimes molybdenum (Mo) elements were collected using energy-dispersive spectrometers. For the high-resolution element maps, 1024 pixels per line, 40 micron beam size, and 10 milliseconds (ms) dwell time were used; for the medium-resolution element maps, 512 pixels per line, 80 micron beam size, and 20 ms dwell time were used.

### 3.3 Carbonate clumped isotope analysis

Carbonate clumped isotope ( $^{13}\text{C}$ - $^{18}\text{O}$  bonds,  $\Delta_{638}$ ) content in excess of the stochastic distribution was measured at the Environmental Isotope Laboratory at the University of Arizona, using a tunable infrared laser differential spectrometer (TILDAS) constructed by Aerodyne Research, Boston. The term  $\Delta_{638}$  is the laser measurement equivalent of  $\Delta_{47}$  in mass spectrometry-based analysis.

About 2 mg of powdered carbonate was reacted with dehydrated phosphoric acid under vacuum at 70 °C. The conventional isotope ratio measurement relative to VPDB was calibrated based on repeated measurements of International Atomic Energy Agency (IAEA) reference materials. Clumped isotope values ( $\Delta_{638}$ ) are reported in the carbon dioxide equilibrium scale (CDES) theoretical reference frame defined by water-equilibrated gases, heated gases, and ETH 1–4 carbonate standards (Bernasconi et al., 2021; Dennis et al., 2011), and are reported for acid digestion at 70 °C (CDES<sub>70</sub>). The precisions for these measurements are  $\pm 0.023\text{‰}$  for  $\Delta_{638}$ ,  $\pm 0.04\text{‰}$  for  $\delta^{18}\text{O}$ , and  $\pm 0.03\text{‰}$  for  $\delta^{13}\text{C}$  (pooled reproducibility, 1-sigma), respectively. The laser-based  $\Delta_{638}$  – temperature relationship for carbonates is based on fifty-one synthetic calcites that equilibrated at temperatures from 6 °C to 1100 °C (Yanay et al., 2022):

$$\Delta_{638\text{CDES}} = (0.0409 \pm 0.0003) \times (10^6/T^2) + (0.1776 \pm 0.0031), R^2 = 0.997 \quad \text{equation (1)}$$

T in this equation is referred to throughout the text as  $T_{(\Delta_{638})}$ , thus distinguishing measurements made by the laser system versus mass spectrometry,  $T_{(\Delta_{47})}$  (Ghosh et al., 2006), although  $T_{(\Delta_{47})}$  and  $T_{(\Delta_{638})}$  have been shown to be statistically equivalent (Yanay et al., 2022). Equation (1) is within error of recent mass spectrometry-based  $\Delta_{47}$  – temperature relationships and

correctly predicted precipitation temperatures for a suite of seventeen natural carbonates for both calcite and aragonite (Yanay et al., 2022). Complete details of this method and the calibration of the temperature –  $\Delta_{638}$  relationship are described in Wang et al. (2020) and Yanay et al. (2022).

For two of the samples, 4DC34 and 4DC41B, which contain both calcite and dolomite components, we used 0.5 mol acetic acid to process the bulk micrite to preferentially remove the calcite component from the dolomite component. Excess ( $>2\text{--}3$  ml) acetic acid was added to  $\sim 200$  mg micrite powders and left at room temperature to react for either 60 minutes or 120 minutes. The remaining powders containing the dolomite component were cleaned with deionized water and dried for clumped isotope analysis. We acknowledge that this processing method may also dissolve a certain amount of dolomite, however, we consider the amount to be small as the reaction occurred at room temperatures with diluted acetic acid and a shorter duration.

All clumped isotope samples were analyzed for 5–7 replicates. Each replicate measurement was based on four comparisons (sub-cycles) of the sample and reference gas. We excluded replicates with fewer than two sub-cycles and outliers to calculate the mean value of each sample. The outlier was defined as follows: first, we calculated the average  $\Delta_{638}$  value of all replicates for each sample, then we calculated the difference of  $\Delta_{638}$  between each replicate with the average; and finally, we considered differences of  $>0.023$  ( $\Delta_{638\text{CDES}}$  external standard deviation of references) as outliers, which corresponds to  $\sim 7^\circ\text{C}$   $T_{(\Delta_{638})}$  temperatures in the range of  $0\text{--}100^\circ\text{C}$ . In total, seventy-six replicates were measured and ten replicates were excluded. All reported clumped isotope values were averaged from 4–5 replicates. Supplementary Data S1 lists all clumped isotope values, including excluded replicates, of all new samples; Supplementary Data S2 lists all clumped isotope data of standards (carbonate standards ETH1–4 and equilibrated gas) used for calibration.

### 3.4 Mixing model of stable and clumped isotopes

For samples containing both dolomite and calcite components, i.e., 4DC34 and 4DC41B, we measured the clumped isotopes for both the bulk sample and the dolomite component (section 3.3). We then calculated the  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $\Delta_{638}$  values of the calcite component using the mixing model of Defliese and Lohmann (2015). Leached dolomite samples that had been reacted with acetic acid to remove calcite were treated as end-member one, while the bulk carbonate was treated as the final mixture. The unknown calcite isotopic values constituted end-member two. Percent contributions of each mineral end-member were estimated from XRD analysis (section 3.1). A goal-seeking algorithm was used to find the correct end-member values for the calcite in each sample that resulted in the measured bulk sediment isotopic values, solving in order for  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and finally  $\Delta_{638}$ . All mixing model results are presented in Supplementary Table S1.

### 3.5 Clumped isotope bond reordering modeling

Potential carbonate clumped isotope bond reordering due to burial was evaluated for samples in the 4DC section of the Nima Basin by constructing several thermal (burial and exhumation) histories and then analyzing them using the Isotopylog package for python from Hemingway and Henkes (2021) and using the kinetic parameters for either calcite or dolomite of Hemingway and

Henkes (2021), here referred to as “HH21” model. The HH21 model was chosen because it contains reordering kinetic parameters for both calcite and dolomite minerals and is also the most ‘general’ bond reordering model. The  $\Delta_{638}$  – temperature equation of Yanay et al. (2022) (equation 1 in this paper) was used for the equilibrium  $\Delta_{47}$  – temperature relationship, replacing the default equation of Anderson et al. (2021) in Hemingway and Henkes (2021). This may result in a small amount of error due to the differences between  $\Delta_{638}$  and  $\Delta_{47}$ , however, as shown in Yanay et al. (2022), such differences are minimal. Test runs using these two different clumped isotope temperature calibration equations yielded nearly identical results, as the much larger source of error is the uncertainty in the kinetic parameters of bond reordering. For this study, we conducted the following three groups of modeling runs.

The first group of modeling runs was for calcite. As the exact exhumation history of the 4DC section is unknown, we ran the models assuming the following three different burial and exhumation histories: S1, gradual burial of the 4DC section to maximum depth with maximum temperatures (varied by run) between 25 and 11 Ma, staying at maximum burial depth and temperature between 11 and 10 Ma, and exhumation to Earth-surface between 10 and 0 Ma; S2, gradual burial to maximum depth between 25 and 20 Ma, staying at maximum burial depth and temperature between 20 and 10 Ma, and exhumation to Earth-surface between 10 and 0 Ma; S3, gradual burial to maximum depth and temperature between 25 and 20 Ma, staying at maximum burial depth and temperature between 20 and 5 Ma, and exhumation to Earth-surface between 5 and 0 Ma. For each of the burial and exhumation scenarios, we first considered a 130 °C maximum burial temperature, assuming that the clumped isotope temperatures of the vein calcites represent the maximum burial temperature. The purpose of this run is to figure out the final clumped isotope temperatures of calcite under a 130 °C maximum burial temperature. Then we assumed that the  $T_{(\Delta_{638})}$  values of 50 °C and 60 °C of the two lacustrine micritic calcite samples, i.e., 4DC51 and 4DC64, were caused by solid-state bond reordering, and solved for the maximum burial temperatures needed. As we also do not know the syndepositional  $T_{(\Delta_{638})}$  temperatures, we assumed two possibilities, 20 °C or 30 °C, based on our studies of lacustrine carbonates of similar ages in the adjacent Lunpola Basin (Fig. 1A; data under review in another journal). In total, there are 18 separate model runs in this group (C1–C18 in Supplementary Table S2).

The second group of modeling runs was for dolomite. We first conducted eighteen model runs with configurations that are the same as C1–C18 but for dolomite (D1–D18 in Supplementary Table S2). In addition, we also carried out four more runs under the burial and exhumation scenario S2. We set the maximum burial temperatures in these runs the same as those needed to reorder calcite to 50 °C or 60 °C, i.e., similar maximum burial temperatures as in model runs C8, C11, C14, and C17. The purpose of these model runs was to figure out how much bond reordering dolomite would experience under the maximum burial temperatures that can reorder 20 ° or 30 °C calcite to 50 °C or 60 °C (D19–D22 in Supplementary Table S2).

The third group of modeling runs was designed to compare the differences between different models for calcite reordering. We compared three models that differ in their mechanistic interpretations of the solid-state bond reordering: the transient defect/equilibrium defect model (Henkes et al., 2014; Passey and Henkes, 2012), here referred to as “Hea14” model; the paired exchange-diffusion model (Stolper and Eiler, 2015), here referred to as “SE15” model; and the disordered kinetic model (“HH21” model) (Hemingway and Henkes, 2021). We compared the HH21, Hea14, and SE15 model results using the Isotopylogy software of Hemingway and Henkes

(2021). To minimize the influence of thermal history, for these model runs, we assumed the same burial and exhumation scenario S2 and maximum burial temperatures of 130 °C (C19–C22 in Supplementary Table S2).

### 3.6 Carbonate LA-ICPMS analysis

Carbonate U-Pb analyses of three micrite and two vein calcite samples were performed at the University of California, Santa Barbara using a Photon Machines Excite 193 laser ablation system coupled to a Nu Instruments Plasma3D MC-ICP-MS, following the analytical procedures of Kylander-Clark (2020). Samples were analyzed in polished, one-inch epoxy mounts, using an 85 µm spot run at 10 Hz for 15 s following a 20 s baseline. Unknown analyses were corrected for instrument drift and mass bias in a two-step procedure using a combination of analyses from NIST614 glass and calcite standard WC-1 (254 Ma; Roberts et al., 2017) that were measured periodically throughout the analytical session; NIST614 was first used to correct for instrument drift of all isotopic ratios and the mass and detector bias of the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio using Iolite v2.5 (Paton et al., 2011), and a correction for the mass and detector bias of the  $^{206}\text{Pb}/^{238}\text{U}$  ratio was corrected such that, using an initial  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of 0.85, WC-1 yields 254 Ma. Analyses of calcite standards ASH 15D (2.965 Ma; Nuriel et al., 2021), and Duff Brown Tank (64 Ma; Hill et al., 2016) analyzed throughout the analytical session yielded ages that overlap within uncertainties of their accepted values. All data are presented in Supplementary Data S3.

## 4. Results

### 4.1 Petrographic, CL, SEM, and mineralogical results

Several different types of carbonate textures were observed under petrographic microscopes (Fig. 2C–F). For most of the samples, the bulk carbonate samples are dominated by micrite (Fig. 2D and 2F), while calcite veins are abundant in some samples (Fig. 2C). A few other samples, e.g., 4DC64, are dominated by microspars (Fig. 2E). No significant luminescence difference was observed between the vein calcite and adjacent micrite (Supplementary Fig. S1). SEM images show micro-crystals in the micrite adjacent to the vein calcite in sample 4DC41B (Fig. 2G), while 4DC51 is composed largely of calcite nanoparticles (Fig. 2H). See Supplementary Fig. S2 for more SEM images.

XRD analysis indicates that the analyzed carbonate samples have carbonate contents between 73% and 91%, with one exception (45%) (Table 1). Most of the lacustrine micrites are dominated by dolomite (61% to 93% of the carbonate content, with a mean of 74%); whereas samples 4DC51 and 4DC64 are nearly pure calcite (Table 1 and Fig. 3A). In the following, wherever “micritic calcite” is indicated, it refers to samples 4DC51 and 4DC64 that are nearly pure calcite in composition; wherever “calcite component” and “dolomite component” are indicated, they refer to the different carbonate species in micritic carbonates that contain both calcite and dolomite components, such as samples 4DC34 and 4DC41B. The one paleosol carbonate consists of pure calcite. Although we do not have XRD results for the vein carbonate, EPMA element analysis (see below) indicates that the veins are pure calcite, henceforth referred to as vein calcite.



## 4.2 EPMA element maps

For sample 4DC41A (collected at the same location as 4DC41B, but from two different hand samples), the EPMA element maps show clear differences between micrite and vein calcite (Fig. 2I–J). For example, the vein calcites show a distinct red color on the Ca map (Fig. 2I) and a black color on the Mg map (Fig. 2J), indicating a pure calcite component. The boundary between vein calcite and micrite is sharp with differences in concentration of Ca and Mg (Fig. 2I–J). Within micrite, the distribution of different elements is rather homogeneous. Sample 4DC47.2 shows a relatively homogeneous color in the Ca map (Fig. 2K), but visible changes in the Mg map (Fig. 2L) that probably reflect an inter-lamination compositional difference. Supplementary Figs. S3–S5 shows maps of other minor elements of these two samples, including another larger-scale element maps of 4DC41A.

## 4.3 Carbonate stable isotope data

Carbonate  $\delta^{18}\text{O}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values were measured at the same time as the clumped isotopes (Table 2). We combine these new stable isotopic data with those published in DeCelles et al. (2007b) to discuss the stable isotopic signatures (Fig. 3B–F; note that only lacustrine carbonates were considered here).

For the  $\delta^{18}\text{O}_{\text{carb}}$  values (VPDB) of micrites (Fig. 3C), the following features are observed: 1) large variations between -9‰ and -14‰ within a single hand sample but different laminae, e.g., at the stratigraphic level of 130 m; 2) excluding the bottom sample (4DC34) and another two in the lower part (4DC51 and 4DC64, outlined by a gray circle), the lowest  $\delta^{18}\text{O}_{\text{carb}}$  values show an upward decrease in  $\delta^{18}\text{O}_{\text{carb}}$  values (from -11.7‰ to -13.4‰); and 3) samples 4DC51 and 4DC64 have the lowest  $\delta^{18}\text{O}_{\text{carb}}$  values of  $\sim$ -16.5‰. The  $\delta^{13}\text{C}_{\text{carb}}$  values (VPDB) of micrites show the following features (Fig. 3D): 1) variations as large as 2‰ exist within a single hand sample but different laminae; 2) the bottom two samples (4DC34 and 4DC41A/B) show lower  $\delta^{13}\text{C}_{\text{carb}}$  values between -2‰ and -5‰; and 3) all the other samples show similar  $\delta^{13}\text{C}_{\text{carb}}$  values between -1‰ and +1‰, including 4DC51 and 4DC64.

For vein calcites, both their  $\delta^{18}\text{O}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values are consistent throughout the stratigraphic levels (Fig. 3E–F). The  $\delta^{18}\text{O}_{\text{carb}}$  values of vein calcites are lower (-14‰ to -19‰) than those of micrites (Fig. 3B) while their  $\delta^{13}\text{C}_{\text{carb}}$  values (-2‰ to 0‰) are similar to those of micrites but with a smaller range (Fig. 3B). On the  $\delta^{18}\text{O}_{\text{carb}}$  versus  $\delta^{13}\text{C}_{\text{carb}}$  graph (Fig. 3B), micrite and vein calcite samples generally do not overlap, although two of the micrite values (4DC51 and 4DC64, circled in gray) fall within the vein calcite domain.



#### 4.4 Carbonate clumped isotope data

Previously, Huntington et al. (2014) also reported clumped isotope temperatures ( $T_{(\Delta 47)}$ ) of lacustrine carbonates from the same 4DC section. It is noted that although not exactly the same, for most bulk samples that are analyzed in both Huntington et al. (2014) (solid blue circles, Fig. 4) and this study (solid orange circles), the  $T_{(\Delta 638)}$  and  $T_{(\Delta 47)}$  temperatures agree with each other within uncertainty. Supplementary Fig. S6 exhibits the  $T_{(\Delta 638)}$  temperatures of the new samples that include all replicates (i.e., no outliers were removed), which shows nearly the same temperatures and trends compared to the data reported in Fig. 4. This comparison indicates that our method of removing outliers did not result in a bias to the data.

The new measurements of this study include two distinct groups of  $T_{(\Delta 638)}$  temperatures: the vein calcites have  $T_{(\Delta 638)}$  temperatures between  $119.5 \pm 8.0$  °C and  $125.6 \pm 8.6$  °C (solid red circles, Fig. 4) while the bulk micrites have relatively lower, but still higher than plausible Earth-surface  $T_{(\Delta 638)}$  temperatures, between  $40.8 \pm 4.3$  °C and  $63.2 \pm 5.1$  °C (solid orange circles, Fig. 4). For samples that were treated with acetic acid to remove the calcite component, we note the remaining dolomite component has lower  $T_{(\Delta 638)}$  temperatures than the bulk sample, but is still higher than plausible Earth-surface temperatures between  $40.1 \pm 4.2$  °C and  $43.8 \pm 4.4$  °C, except one lower value of  $34.4 \pm 3.9$  °C (open orange circles, Fig. 4). The two lacustrine micritic calcite samples, 4DC51 and 4DC64, yielded  $T_{(\Delta 638)}$  temperatures of  $49.7 \pm 3.7$  °C and  $58.5 \pm 4.0$  °C (Fig. 4, solid orange circles denoted by green arrows), and the one paleosol calcitic carbonate yielded a  $T_{(\Delta 638)}$  temperature of  $41.1 \pm 4.2$  °C (solid orange diamond denoted by a green arrow, Fig. 4).

#### 4.5 Results of mixing model

Using the mixing model described in section 3.4, we calculated the  $\Delta_{638}$  values and  $T_{(\Delta 638)}$  temperatures for the calcite component of samples 4DC34 and 4DC41B, based on the measured  $\Delta_{638}$  values of the bulk sample and the dolomite component. For sample 4DC34, the dolomite component of which accounts for 79% (Table 1), we calculated the  $T_{(\Delta 638)}$  temperature of the calcite component to be  $102.9 \pm 36.7$  °C and  $68.5 \pm 39.0$  °C (Fig. 4; open green circles; Supplementary Table S1). The two calculated values correspond to the two measured dolomite  $T_{(\Delta 638)}$  temperatures (Table 2). For sample 4DC41B, which contains 66% dolomite component (Table 1), we calculated four  $T_{(\Delta 638)}$  temperatures for the calcite component, as we obtained two  $T_{(\Delta 638)}$  temperatures for the bulk sample and dolomite component, respectively (Table 2). The four calculated  $T_{(\Delta 638)}$  temperatures of the calcite component of 4DC41B range between  $98.3 \pm 22.9$  °C and  $127.8 \pm 21.8$  °C (Fig. 4, open green circles). The large errors are associated with error propagation during calculations and incorporate the errors in the  $\Delta_{638}$  measurements.

#### 4.6 Results of clumped isotope solid-state bond reordering

For model runs under different burial and exhumation histories (S1, S2, and S3), we observed, as expected, that under the same maximum burial temperatures, the longer the duration

of maximum burial, the higher the final modeled  $\Delta_{638}$  temperature is; and to obtain the same final modeled  $T_{(\Delta_{638})}$  temperatures, it requires lower maximum burial temperatures for scenarios with longer durations of maximum burial (Supplementary Table S2). The differences in temperatures produced by different burial and exhumation histories are small (2–10 °C) compared to the measured  $T_{(\Delta_{638})}$  temperature range, which also does not influence the following discussion of diagenetic history. We choose the modeling results of burial and exhumation scenario S2 (i.e., 25–20 Ma gradual burial, 20–10 Ma maximum burial at a constant temperature, 10–0 Ma exhumation to Earth-surface) for the following description and discussion, which we deem to be the most reasonable burial and exhumation history for the 4DC section based on our understanding of regional tectonic history.

According to the disordered kinetic model (“HH21” model) (Hemingway and Henkes, 2021), it was found that under 130 °C maximum burial temperatures, calcite with 30 °C (20 °C) temperatures would be reordered to 40 °C (31 °C) (Fig. 5A–B). It requires 144 °C (153 °C) maximum burial temperatures to reorder 30 °C (20 °C) calcite to 50 °C, while 154 °C (160 °C) is required to reorder 30 °C (20 °C) calcite to 60 °C (Fig. 5A–B). For dolomite, the model runs indicate that under 130 °C, 144 °C, and 154 °C maximum burial temperatures, 30 °C dolomite would be reordered to 31 °C, 33 °C, and 37 °C, respectively (Fig. 5C). If the dolomite temperature is 20 °C, under maximum burial temperatures of 130 °C, 153 °C, and 160 °C, the corresponding reordered temperatures are 21 °C, 27 °C, and 30 °C, respectively (Fig. 5D).

We found different results using different kinetic models (Fig. 6). Under 130 °C maximum burial temperatures, 30 °C calcite would be reordered to 40 °C, 53 °C, and 64 °C, respectively, using HH21, Hea14, and SE15 models (Fig. 6A–C). The reordered temperatures are 31 °C, 42 °C, and 57 °C for 20 °C calcite.

#### 4.7 Carbonate LA-ICPMS data

Carbonate LA-ICPMS analyses were conducted with two main purposes: first, to constrain the depositional ages of micrite and precipitation ages of vein calcite using the U-Pb dating system; and second, to use the trace element concentration to characterize the fluid in which micrite and vein calcite were deposited. Due to the abundance of common Pb, as well as the small range of  $^{238}\text{U}/^{206}\text{Pb}$  ratios, the calculated carbonate U-Pb ages yield large uncertainties (Supplementary Fig. S7). Nonetheless, two of the samples (4DC34 and 4DC41B) yielded dates of  $30.0 \pm 6.5$  Ma and  $39.2 \pm 13.3$  Ma, older than but within uncertainty of the inferred ~26 Ma depositional age of the studied strata (DeCelles et al., 2007b). The vein calcites yielded precipitation ages of  $12.9 \pm 11.9$  Ma. We emphasize that the imprecise ages of the 4DC section do not influence the diagenetic history that will be discussed later.

Trace elements U and Th show distinct differences between micrites and vein calcites (Fig. 7). All three micrite samples have high U content with means at  $7.8 \pm 1.1$  ppm,  $28.1 \pm 3.2$  ppm, and  $46.0 \pm 4.6$  ppm, respectively. Similarly, all three micrite samples also have high Th content with means at  $2.8 \pm 1.8$  ppm,  $31.5 \pm 7.3$  ppm, and  $30.9 \pm 6.8$  ppm, respectively (Fig. 7). In contrast, the vein calcites have much lower U and Th content, with means at  $2.5 \pm 1.8$  ppm and  $0.5 \pm 0.2$  ppm for U, and  $0.1 \pm 0.3$  ppm and  $0.2 \pm 0.3$  ppm for Th (Fig. 7).

## 5. Discussion

### 5.1 Diagenetic history

Nearly all the analyzed carbonates in the 4DC section, whether lacustrine or paleosol carbonate in origin, and whether dolomite or calcite in composition, show higher-than-plausible Earth-surface  $T_{(\Delta 638)}$  temperatures of  $>40$  °C (Fig. 4), which are signs of diagenesis. The much higher 120–130 °C  $T_{(\Delta 638)}$  temperatures of the vein calcites also indicate the existence of high-temperature thermal fluid, which may have also exerted diagenetic influences on adjacent micritic carbonates. In the following, we aim to identify possible processes that caused the diagenesis of the 4DC section carbonates. More specifically, we try to explain the following observations: 1) the dolomite components have  $T_{(\Delta 638)}$  temperatures of 34–43 °C; 2) the associated calcite components have  $T_{(\Delta 638)}$  temperatures of  $\sim 100$ –130 °C; 3) the two lacustrine micritic calcite samples have  $T_{(\Delta 638)}$  temperatures of  $\sim 50$ –60 °C while the one paleosol calcitic carbonate has  $T_{(\Delta 638)}$  temperature of  $\sim 41$  °C; and 4) the vein calcites have  $T_{(\Delta 638)}$  temperatures of  $\sim 120$ –130 °C (Fig. 4 and Table 2).

#### 5.1.1 Shallow burial diagenesis (partial dolomitization)

XRD analysis indicates that except for the paleosol carbonate (4DC16) and two lacustrine micrites (4DC51 and 4DC64) that are calcite in composition, most analyzed lacustrine micrites are composed predominantly of dolomite (61–93%), with a smaller amount of calcite component (Table 1). Although modern Earth-surface conditions make direct dolomite precipitation difficult, ample evidence of dolomite precipitation from surface waters in the geologic past has been documented (Vasconcelos et al., 1995; Warren, 2000). As a result, it is possible that both the calcite and dolomite components were primarily deposited from lake water; or alternatively, the calcite component was primarily deposited, while the dolomite component was formed by partial dolomitization of the calcite in a later stage (Machel, 2004; Warren, 2000).

The trace element concentration of the micrites indicates that the dolomite was probably not primarily precipitated from lake water. The three micrite samples have high to very high concentrations of U, i.e.,  $7.8 \pm 1.1$  ppm,  $28.1 \pm 3.2$ , and  $46.0 \pm 4.6$  ppm, respectively (Fig. 7). Similarly, the Th concentration is also high to very high between  $2.8 \pm 1.8$  ppm and  $31.5 \pm 7.3$  ppm (Fig. 7). Normally, carbonate precipitated from Earth-surface lake waters contain U and Th concentrations that are no more than 1 ppm (Elisha et al., 2021; Roberts et al., 2020) due to the fact that lake water contains very low amounts of U and Th, i.e., a few to tens of ppb (Smedley and Kinniburgh, 2023; Waseem et al., 2015). This suggests that the dolomite is most likely formed by partial dolomitization in fluid that is different from surface lake waters and is a significant source of trace elements and other elements, such as Mg. Numerous studies have shown that when the supply of  $Mg^{2+}$  ions in surrounding fluids is sufficient, calcite minerals may experience dolomitization (Machel, 2004; Warren, 2000).

Among the four measured  $T_{(\Delta 638)}$  temperatures of the dolomite component, three of them are between 40–43 °C, and the other one is  $\sim 34$  °C (Fig. 4 and Table 2). This indicates that the

dolomitization process occurred during shallow burial with slightly elevated ambient temperatures. As will be discussed in the next section, we consider that the 4DC section was further buried to a depth with a maximum temperature of  $\sim 130$  °C. Under this burial temperature, the dolomite component would experience minimal bond reordering, i.e.,  $\sim 1$  °C increase of  $T_{(\Delta 638)}$  temperatures (Fig. 5C–D). Thus, we suggest that partial dolomitization occurred at shallow depths equivalent to ambient temperatures of  $\sim 34$ – $40$  °C and that the dolomite component was largely unaffected by subsequent diagenetic events.

Although shallow burial partial dolomitization is our preferred explanation, it is conceivable that the measured  $34$ – $40$  °C  $T_{(\Delta 638)}$  temperatures represent a mixture of depositional ( $\sim 20$ – $30$  °C) and early diagenetic secondary dolomite (e.g.,  $\sim 50$  °C). The exact burial temperatures at which partial dolomitization occurred would then be determined by the mixing ratios of these two stages of dolomite, although there is no firm evidence at this time for two stages of dolomite precipitation.

### 5.1.2 Deep burial diagenesis (solid-state bond reordering and open-system recrystallization)

Using mixing models (section 4.5), it is shown that the calcite component of samples 4DC34 and 4DC41B have  $T_{(\Delta 638)}$  temperatures mainly ranging between  $100$  and  $130$  °C (Fig. 4, open green circles; Supplementary Table S1). However, the measured  $T_{(\Delta 638)}$  temperatures of two lacustrine micritic calcite samples (4DC51 and 4DC64) of the same section are only  $50$ – $60$  °C (Fig. 4, solid orange circles denoted by green arrows; Table 2). What caused the diverging  $T_{(\Delta 638)}$  temperatures of the micritic calcite versus calcite component?

Solid-state bond reordering modeling indicates that if the 4DC section was buried to temperatures of  $144$ – $160$  °C,  $20$ – $30$  °C calcite would be reordered to  $50$ – $60$  °C, e.g., 4DC51 and 4DC64 (Fig. 5A–B). The dominance of nanoparticles of sample 4DC51 under SEM (i.e.,  $10$ s– $100$ s nanometers in scale; Fig. 2H) indicates the lack of post-depositional recrystallization, supporting this inference of bond-reordering only. Solid-state bond reordering can explain the  $T_{(\Delta 638)}$  temperatures of 4DC51 and 4DC64, however, it cannot explain the  $100$ – $130$  °C  $T_{(\Delta 638)}$  temperatures of the calcite component of 4DC34 and 4DC41B. We note that 4DC34 and 4DC41B contain abundant vein calcites (Fig. 2C), which exhibit  $120$ – $130$  °C  $T_{(\Delta 638)}$  temperatures (Fig. 4, solid red circles), indicating the presence of high-temperature thermal fluid. Thus, a possible explanation is that the calcite component of these two samples experienced open-system recrystallization (dissolution and reprecipitation) in the presence of high-temperature thermal fluids. As a result, the recrystallized calcite component would record similar  $120$ – $130$  °C temperatures as the thermal fluid. The lower  $T_{(\Delta 638)}$  temperatures of the calcite component, i.e.,  $\sim 100$  °C and  $68$  °C (Supplementary Table S1), can be explained as a mixing of depositional calcite and recrystallized calcite. This explanation receives support from SEM observations, which show micro-crystals probably formed during recrystallization (Fig. 2G). Additional supporting evidence of open-system recrystallization is the positive  $\delta^{18}\text{O}_{\text{mw}}$  values ( $-0.4 \pm 2.6$  ‰, VSMOW) of water calculated from the  $\delta^{18}\text{O}_{\text{carb}}$  and  $T_{(\Delta 638)}$  temperatures of the calcite component (Supplementary Table S1), which is similar to the fluid in which vein calcite precipitated ( $-1.7 \pm 0.5$  ‰, Table 2), but different from those in which the dolomite component precipitated ( $-8.8 \pm 2.2$  ‰, Table 2).

Although the calcite component of these samples experienced open-system recrystallization, we argue that the dolomite component in the same micrite samples did not recrystallize, based on the observation that these dolomites exhibit 34–40 °C  $T_{(\Delta 638)}$  temperatures (Fig. 4, open orange circles). Compared to calcite, dolomite has a higher resistance to dissolution (Langmuir, 1997) and thus a higher potential to remain unaltered (i.e., Mueller et al., 2020). Open-system recrystallization did not influence the two micritic calcite samples that lack vein calcite (4DC51 and 4DC64; Fig. 2E), further implicating the influence of high-temperature fluids in altering samples that do contain vein calcite.

The above discussion of solid-state bond reordering is based on the HH21 model of Hemingway and Henkes (2021), which requires 140–160 °C maximum burial temperatures to reorder 20–30 °C calcite to 50–60 °C (Fig. 5A–B). However, if using different models, such as Hea14 (Henkes et al., 2014) and SE15 (Stolper and Eiler, 2015), the results are slightly different. For example, under a 130 °C maximum burial temperature, the Hea14 model predicts that 30 °C calcite could be reordered to 53 °C (Fig. 6B); while the SE15 model predicts that 20 ° and 30 °C calcite could be reordered to 57 °C and 64 °C, respectively (Fig. 6C). The differences between these different models lie in their different mechanistic interpretations of solid-state bond reordering in calcite. If the kinetic parameters of the micritic calcite of 4DC51 and 4DC64 are more similar to those of Hea14 and SE15 models, it would indicate that the 4DC section does not need to be buried to the depth with 144–160 °C temperatures (as inferred from the HH21 model, Fig. 5A–B), but rather a temperature of 130 °C would be sufficient to reorder 20–30 °C micritic calcite to 50–60 °C (Fig. 6B–C).

Although both 144–160 °C and 130 °C maximum burial temperatures are possible to explain the 50–60 °C  $T_{(\Delta 638)}$  temperatures of 4DC51 and 4DC64, we prefer the 130 °C scenario, as it is a simpler explanation for all the following three observations: 1) reorder micritic calcite samples 4DC51 and 4DC64 to 50–60 °C by solid-state bond reordering; 2) form the 120–130 °C vein calcite; and 3) reset the temperatures of the calcite component of samples 4DC34 and 4DC41B to 100–130 °C through open-system recrystallization. Considering the total measurable overburden of ~3 km or less based on the maximum thickness of younger strata in the Nima area (DeCelles et al., 2007a; Huntington et al., 2014), as well as possible thrust loading of the north-verging GSBT (Fig. 1A) (DeCelles et al., 2007a; DeCelles et al., 2007b; Kapp et al., 2007), it is reasonable that the 4DC section was buried to ~3.3–4.4 km depth with maximum burial temperatures of 120–130 °C, assuming a surface temperature of 20–30 °C, and a thermal gradient of 25–30 °C/km.

### 5.1.3 Summary of a multi-stage diagenetic history

Based on the above discussion, we summarize the most likely diagenetic history for the Nima Basin 4DC section carbonates (Fig. 8), as well as changes in both the  $\delta^{18}\text{O}_{\text{carb}}$  and  $T_{(\Delta 638)}$  temperatures (Table 3).

During the late Oligocene (~26–25 Ma), limestones were deposited in the Nima Lake (T0 in Table 3 and Fig. 8) at Earth-surface conditions, such that both the stable and clumped isotopes of the limestone (micritic calcite) recorded the isotopic composition and temperature of lake water. Later, when the lacustrine limestone was shallowly buried to a depth with temperatures of 34–



40 °C, basinal fluid with  $\text{Mg}^{2+}$  ions and with different chemical compositions from surface lake waters, filled pore spaces and caused partial dolomitization of the micritic calcite (T1 in Table 3 and Fig. 8). Some layers experienced no dolomitization, such as 4DC51 and 4DC64. The newly formed dolomite component recorded the stable and clumped isotopes of the basinal fluid and shallow burial temperatures, respectively, whereas the remaining calcite experienced no changes and its stable and clumped isotopes still recorded surface lake water conditions. Considering the shallow burial depth of dolomitization, i.e., 0.3–0.8 km depth (considering surface temperatures of 20–30 °C, and thermal gradients of 25–30 °C/km), it is likely that the  $\delta^{18}\text{O}_{\text{mw}}$  values of the groundwater are similar as those of surface water, although there are additional inputs of trace elements.

With further burial, probably due to thrust loading from the south (DeCelles et al., 2007a; Kapp et al., 2007), the 4DC section was buried to a depth with temperatures of ~120–130 °C (T2, Table 3 and Fig. 8). Under these burial temperatures, the following diagenetic processes occurred: 1) the formation of 120–130 °C vein calcites, the stable and clumped isotope temperatures of which record those of the thermal fluid; 2) the micritic calcite samples that are far away from and unaffected by thermal fluid, e.g., 4DC51 and 4DC64, were reset to 50–60 °C temperatures by solid-state bond reordering; while their  $\delta^{18}\text{O}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values remain the same as depositional calcite; 3) the calcite components of micrites that are adjacent to and influenced by thermal fluid, e.g., 4DC34 and 4DC41B, were reset to 100–130 °C temperatures by open-system recrystallization; and 4) the associated dolomite components in these samples experienced neither open-system recrystallization nor solid-state bond reordering (i.e., only 1 °C temperature increase; Fig. 5C–D), due to the higher resistance to dissolution and bond reordering.

## 5.2 Implications for paleoelevation estimates of the Nima Basin in central Tibet

DeCelles et al. (2007b) interpreted the micritic texture of the paleosol carbonate (Supplementary Fig. S1A–B) of the 4DC section, in addition to a “conglomerate test”, to reflect the preservation of syndepositional isotopic signals. They found very low  $\delta^{18}\text{O}_{\text{carb}}$  values, which are indistinguishable from the least evaporated  $\delta^{18}\text{O}_{\text{carb}}$  values of modern soil carbonates in the area. As a result, they deduced that the Nima Basin had reached its modern high elevations by at least 26 Ma. Subsequently, Huntington et al. (2014) determined >47 °C clumped isotope temperatures for the 4DC section lacustrine micrites. They concluded that varying degrees of micro-scale mineral recrystallization occurred in a rock-buffered environment and argued against the possibility of solid-state bond reordering.

This study reveals a more complex diagenetic history for the 4DC section carbonate rocks (Fig. 8). Compared to Huntington et al. (2014)’s study, the additional diagenetic processes were identified through: 1) a new XRD mineralogy study to identify both calcite and dolomite components, which is critical for both solid-state bond reordering modeling and differentiating phases of diagenesis; 2) updated model configuration and kinetic parameters for bond reordering, including the different reordering behaviors between calcite and dolomite (Hemingway and Henkes, 2021, and references within); and 3) additional clumped isotope measurements of the vein calcites. We do not favor a rock-buffered cryptic recrystallization explanation, because the process

of dolomitization, as well as the introduction of vein calcites, would require considerable fluid in the system, during both shallow and moderately deep burial.

Although at least two stages of diagenesis were identified for the Nima Basin 4DC section lacustrine carbonates, this does not necessarily negate DeCelles et al. (2007b)'s results, which used the very low  $\delta^{18}\text{O}_{\text{carb}}$  values of paleosol carbonate to infer similar-to-present high paleoelevations. As argued in section 5.1.3, in the 4DC section, the few pure calcite samples, e.g., 4DC16, 4DC51, and 4DC64 (Table 1), only experienced solid-state bond reordering, which would only influence the clumped isotope temperatures, but would not change the syndepositional  $\delta^{18}\text{O}_{\text{carb}}$  values. Thus, the argument for well-preserved  $\delta^{18}\text{O}_{\text{carb}}$  values in DeCelles et al. (2007b) would still hold. This inference confirms the reliability of the “conglomerate test” as originally proposed in DeCelles et al. (2007b) in detecting diagenesis, i.e., similar  $\delta^{18}\text{O}_{\text{carb}}$  values between newly deposited carbonates and interbedded marine limestone clasts strongly suggest diagenetic alteration.

As pointed out by Li et al. (2022), although the  $\delta^{18}\text{O}_{\text{carb}}$  values of soil carbonates are similar between 25–26 Ma and the present, this does not require that the region arrived at exactly the present elevation, as the temperature of soil carbonate formation is probably different between 25–26 Ma and the present. If using the  $33.4 \pm 3.0^\circ\text{C}$  ( $n=3$ ,  $1\sigma$ ) clumped isotope temperatures of the upper Niubao paleosol carbonate in the adjacent Lunpola Basin (Ingalls et al., 2020), which has similar depositional ages of 26–23 Ma (Fang et al., 2020), this would suggest elevations of only  $3.3 \pm 0.5$  km following the calculation method outlined in Li et al. (2022). This indicates an additional  $>1$  km elevation increase in the Nima Basin ( $\sim 4.6$  km modern elevation) after  $\sim 25$  Ma.

This new moderate paleoelevation inference ( $3.3 \pm 0.5$  km at 25–26 Ma for the Nima Basin) agrees with recent paleoelevation estimates in the nearby Lunpola Basin (Fig. 1A) (Li et al., 2022; Sun et al., 2022). Together, these studies suggested: 1) the existence of a moderately high central valley not only in the Lunpola Basin, but also in the nearby Nima Basin, which probably extended farther west along the Bangong suture zone (Li et al., 2022); and 2) the central valley was uplifted to its current high elevations (4.5–4.7 km) during the Neogene, but not during the Oligocene (Xiong et al., 2022), or even the late Eocene (Ingalls et al., 2020; Rowley and Currie, 2006). As there is no evidence for major upper-crustal shortening in central Tibet since  $\sim 23$  Ma (Kapp et al., 2007), Neogene surface uplift may be attributed to northward underthrusting of the Indian lower crust and/or middle-lower crustal flow from surrounding high-elevation mountain ranges, e.g., Gangdese and Tanggula (Fig. 1A) (Li et al., 2022). In addition, considering the thin lithosphere beneath central Tibet (McNamara et al., 1997), the convective removal of the lower lithosphere might have also contributed to the Neogene surface uplift.

### 5.3 Implications for carbonate diagenesis studies

The results of this study and many other studies (e.g., Ingalls, 2019; Lacroix and Niemi, 2019; Leier et al., 2009; Winkelstern and Lohmann, 2016) indicate that micritic carbonates may have experienced complex diagenetic alterations. However, the recording of higher than plausible Earth-surface clumped isotope temperatures is also not confirming evidence of the loss of syndepositional stable isotopic signals. The retention of micritic textures with higher clumped isotope temperatures could be formed by several different processes that have different influences

on the syndepositional stable isotopic values: 1) closed-system cryptic-recrystallization, 2) open-system cryptic-recrystallization, and 3) solid-state bond reordering. Closed-system recrystallization and solid-state bond reordering would only alter the clumped isotope values but exert no influence on the syndepositional stable isotopic signals, which is not the case for open-system recrystallization.

Petrographic and CL observations are useful tools in identifying the existence of external fluid (a sign of open-system diagenesis), which usually leaves vein calcite as a product. However, it is also possible that the fluid exerts no influence on host carbonate rocks if the fluid activity is transient or the host materials are resistant to dissolution, i.e., dolomite. The measurement of clumped isotope temperatures and U-Pb dating (MacDonald et al., 2019; Mangenot et al., 2018; Mueller et al., 2020; Pagel et al., 2018) on both host and vein carbonate, could provide additional constraints to evaluate the diagenesis history. It is suggested that in studies of carbonate diagenesis, when vein calcite is present, the measurement of both the temperature and timing of vein calcite formation is beneficial. Fluid inclusions may also be abundant in micrites and vein calcites. Analyses of the stable isotopes, trace elements, and temperatures of the fluids (Pettke et al., 2012) provide direct information about ancient fluid in which carbonate precipitated and thus could also help explore diagenetic history (e.g., Mueller et al., 2020; Mueller et al., 2022).

Clumped isotope solid-state bond reordering modeling (Hemingway and Henkes, 2021; Henkes et al., 2014; Stolper and Eiler, 2015) provides an additional powerful tool to examine the causes of diagenesis. There has been some recent data indicating that water and/or the exchangeable fraction of water can increase reordering rates (Brenner et al., 2018; Looser et al., 2023; Nooitgedacht et al., 2021; Perez-Beltran et al., 2023; Sun et al., 2023). However, the currently available bond reordering models are all based on the heating experiments of optical calcite and biogenic calcite, i.e., branchiopod and belemnite (Hemingway and Henkes, 2021; Henkes et al., 2014; Looser et al., 2023; Stolper and Eiler, 2015). Lacustrine micrites and soil carbonates may have increased surface area and/or biological matter that can help speed up bond reordering, but how that compares to optical calcites and organic-matrix biogenic calcites is unclear at this time. It is necessary to conduct more heating experiments on natural lacustrine micrite and soil carbonate samples. The one paleosol calcite sample (4DC16) has a  $T_{(\Delta 638)}$  temperature of 41 °C, which is more than 10 °C lower than those of lacustrine micritic calcite samples (4DC51 and 4DC64) at 50–60 °C, further exemplifies the likely difference in kinetic parameters between different types of calcites that were formed in varying environments.

## 6. Conclusions

In this study, we applied an integrated suite of tools to explore micrite diagenesis, including: mineralogy identification (XRD analysis), petrographic, CL, SEM, and EPMA imaging, LA-ICPMS trace element analysis and U-Pb dating, stable isotopes, clumped isotopes, as well as mixing models and solid-state bond reordering modeling. Our results demonstrate two stages of diagenesis for the Nima Basin 4DC section carbonates: shallow burial (34–40 °C) partial dolomitization, and moderately deep burial (120–130 °C) bond reordering and open-system recrystallization.

For the Nima Basin, our new results indicate that the  $\delta^{18}\text{O}_{\text{carb}}$  values of paleosol carbonates (DeCelles et al., 2007b) recorded the syndepositional Earth-surface water stable isotope signals. However, the Nima Basin was probably only  $\sim 3.3$  km high during the late Oligocene, requiring an additional  $>1$  km of surface uplift during the Neogene. This is consistent with recent paleoelevation studies in the nearby Lunpola Basin, which requires subsurface geodynamic processes other than shortening for the Neogene surface uplift along the Bangong suture zone in central Tibet (Li et al., 2022).

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## Data Availability

All data associated with this paper (Data S1: clumped isotope data of new samples; Data S2: clumped isotope data of standards; Data S3: carbonate LA-ICPMS U-Pb data) are available through Zenodo at: <https://doi.org/10.5281/zenodo.10523691>.

## Appendix A. Supplementary material

The supplementary file includes two tables and five figures: Table S1: Calculation of stable and clumped isotopes of calcite component using mixing model. Table S2: Summary of solid-state bond reordering modeling results. Fig. S1 shows the CL images of samples 4DC16 and 4DC41A. Fig. S2 shows the SEM images of samples 4DC41B and 4DC51. EPMA maps of all measured elements (Ca, Mg, Si, Fe, Mn, Sr, Cr, and Ba) for sample 4DC41A\_coarse scale (Fig. S2), 4DC41A\_fine scale (Fig. S3), 4DC47.2\_coarse scale (Fig. S4). Fig. S5 shows the comparison of clumped isotope values using different data processing methods. Fig. S6 shows the Tera-Wasserburg plots of carbonate U-Pb data. The supplementary file can be found online at xxx.

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## Figure captions

**Figure 1.** Geologic background. **(A)** Shaded relief map of the south-central Tibetan Plateau. Dashed lines are suture zones; solid lines with barbs are thrust faults. The white box shows the location of the southern Nima Basin in Fig. 1B. Explanations of abbreviations are embedded in B. **(B)** Simplified geologic map of the southern Nima Basin, showing sedimentary sections (1DC, 4DC) and tuff zircon U-Pb ages of DeCelles et al. (2007b). Adapted from Kapp et al. (2007). **(C)** Simplified stratigraphy of the 4DC section, showing stratigraphic heights of analyzed samples. Adapted from DeCelles et al. (2007b). Open circles on the right indicate carbonate samples and their stratigraphic heights. Note that the majority of samples are lacustrine micrites, except 4DC16 (soil carbonate). The letter “V” denotes vein calcite samples.

**Figure 2.** Macro- and micro-textures of analyzed carbonate samples. **(A)** field outcrops showing lacustrine micrite interlayered with massive red siltstones. **(B)** A micritic carbonate hand sample with vein calcite (4DC41B). **(C–F)** Petrographic microscope images of representative samples under cross-polarized light. **(G–H)** SEM images of samples 4DC41B and 4DC51, respectively. EPMA maps of sample 4DC41A **(I–J)** and 4DC47.2 **(K–L)** for Ca and Mg elements, respectively. The color bar indicates counts of Ca or Mg element: the red color indicates high counts (high content), and the black color indicates 0 count.

**Figure 3.** Carbonate  $\delta^{13}\text{C}_{\text{carb}}$  (VPDB) and  $\delta^{18}\text{O}_{\text{carb}}$  (VPDB) results. **(A)** The dolomite ratio of representative samples. The dolomite ratio is calculated as dolomite/(dolomite+calcite) (wt%); **(B)**  $\delta^{13}\text{C}_{\text{carb}}$  vs.  $\delta^{18}\text{O}_{\text{carb}}$  relationship; **(C)**  $\delta^{18}\text{O}_{\text{carb}}$  values vs. stratigraphic heights of micrite; **(D)**  $\delta^{13}\text{C}_{\text{carb}}$  values vs. stratigraphic heights of micrite; **(E)**  $\delta^{18}\text{O}_{\text{carb}}$  values vs. stratigraphic heights of vein calcite; **(F)**  $\delta^{13}\text{C}_{\text{carb}}$  values vs. stratigraphic heights of vein calcite. The two micritic calcite samples (4DC51 and 4DC64) are marked with gray ovals.

**Figure 4.** Measured and calculated clumped isotope temperatures of different types of carbonates. The green arrows point to pure calcite samples.

**Figure 5.** Model results of solid-state bond reordering of both calcite (A–B) and dolomite (C–D) using the HH21 model (Hemingway and Henkes, 2021). Solid thick and dotted thin lines are the mean and 95% confidence of forward modeled data; dashed thick lines are equilibrium values. Also labeled are the initial and final clumped isotope temperatures of carbonate, as well as maximum burial temperatures. All simulations are of the same burial and exhumation scenarios: 25–20 Ma gradual burial, 20–10 Ma deep burial to different maximum temperatures (differentiated by different colors, i.e., blue, orange, and black), and 10–0 Ma exhumation to surface. See Supplementary Table S2 for results of all modeling runs.

Figure 6. Model results of solid-state bond reordering of calcite using different models: (A) HH21 (Hemingway and Henkes, 2021), (B) Hea14 (Henkes et al., 2014), and (C) SE15 (Stolper and Eiler, 2015) models.

**Figure 7.** Carbonate U and Th content (ppm) analyzed using the LA-ICPMS method. Note the changing scale of the U content. The inset shows an enlarged area for the 0–1 ppm range of U.

**Figure 8.** Proposed carbonate diagenetic history for the 4DC section of the Nima Basin. The thick black arrow indicates sequential burial/diagenetic history. Limestone was deposited in the Nima Lake at 26–25 Ma (T0); later, when the section was shallowly buried at 34–40 °C, partial dolomitization occurred in fluid that is likely different from surface water (T1); further burial to a depth of 120–130 °C temperatures (T2) caused the formation of high-temperature vein calcite; solid-state bond reordering of the micritic calcite that is unaffected by thermal fluid to 50–60 °C; open-system recrystallization of the calcite component of micrites that are close to thermal fluid to record 100–130 °C temperatures, while the associated dolomite component experienced neither open-system recrystallization nor significant solid-state bond reordering. See text for more details.

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**Table 1.** Summary of XRD results.

| Sample ID             | Dolomite (wt%) | Calcite<br>(wt%) | Quartz<br>(wt%) | Others<br>(wt%) | Dolomite+Calcite<br>(wt%) | Dolomite ratio*<br>(%) |
|-----------------------|----------------|------------------|-----------------|-----------------|---------------------------|------------------------|
| 4DC16 <sup>†, #</sup> | 0              | 88               | 12              | 0               | 88                        | 0                      |
| 4DC34                 | 64             | 17               | 16              | 3               | 81                        | 79                     |
| 4DC47                 | 56             | 17               | 24              | 3               | 73                        | 77                     |
| 4DC41B                | 55             | 28               | 15              | 2               | 83                        | 66                     |
| 4DC47.2               | 53             | 26               | 17              | 4               | 79                        | 67                     |
| 4DC51 <sup>#</sup>    | 0              | 91               | 6               | 3               | 91                        | 0                      |
| 4DC64 <sup>#</sup>    | 1              | 44               | 43              | 12              | 45                        | 2                      |
| 4DC105                | 54             | 35               | 8               | 3               | 89                        | 61                     |
| 4DC112                | 70             | 6                | 19              | 5               | 76                        | 93                     |

Note: wt% indicates weight percentage.

\*dolomite ratio is defined as dolomite/(dolomite+calcite).

<sup>†</sup> Note that 4DC16 is a paleosol carbonate sample, while all others are lacustrine micrite.

<sup>#</sup> Note that these three samples have distinctly low to no dolomite content compared to other samples.

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**Table 2.** Summary of carbonate clumped isotope data<sup>#</sup>.

| Sample<br>name     | Rep.<br>no. | $\delta^{13}\text{C}_{\text{carb}}$<br>(VPDB<br>/‰) | SD<br>(‰) | $\delta^{18}\text{O}_{\text{carb}}$<br>(VPDB<br>/‰) | SD<br>(‰) | $\Delta 638_{\text{CDES}}$<br>(‰)* | SD<br>(‰) | 1 SE<br>(‰) | 95%<br>conf. | Temp.^<br>(°C) | error <sup>¶</sup><br>(°C) | $\delta^{18}\text{O}_{\text{w}}$<br>(VSMOW<br>/‰) | Error<br>(‰) |
|--------------------|-------------|-----------------------------------------------------|-----------|-----------------------------------------------------|-----------|------------------------------------|-----------|-------------|--------------|----------------|----------------------------|---------------------------------------------------|--------------|
| <u>Micrite</u>     |             |                                                     |           |                                                     |           |                                    |           |             |              |                |                            |                                                   |              |
| 4DC16 <sup>§</sup> | 5           | -3.82                                               | 0.03      | -16.86                                              | 0.04      | 0.592                              | 0.018     | 0.004       | 0.007        | 41.0           | 3.1                        | -11.75 <sup>‡</sup>                               | 0.69         |
| 4DC34              | 5           | -5.02                                               | 0.01      | -12.89                                              | 0.02      | 0.580                              | 0.011     | 0.004       | 0.007        | 45.5           | 3.2                        | -6.95 <sup>‡</sup>                                | 0.69         |
| 4DC41B-1           | 4           | -2.86                                               | 0.02      | -11.68                                              | 0.04      | 0.549                              | 0.004     | 0.004       | 0.007        | 58.8           | 3.8                        | -3.47 <sup>‡</sup>                                | 0.73         |
| 4DC41B-2           | 4           | -2.60                                               | 0.01      | -11.66                                              | 0.04      | 0.540                              | 0.012     | 0.004       | 0.008        | 62.8           | 4.0                        | -2.81 <sup>‡</sup>                                | 0.74         |
| 4DC47.2            | 4           | -0.89                                               | 0.01      | -9.22                                               | 0.02      | 0.559                              | 0.014     | 0.004       | 0.008        | 54.4           | 3.8                        | -1.72 <sup>‡</sup>                                | 0.75         |
| 4DC51              | 5           | -0.44                                               | 0.03      | -16.78                                              | 0.02      | 0.550                              | 0.013     | 0.002       | 0.004        | 58.1           | 2.5                        | -8.72 <sup>‡</sup>                                | 0.56         |
| 4DC64              | 5           | -1.65                                               | 0.14      | -17.40                                              | 0.31      | 0.571                              | 0.017     | 0.002       | 0.004        | 49.4           | 2.3                        | -10.80 <sup>‡</sup>                               | 0.56         |
| 4DC112             | 4           | -1.13                                               | 0.02      | -12.85                                              | 0.00      | 0.593                              | 0.012     | 0.004       | 0.007        | 40.7           | 3.3                        | -7.76 <sup>‡</sup>                                | 0.71         |



Vein calcite

|          |   |       |      |        |      |       |       |       |       |       |     |       |      |
|----------|---|-------|------|--------|------|-------|-------|-------|-------|-------|-----|-------|------|
| 4DC41B-V | 4 | -2.63 | 0.01 | -18.52 | 0.02 | 0.445 | 0.005 | 0.004 | 0.008 | 118.1 | 6.5 | -2.17 | 0.84 |
| Nima10-V | 4 | -0.57 | 0.02 | -18.41 | 0.03 | 0.437 | 0.014 | 0.004 | 0.008 | 124.1 | 7.0 | -1.37 | 0.88 |
| Nima11-V | 4 | -0.73 | 0.02 | -18.12 | 0.03 | 0.441 | 0.017 | 0.004 | 0.008 | 121.0 | 6.8 | -1.43 | 0.87 |

Dolomite only<sup>†</sup>

|           |   |       |      |        |      |       |       |       |       |      |     |        |      |
|-----------|---|-------|------|--------|------|-------|-------|-------|-------|------|-----|--------|------|
| 4DC34-D1  | 4 | -4.96 | 0.01 | -12.68 | 0.03 | 0.610 | 0.004 | 0.003 | 0.007 | 34.4 | 2.9 | -11.37 | 0.68 |
| 4DC34-D2  | 4 | -4.81 | 0.04 | -12.31 | 0.03 | 0.593 | 0.013 | 0.004 | 0.007 | 40.7 | 3.1 | -9.86  | 0.69 |
| 4DC41B-D1 | 5 | -2.61 | 0.02 | -9.73  | 0.03 | 0.595 | 0.024 | 0.004 | 0.007 | 40.0 | 3.2 | -7.40  | 0.71 |
| 4DC41B-D2 | 5 | -2.60 | 0.01 | -9.57  | 0.03 | 0.585 | 0.014 | 0.004 | 0.007 | 43.7 | 3.3 | -6.60  | 0.71 |

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Note: Rep. no., replicate number; SD, standard deviation; SE, standard error; 95% conf., 95% confidence interval; Temp., temperature.

# See Supplementary Data S1 for the full data set, including removed outliers; Supplementary Data S2 for data of all standards.

\* In the new TILDAS system,  $\Delta_{638}$  is equivalent to the conventional  $\Delta_{47}$ . See method section 3.3 for more information.

^ The temperature calibration equation is:  $\Delta_{638}_{\text{CDES}} = 0.0409 \pm 0.0003 \times (10^6/T^2) + 0.1776 \pm 0.0031$ ,  $R^2 = 0.997$  (Yanay et al., 2022).

<sup>¶</sup>The temperature error is calculated using the "pooled" standardization approach of Daëron (2021).

<sup>‡</sup> Note that although the stable isotope values of paleo-fluids of these samples were provided, we emphasize that these measured bulk samples contain a calcite component that experienced open-system recrystallization or solid-state bond reordering, and thus records elevated temperatures, and as a result, the calculated water isotopes are meaningless.

<sup>§</sup> 4DC16 is a soil carbonate, and all the others are lacustrine carbonates.

<sup>†</sup> D1 indicates micrites reacted with acetic acid for 60 minutes, while D2 indicates a reaction time of 120 minutes.

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**Table 3.** Summary of the diagenetic history and changes in mineralogy, stable and clumped isotopes.

| Stages* | Settings                         | Deposition/<br>diagenesis                                                                     | $\delta^{18}\text{O}_{\text{carb}}$ values                                                                                                                                                                                                                                                                                                    | Clumped isotope temperatures                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
|---------|----------------------------------|-----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| T0      | Earth-surface<br>(20–30 °C)      | Primary deposition of limestone                                                               | <ul style="list-style-type: none"> <li>Record those of lake water</li> </ul>                                                                                                                                                                                                                                                                  | <ul style="list-style-type: none"> <li>Record those of lake water</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                         |
| T1      | Shallow burial at 34–40 °C depth | Partial dolomitization                                                                        | <ul style="list-style-type: none"> <li>Newly formed dolomite component records those of basinal fluid</li> <li>Remaining calcite component records those of surface lake water</li> </ul>                                                                                                                                                     | <ul style="list-style-type: none"> <li>Newly formed dolomite component records elevated burial temperatures of 34–40°C</li> <li>Remaining calcite component records surface lake water temperatures</li> </ul>                                                                                                                                                                                                                                                                                       |
| T2      | Deep burial at ~120–130 °C depth | Solid-state bond reordering, open-system recrystallization, and precipitation of vein calcite | <ul style="list-style-type: none"> <li>Vein calcites record those of thermal fluid</li> <li>No stable isotope changes to the few micritic calcite samples<sup>†</sup></li> <li>The stable isotopes of the calcite component record those of thermal fluid<sup>†</sup></li> <li>No stable isotope changes to the dolomite component</li> </ul> | <ul style="list-style-type: none"> <li>Vein calcites record high temperatures of thermal fluid (120–130°C)</li> <li>The few micritic calcites experienced bond reordering to 50–60 °C temperatures<sup>†</sup></li> <li>The calcite component experienced open-system recrystallization to record 100–130 °C temperatures<sup>†</sup></li> <li>The dolomite component experienced neither open-system recrystallization nor significant solid-state reordering (i.e. only ~1 °C increase)</li> </ul> |

\* The T0–T2 stages (from old to young) correspond to those in Fig. 8.

<sup>†</sup> The different behaviors between the micritic calcite (e.g., 4DC51 and 4DC64) and the calcite component (e.g., 4DC34 and 4DC41B) are probably due to the fact that the former is far away from and unaffected by thermal fluid, and the latter is adjacent to and influenced by thermal fluid.

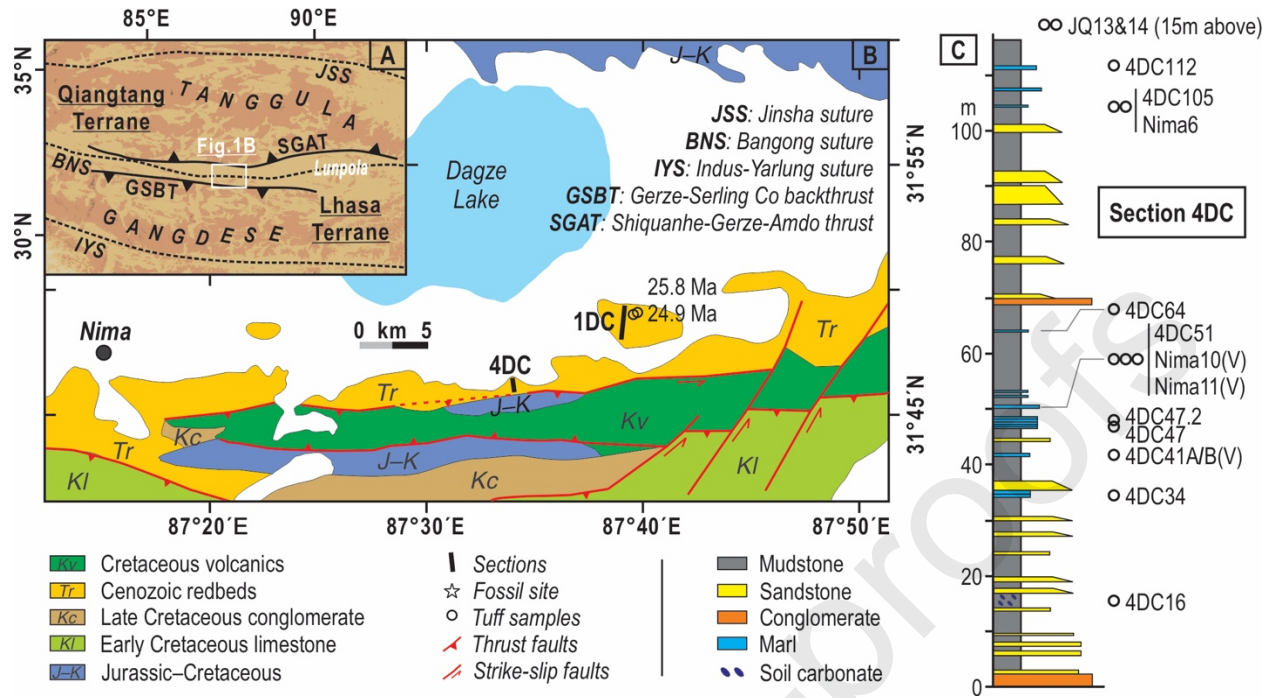


Figure 1



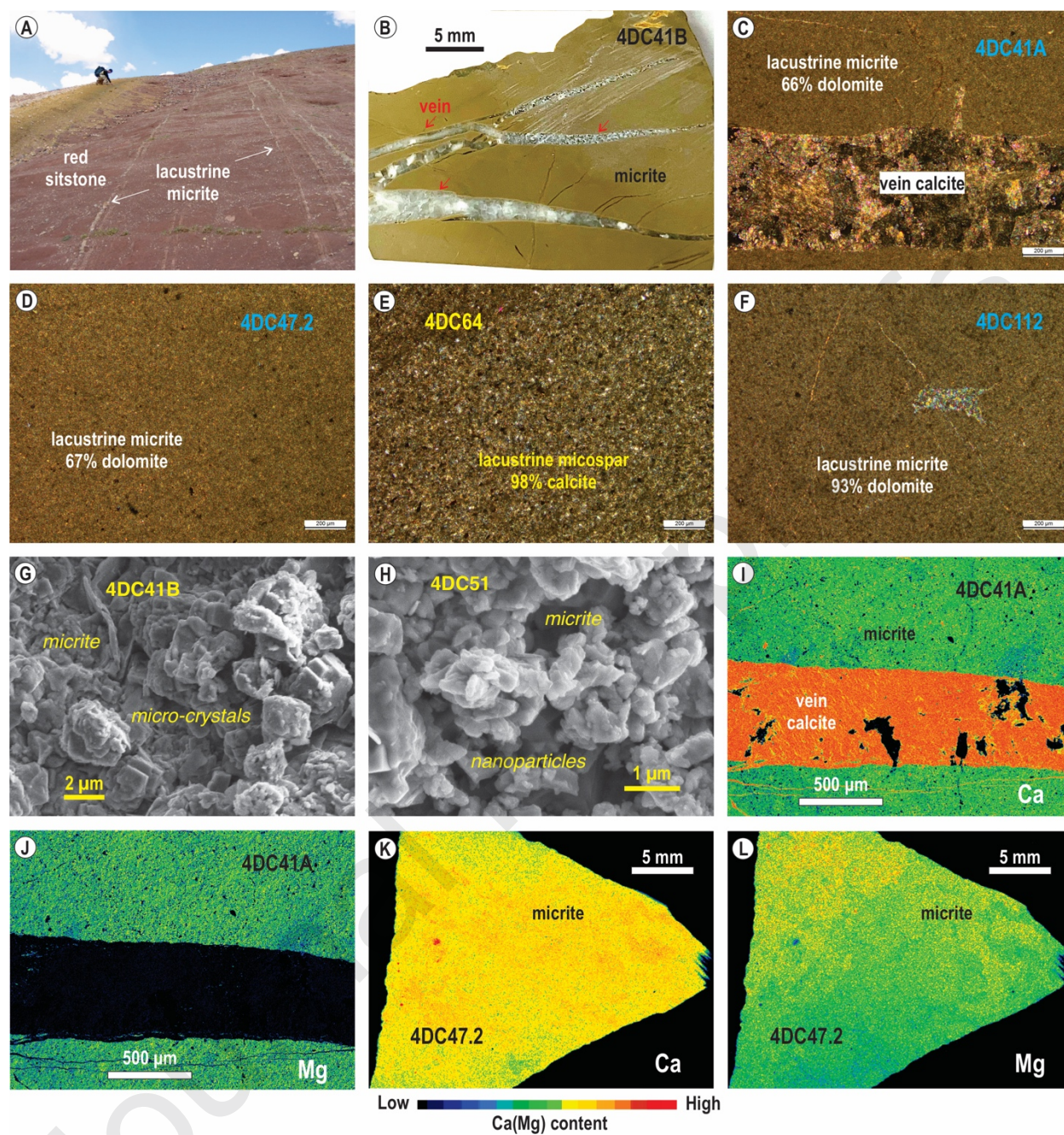


Figure 2

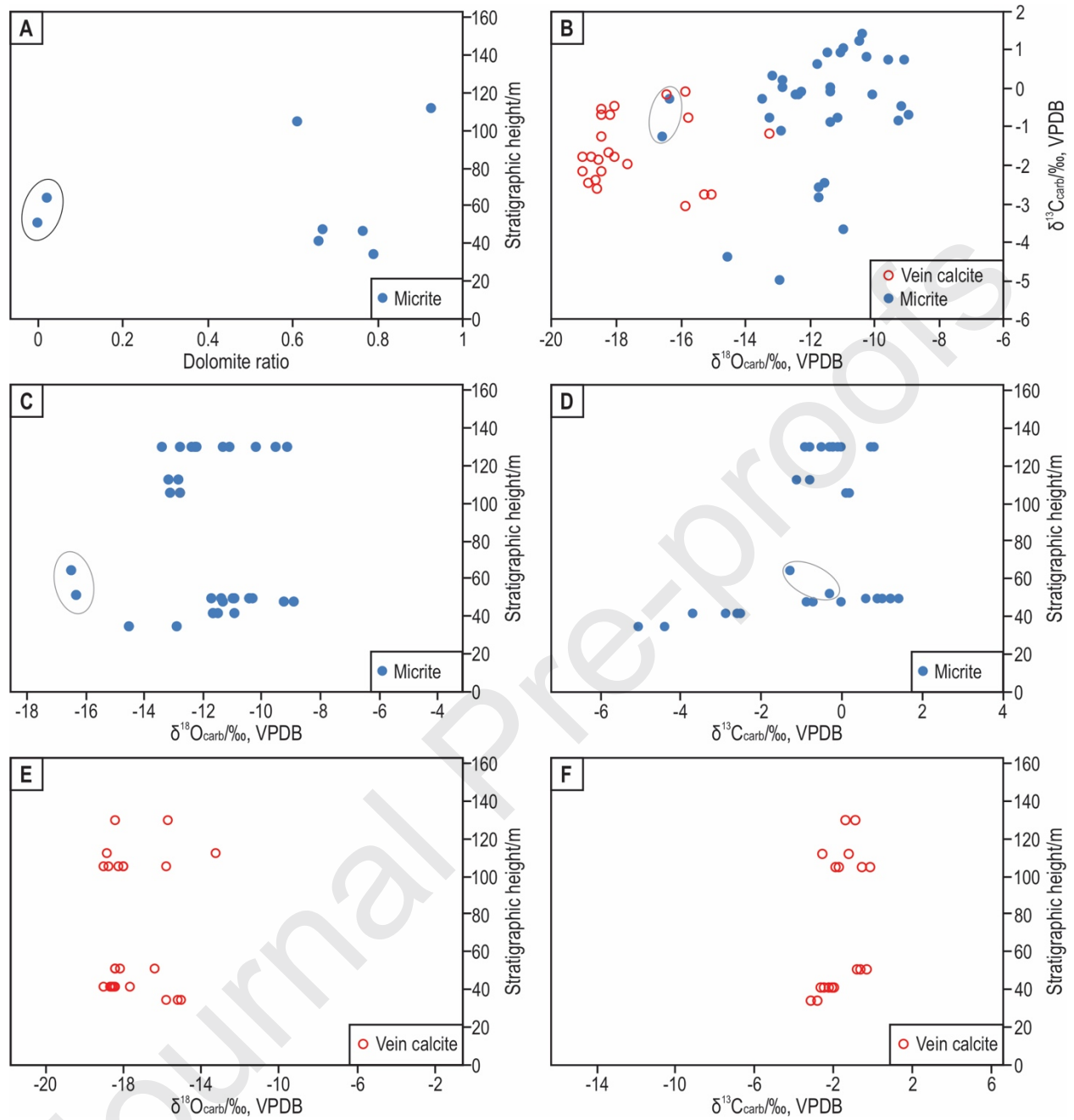
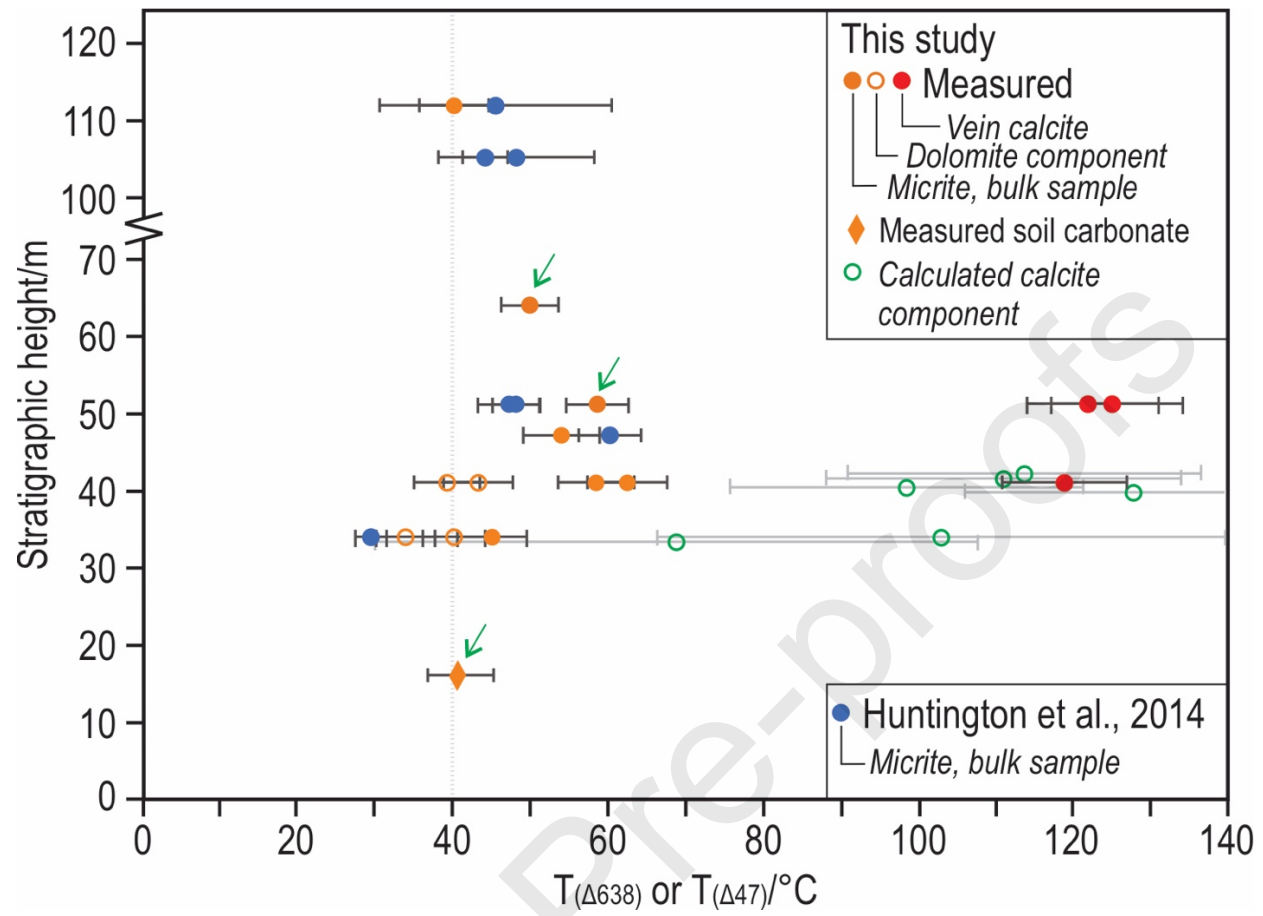


Figure 3





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1030 Figure 4

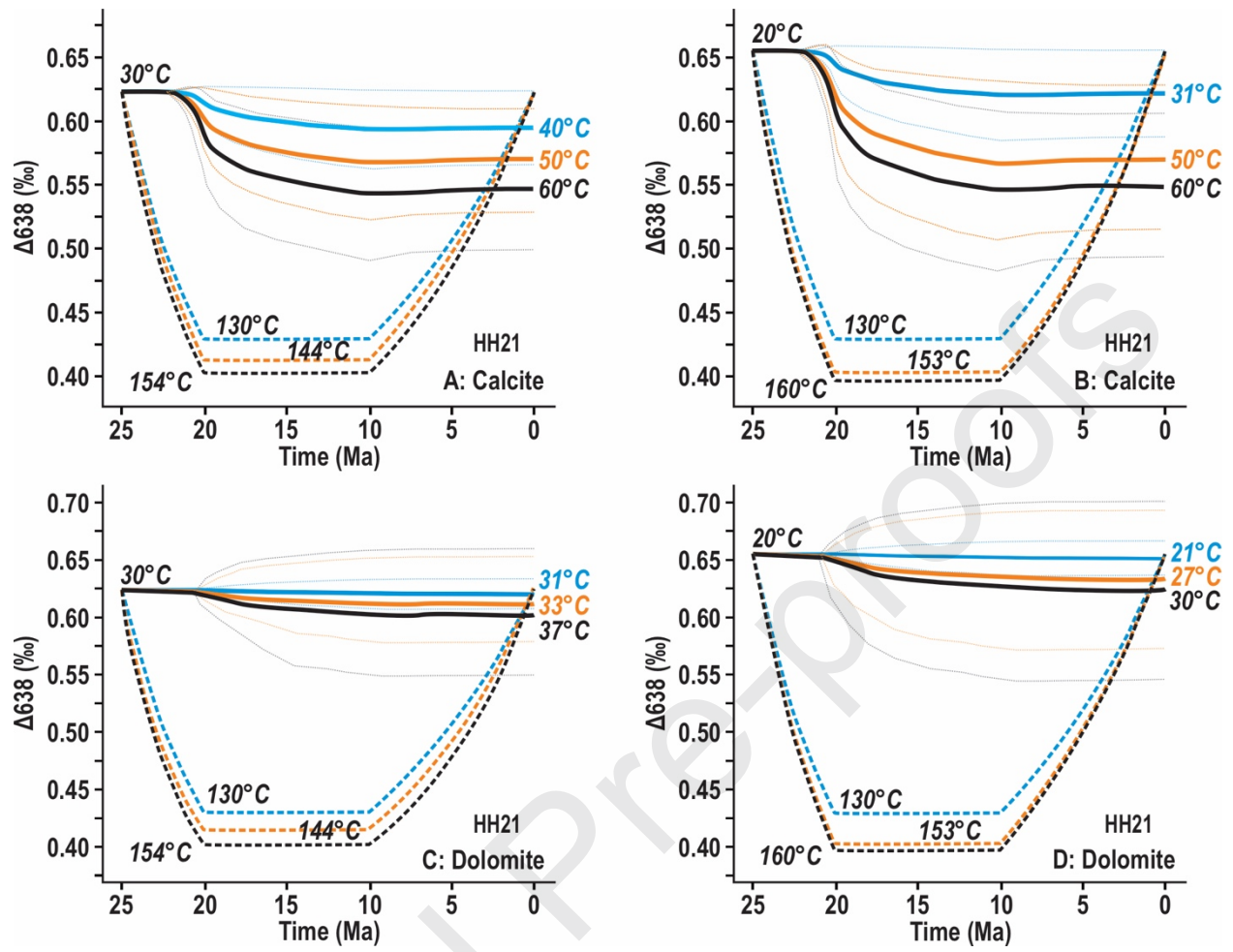


Figure 5

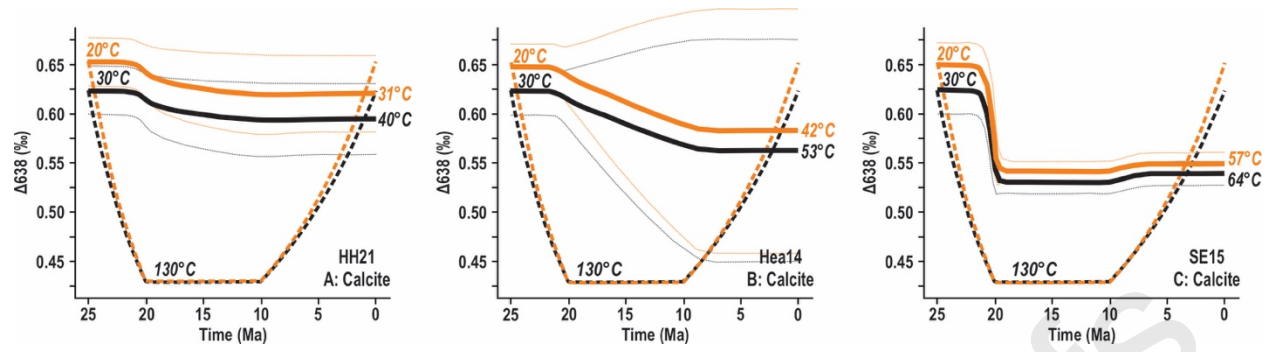
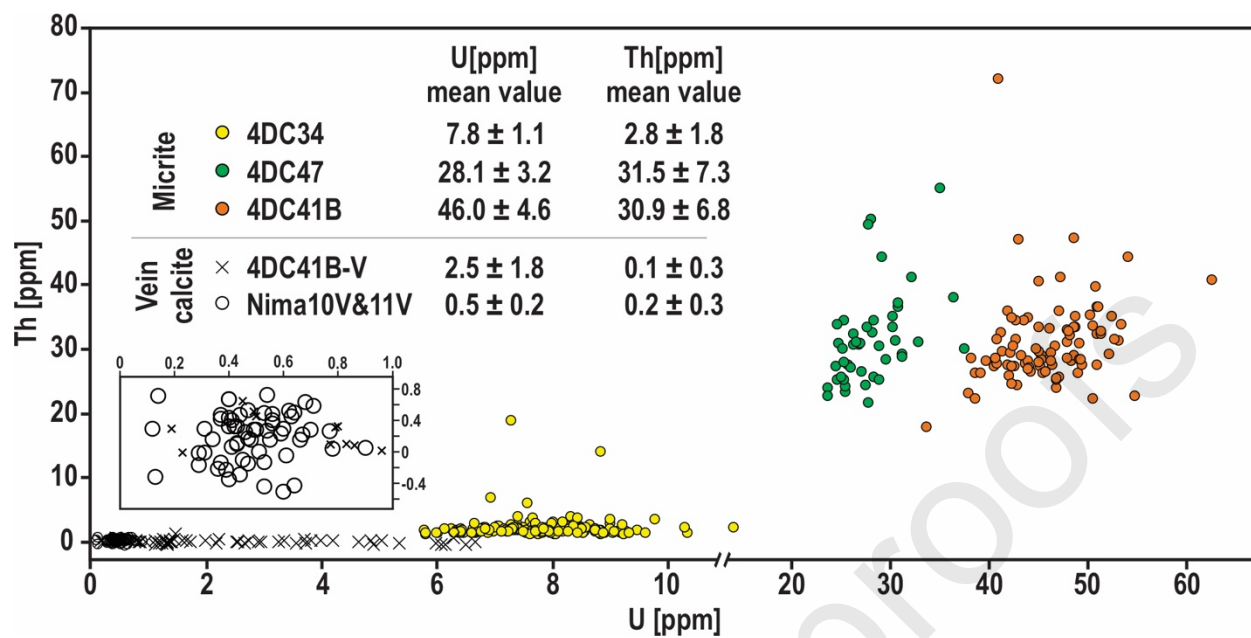


Figure 6



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1036 Figure 7

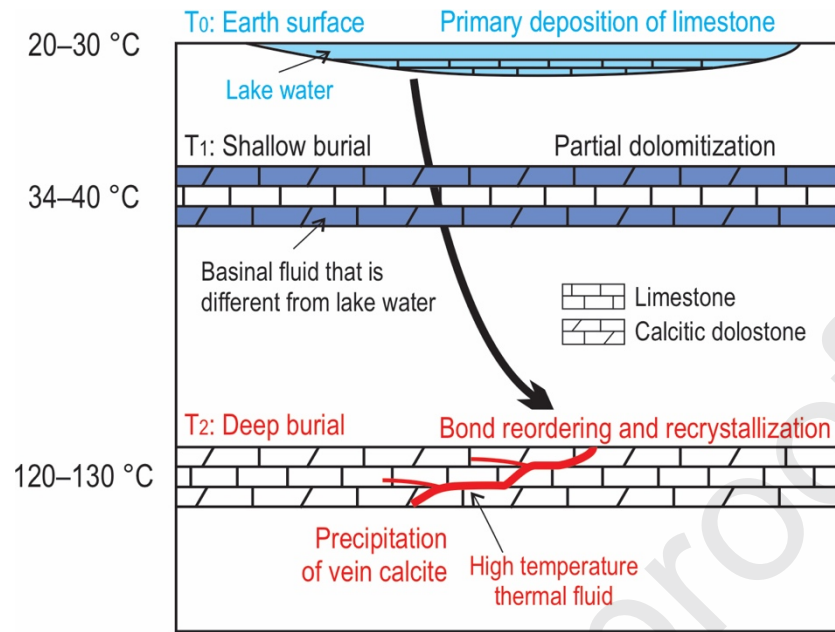
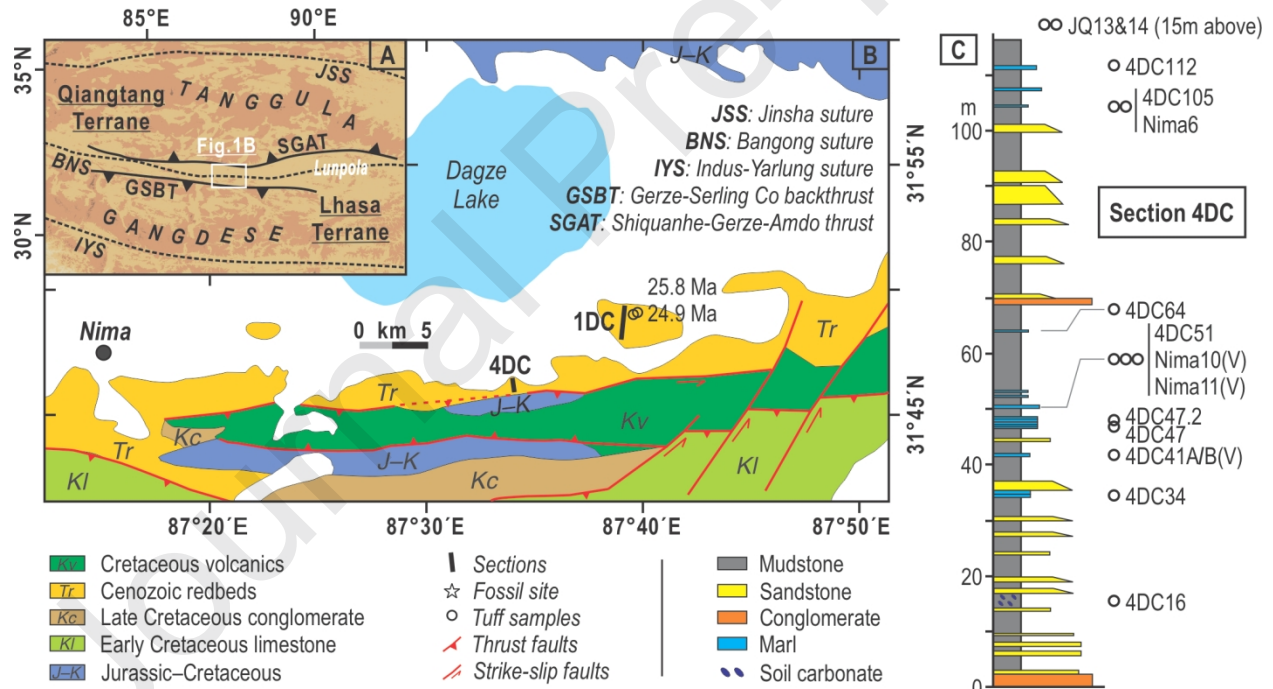
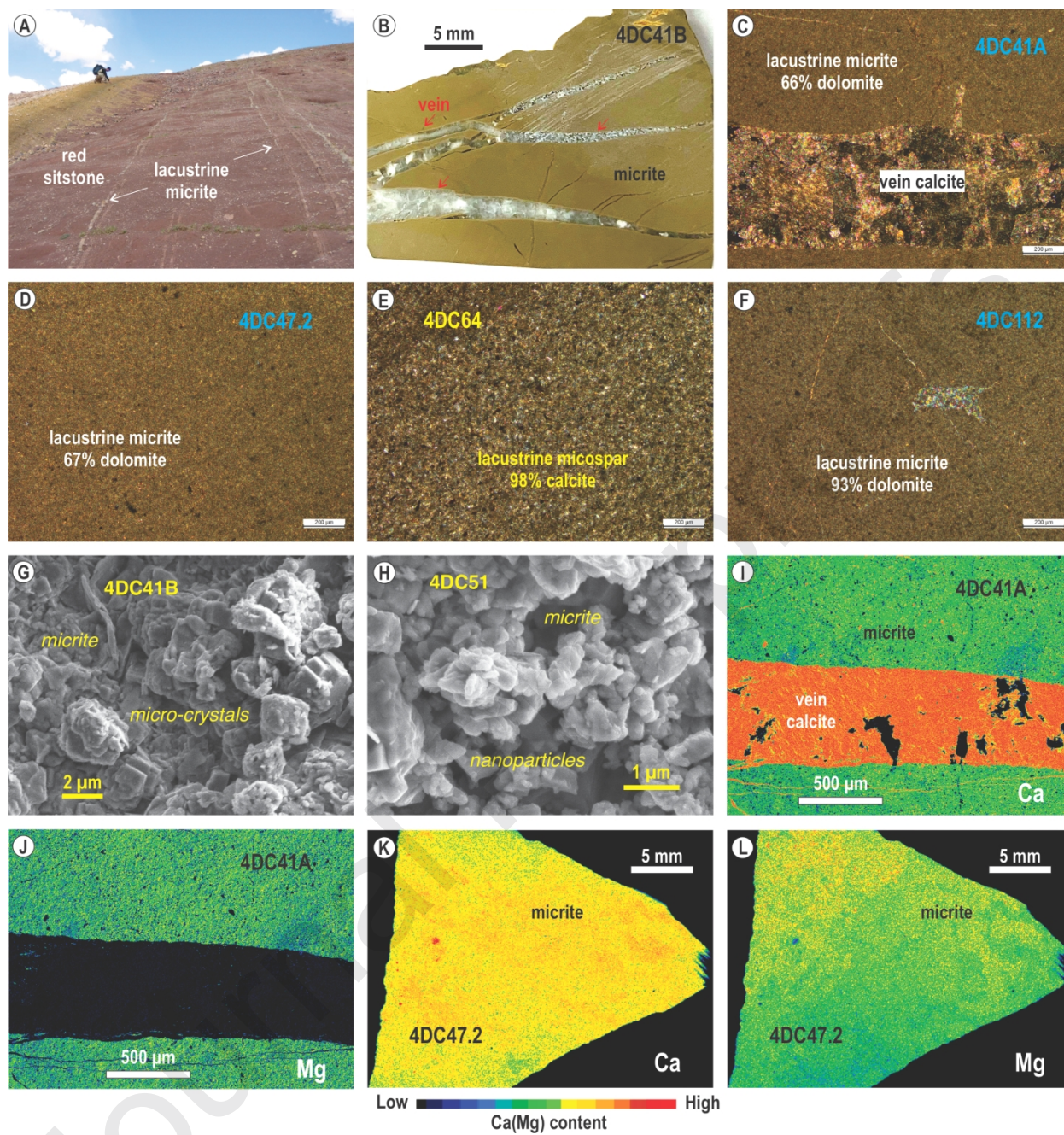
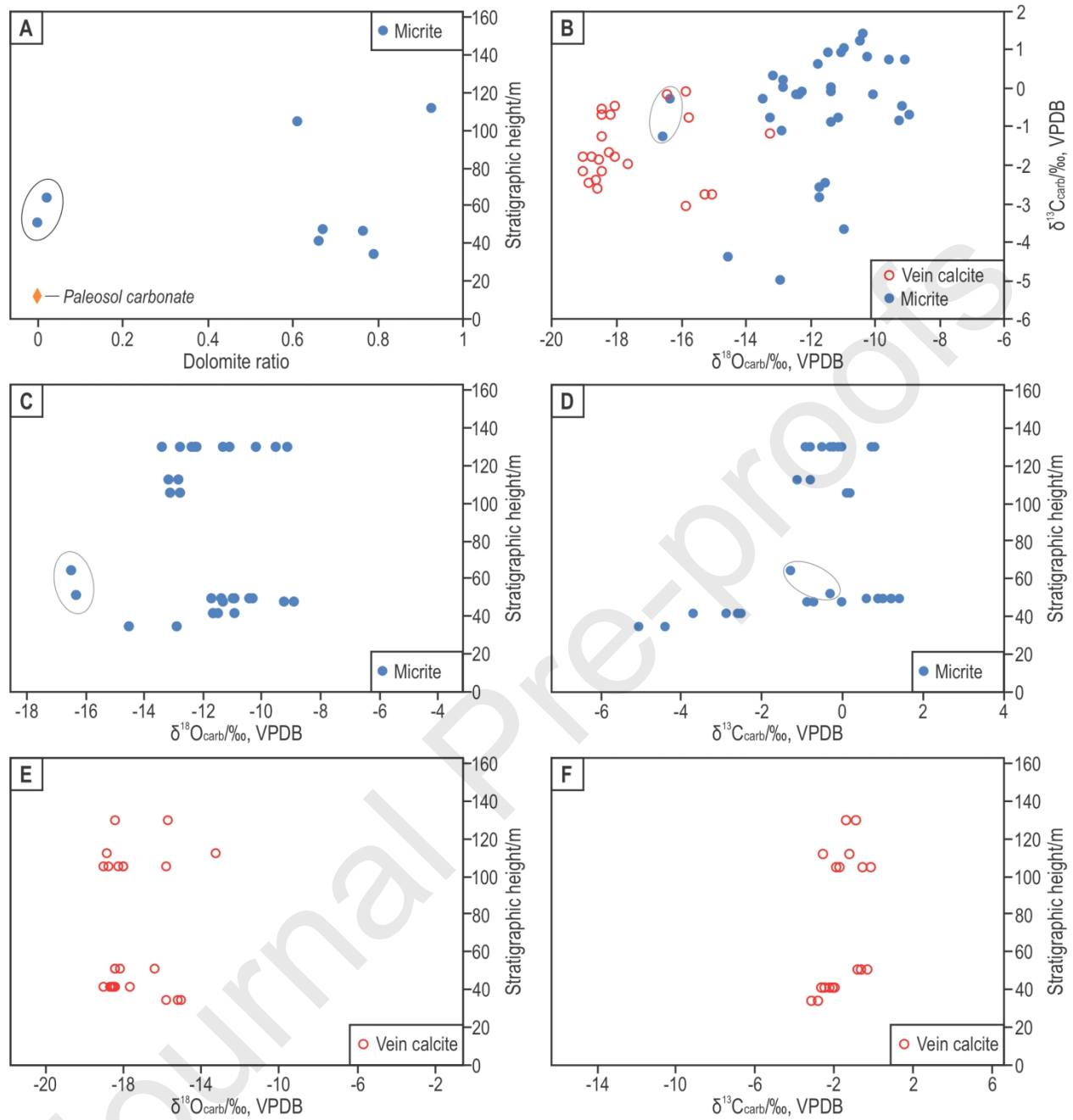


Figure 8

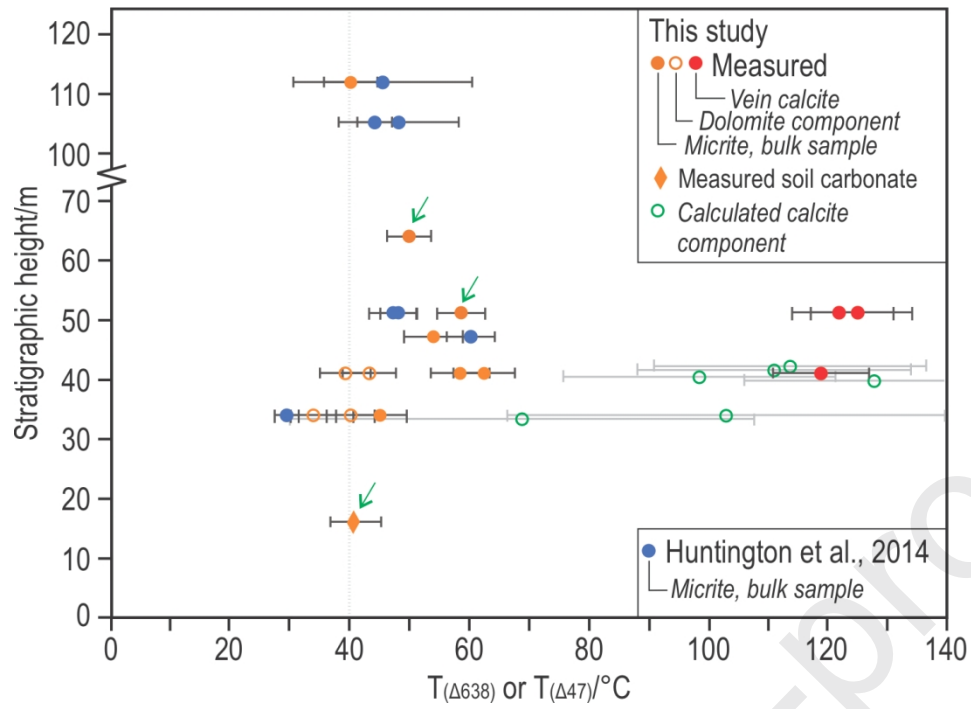




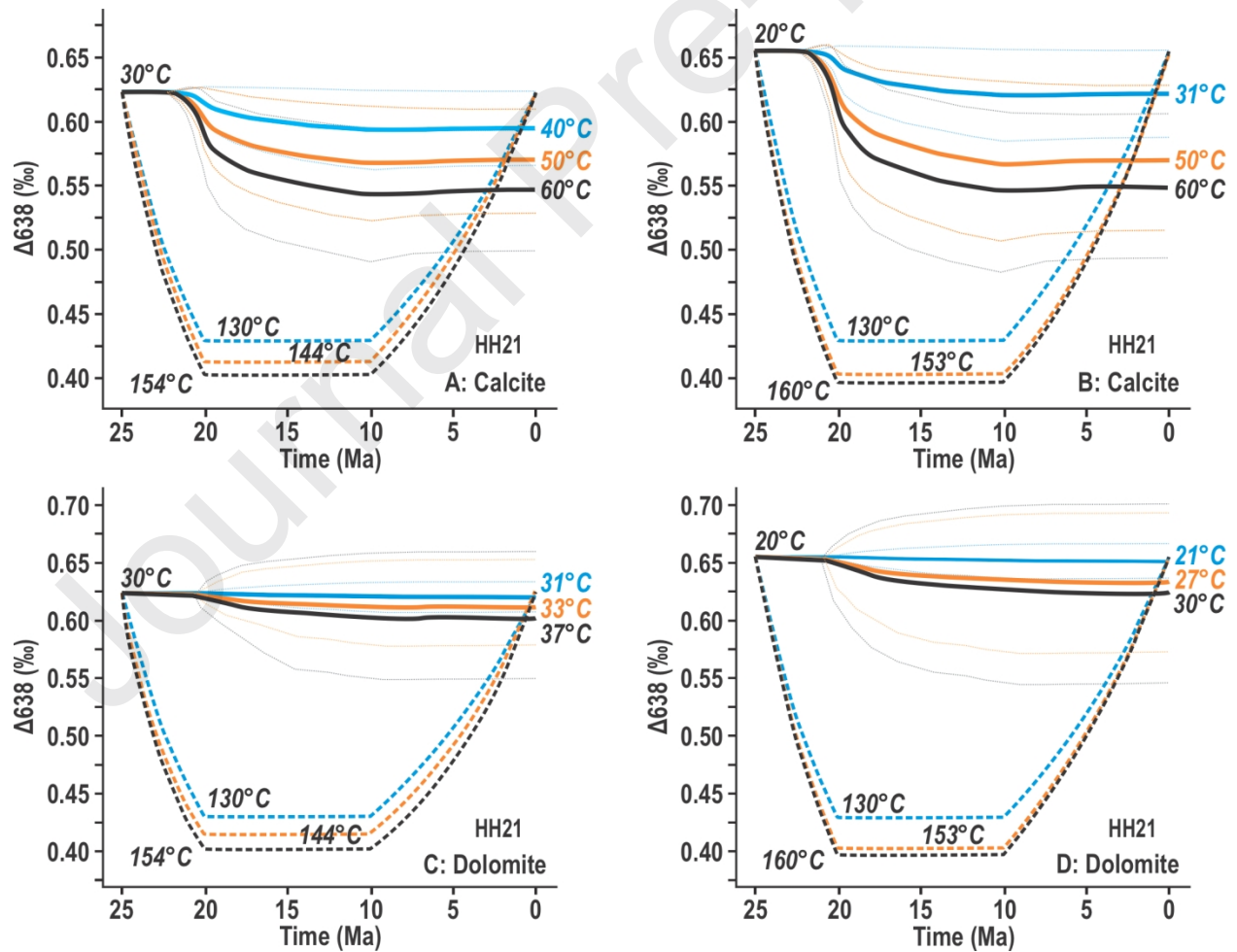




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