Tools for Comprehensive Assessment of Fluid-Mediated and Solid-State Alteration of Carbonates Used to Reconstruct Ancient Elevation and Environments

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Carbonates are ubiquitous in the rock record and provide a broad array of stable isotope-based paleoclimatic proxies (i.e., $\delta^{18}$O, $\delta^{13}$C, $\Delta^{17}$O, $\Delta^{47}$, $\Delta^{48}$) that provide information on stratigraphy, carbon cycling, temperature, hydrology, and the altitude of ancient land surfaces. Thus, carbonates are an essential archive of environmental and topographic histories of continental terranes. However, carbonate minerals are highly susceptible to post-depositional alteration of primary isotopic values via fluid-mediated and solid-state reactions. We propose a hierarchical suite of techniques to comprehensively assess alteration in carbonates, from essential and readily accessible tools to novel, high-resolution techniques. This framework provides a means of identifying preserved textures in differentially altered samples that contain high-value environmental information. To illustrate this progressive approach, we present a case study of Tethyan nearshore carbonates from the Paleocene Tso Jianding Group (Tibet). We demonstrate the utility of each technique in identifying chemical and crystallographic indicators of post-depositional alteration at progressively finer spatial scales. For example, secondary ionization mass spectrometry (SIMS) oxygen isotope maps of micrite and bioclasts reveal significant isotopic heterogeneity due to grain-scale water-rock exchange in textures that were labeled “primary” by optical inspection at coarser spatial resolution. Optical and cathodoluminescence microscopy should be the minimum required assessment of carbonate samples used in stable isotope analyses, but supplemented when necessary by SIMS, PIC mapping, and other yet untapped technologies that may allow distinction of primary and altered fabrics at finer spatial resolutions.

Keywords: carbonate alteration, carbonate diagenesis, oxygen isotope ($\delta^{18}$O), paleoaltimetry, petrography, clumped isotope thermometry

INTRODUCTION

Carbonate rocks provide an archive of geochemical information related to the climatic and tectonic setting of their depositional environment. In particular, oxygen isotopes of terrestrial carbonates ($\delta^{18}$O) have been used as a proxy for ancient rainwater ($\delta^{18}$O$_{\text{w}}$) in the field of stable isotope paleoaltimetry. The relationship between altitude and meteoric water composition is defined by the
Climate and tectonics, and improve our understanding of carbonate alteration mechanisms. Finally, to provide an example of the utility of the analytical framework presented herein, we apply the framework to Tethyan shallow marine carbonates from the Paleocene Jialazi Formation of southern Tibet to characterize the extent of textural and chemical alteration.

Hierarchical Framework for Alteration Assessment Techniques

The assessment techniques are categorized by spatial resolution, which generally coincides with ease of access and cost (Table 1). Category one techniques should be applied in all carbonate proxy research, whereas Category three techniques, which are costlier and/or available at a limited number of institutions, are meant to be reserved for assessing and obtaining high-value geochemical information not available by other means. Our intention is to provide a brief overview of the techniques that illustrate their primary utility and caveats for assessing diagenesis, and to show how they can be used hierarchically to holistically. Further information about the techniques can be found in the Supplement and in the references herein.

It is important to note that terrestrial carbonates are typically more variable geochemically than marine carbonates, and are generally less well characterized than marine carbonates. To maximize the ability to interpret data from any of the techniques mentioned below, it will be helpful to measure modern analogs of specific terrestrial carbonates or biogenic material to establish an informative baseline for a given sample.

Category 1—mm- to μm-Scale Optical Petrography

Optical microscopy of carbonate thin sections is the most essential and accessible method for qualitative assessment of alteration. With plane polar (PPL) and cross polarized light (XPL), one can identify mineralogy, crystal domains and habit, and textures that can be associated with primary formation or water-rock alteration. Some features that may indicate water-rock alteration are secondary porosity, microfractures, meteoric and vadose zone blocky or meniscus cements, pressure dissolution stylolites, dolomitization and microspar or spar-filled veins crosscutting the host rock (Wanless, 1979; Buxton and Sibley, 1981; Moore, 1989; Budd and Land, 1990; Budd et al., 2002; Moore, 2002).

Optical identification of primary domains allows for fabric-specific subsampling from the corresponding slab for geochemical analyses (Table 1). In marine or lacustrine limestones, a dense micritic fabric is often considered a primary fabric, and commonly preferred in stable isotope studies. However, micrite can also represent diagenesis via
TABLE 1 | A toolbox of optical and microanalytical techniques for studying the alteration history of a carbonate sample. Spatial resolutions and optimal spot sizes are dependent on the analytical conditions, materials analyzed, and instrumentation, but commonly accepted resolutions are given. Examples of necessary instrumentation are given, although there are often multiple options from different companies for a given instrument. Similarly, we present relative data acquisition time for one datum, but this will vary significantly depending on whether the analysis is a single point or a compositional map, and with user-determined measurement resolution. The techniques are categorized by increasing spatial resolution, which typically coincides with decreasing accessibility and increasing fees.

| Ranked accessibility | Technique | Spatial resolution or spot size | Sample preparation | Destructive? | Relevant information obtainable | Instrumentation | Analytical time |
|----------------------|-----------|--------------------------------|--------------------|-------------|---------------------------------|----------------|----------------|
| 1                    | Optical petrography | ∼30 µm | Thin sections | Non-destructive | Preservation of primary texture/fabric; Mineralogy; Alteration fabrics (e.g., veins, grain ripening) | Petrographic binocular microscope | Immediate |
|                      | Cathodoluminescence | ∼30 µm | Thin section or other polished surface | Non-destructive | Details of internal structures in fossils; Compositional variation between crystal domains or fabrics, indicative of different formation fluids; Microtextures and compositional variation not evident in light microscopy | Petrographic microscope and cathodoluminescence system (i.e., cold cathode electron gun, vacuum chamber) OR CL detector with SEM | Immediate |
| 2                    | SEM-EDS     | 50–100 nm | Cut and polished or raw surface with conductive coating | Minorly destructive (no volume loss) | Mineralogy of secondary phases often indicative of water-rock alteration (e.g., clays); Element composition maps | Scanning electron microscope with EDS detector and carbon or gold coater | Seconds to hours |
|                      | SEM-EBSD  | 50–100 nm | Extra-fine polish and conductive coating of flat surface (thin section or billet) | Minorly destructive (no volume loss) | 3D orientations of individual crystals; Enlarged crystal domains, potentially from dissolution-precipitation at grain boundaries; Statistical distributions of orientations of individual grains of a given phase in pole figures; Preferred orientations of altered crystal domains | Same as above, + EBSD detector | Hours |
|                      | Electron microprobe | 10–20 µm | Extra-fine polish and conductive coating of flat surface | Minorly destructive (no volume loss) | Concentration mapping of elements; partitioning or gradients of elements at grain boundaries; Chemical analysis of microns-sized spot; transects to identify elemental variability tied to source waters | Field-emission electron probe micro-analyzer with wavelength dispersive spectrometers (WDS) and EDS | Minutes (spot analyses) to hours (compositional maps) |

(Continued on following page)
TABLE 1  (Continued) A toolbox of optical and microanalytical techniques for studying the alteration history of a carbonate sample. Spatial resolutions and optimal spot sizes are dependent on the analytical conditions, materials analyzed, and instrumentation, but commonly accepted resolutions are given. Examples of necessary instrumentation are given, although there are often multiple options from different companies for a given instrument. Similarly, we present relative data acquisition time for one datum, but this will vary significantly depending on whether the analysis is a single point or a compositional map, and with user-determined measurement resolution. The techniques are categorized by increasing spatial resolution, which typically coincides with decreasing accessibility and increasing fees.

| Ranked accessibility | Technique | Spatial resolution or spot size | Sample preparation | Destructive? | Relevant information obtainable | Instrumentation | Analytical time |
|----------------------|-----------|--------------------------------|--------------------|-------------|--------------------------------|----------------|----------------|
| 3                    | Synchrotron PIC mapping | >20 nm | Extra-fine polish and conductive coating of flat surface | Destructive (radiation damage) | • Redox states of individual elements • Crystallographic orientation on finer scale than EBSD | Synchrotron beamline capable of x-ray photoelectron emission spectromicroscopy (X-PEEM) and x-ray absorption near-edge structure spectroscopy (XANES) | Hours |
| SIMS                 |           | >10 μm | Extra-fine polish and conductive coating; 1" round set in epoxy | Essentially non-destructive | • in situ trace element abundances and isotopic ratios at ppb levels • Isotopic spatial variability at orders of magnitude smaller scale than bulk analyses • Depth profiling for subsurface variability that may be integrated while drilling for bulk analyses | SIMS and gold coater | Minutes (spot analyses) to hours (compositional maps) |

Note: Spatial resolutions and optimal spot sizes are dependent on analytical conditions, material analyzed, and instrumentation.

*aTechnique is sensitive to composition of epoxy; always check with lab technician prior to sample preparation.*
SEM–Electron Backscatter Diffraction (EBSD)
SEM electron beams can be diffracted by atomic layers within a carbonate crystal to generate visible backscatter patterns as they pass through a phosphor screen. The backscatter patterns are projections of the lattice plane geometry of individual carbonate crystals. These data are used to generate misorientation maps and pole figures displaying statistical distributions of crystallographic c-axis orientations of all individual grains of a given phase (Figure 1), superimposed on the SE and/or EDS images. The statistical data can be used to test alteration hypotheses and reconstruct the history of crystal reorientation related to water-rock alteration, including processes like grain ripening, calcite zonation, and overprinting of a unified c-axis orientation during reprecipitation. For example, micrite in a lacustrine limestone from the Lunpola basin had no preferred c-axis orientation, as seen in the pole figure in Figure 1. Following EBSD and optical petrographic observations, Ingalls et al. (2020) interpreted that this sample likely preserved primary fabrics and isotope values, since alteration would likely produce greater alignment of c-axis orientations within the micrite (e.g., Ryb et al., 2017).

Electron Probe Microanalysis (EPMA)
EPMA is a non-destructive tool that operates by the same principles as SEM, but is capable of quantitative, spatially resolved elemental analyses by wavelength dispersive spectroscopy (WDS). These 2D element maps can be overlaid on SE, BSE, and CL images to directly compare chemical variability between textural, mineralogical, crystallographic, and redox domains. Element maps and <10 µm spot analyses can reveal micron-scale chemical variability (Table 1), thereby serving as a test for subsurface water-rock interaction that may occur from pore fluids at a fine spatial scale. Quantitative analyses of major, minor and trace element ratios (e.g., Mg/Ca, Sr/Ca, Mn/Sr) provide evidence for carbonate formation from a different fluid composition than primary Earth surface water (Figure 1).

Category 3—µm-to 10s of nm-scale Secondary Ionization Mass Spectrometry (SIMS)
SIMS and nanoSIMS provide one of the highest spatial resolution, in situ isotopic and elemental measurements currently available. SIMS provides oxygen and carbon isotope values at <20 µm scale (Table 1), similar to the spatial resolution of EPMA, while nanoSIMS can provide geochemical information on spots as small as 10s of nanometers. A primary positive (133Cs+) or negative (18O2-) ion beam focused on a sample surface generates secondary ions of specific elements that are measured by a mass spectrometer. SIMS analyses enable isotopic differentiation between microtextures and observation of isotopic shifts over areas that are integrated during bulk sample drilling, SIMS could open doors to characterizing extent of water-rock alteration and paragenesis from pore fluids, as well as potentially revealing residual primary carbonate material in differentially altered samples.

Polarization-dependent Imaging Contrast (PIC) Mapping
PIC mapping is an outgrowth of X-ray absorption near-edge structure (Xanes) spectroscopy, in which spectra vary depending on the orientation of a carbonate mineral’s c-axis due to X-ray linear dichroism (Gilbert, 2012; DeVol et al., 2014). Crystallographic orientations can be quantified for domains >20 nm (DeVol et al., 2014), which is why this technique is commonly applied to biogenic carbonates to investigate biomineralization. Different modes of alteration result in different distributions of reoriented c-axes, which can then be explicitly tied to geochemical data from nanoSIMS on a comparable spatial scale. This is analogous to pairing EBSD-derived maps with SIMS on even finer spatial scales. A recent application of PIC mapping revealed reorientations of c-axes in individual nacre within fossil values, which demonstrated that altered biogenic aragonite can preserve original biomineral structures and mineralogy (Gilbert et al., 2017). This type of alteration would not be detectable at the scale of optical petrography, which could result in isotope values from altered material being used erroneously to reconstruct paleoenvironmental conditions. In the future, nanoSIMS analyses could reveal whether geochemical changes correspond to this nanoscale alteration.

Modeling Potential Extent of Solid-State Bond Reordering in Clumped Isotope applications
At high temperatures, atoms can migrate within the carbonate lattice by solid-state diffusion, thereby randomizing the distribution of 13C–18O pairs and altering Δ47, and in turn, the inferred formation temperature (Passey and Henkes, 2012; Stolper and Eiler, 2015; Henkes et al., 2018). Importantly, solid-state alteration retains primary fabrics and bulk δ13C and δ18O while reducing Δ47 via diffusion. Samples experiencing solid-state alteration would pass all previously described assessments of textural and isotopic alteration, making it difficult to identify. Thus, it is critical to sufficiently rule out effects of fluid-based alteration before inferring that solid-state reordering is responsible for erroneous Δ47 temperatures.

Fluid-mediated recrystallization also resets T (Δ47) to the recrystallization temperature. However, the extent of Δ47 alteration by solid-state 13C–18O reordering is dependent on the integrated time above a mineral-specific threshold. For example, calcite held at 75°C for 100 My would only increase T (Δ47) by <1 °C, but would increase T (Δ47) by ~40 °C if held at 120 °C for 100 My (Stolper and Eiler, 2015). Independent constraints on the burial histories of sedimentary basins and application of mineral-specific kinetic parameters in reordering models provide means for assessing the potential extent of solid-state reordering (e.g., Lawson et al., 2018; Lloyd et al., 2018; Lacroix and Niemi, 2019), for samples that show no other signs of fluid-based alteration that could account for erroneous Δ47 values.

Case Study: Differential Alteration of Tethyan Shallow Marine carbonate
The shallow marine Paleocene-Eocene Jialazi Formation of the Tso Jianding Group (southern Tibet) is ideal for investigating the expression of water-rock and solid-state alteration in micritic and biogenic carbonate at a variety of spatial scales because of the incongruity of its isotope values and textural characteristics. The Jialazi Formation records the transition from marine to terrestrial
deposition within the Xigaze forearc basin following the India-
Asia collision (Orme et al., 2014; Orme, 2017). Currently, no low-
altitude $\delta^{18}O_w$ or $\delta^D_w$ estimate of precipitation south of Tibet
exists for Paleogene $\Delta \delta^{18}O_w$-based reconstructions during a
critical period of Tibetan tectonics. Ingalls (2019) aimed to
provide a low-altitude $\delta^D_w$ from terrestrially derived organics
preserved within the nearshore sediments if effects of alteration
could be more concretely assessed.

Ingalls (2019) found that textural and isotopic data presented
contradictory cases for the preservation of primary information in the Jialazi Formation. While primary biofabrics of shells and foraminifera were identified by
traditional optical techniques (Figure 1), $\delta^{18}O_C$ values were
~10–20‰ lower than any primary marine carbonate, and
similar to carbonates that precipitate from Tibetan meteoric
water today (Ingalls, 2019). Specifically, optical petrography
showed preserved primary foraminifera test porosity in plane
polarized light and primary bivalve growth habit with banding
perpendicular to growth laminae crossed polars (T0702-4; Figure 1). Contrary to these indicators of textural
preservation, test edges appeared to be partially dissolved or
weathered and pores were infilled with cements with increased
luminescence (T0702-18; Figure 1; Supplementary Figure S1). The dull luminescence of the tests and micritic matrix

![FIGURE 1](https://example.com/figure1.png)

**FIGURE 1** Optical and geochemical investigations of carbonate alteration increasing in spatial resolution (1–3). (1) Preservation of primary porosity in a foram test (T0702-18) in plane polar light; secondary carbonate precipitation within the test microporosity can be identified by the brighter red luminescence, indicative of elemental chemistry different from the water in which the foram grew. The test walls preserve alternating light and dark banding in CL, although it is patchier than is likely for the original fabric. Preserved primary bivalve growth habit (T0702-4) can be identified in cross polar light. (2) Scanning electron microscopy (SEM) energy dispersive spectroscopy (EDS) of a calcite vein cutting through a mudstone (T0702-14) displays phase mixing on the 10s of microns scale. Electron probe microanalysis (EPMA) shows elevated Sr/Ca at the core of the same vein (T0702-14), potentially indicative of two episodes of water-rock alteration. A sample from the Lunpola basin analyzed by EBSD demonstrates the expected no preferred c-axis orientation for a primary lacustrine limestone composed of micrite. IPF = inverse pole figure. (3) On the finest scale, ~10 to 15‰ variability in carbonate $\delta^{18}O$ values are seen within limestones (T0702-9), and across abiotic and biotic carbonate components (T0702-4 and -18). Generally, micrite and allochems yielded lower $\delta^{18}O$ values than bioclasts. Overall, in this study, bioclasts were more fabric retentive and less divergent from expected values of marine carbonate than other carbonate components.
suggested that those domains may preserve geochemical information of the depositional environment, but the red luminescence within pore spaces indicated carbonate precipitation from a fluid with different redox chemistry. Subsampling material from the Nummulites tests without integrating altered pore-filling carbonate is beyond the spatial capability of a micromill, so traditional isotope analysis would likely integrate primary and altered material.

Instead, using EPMA, we identified secondary carbonate formed from two generations of alteration fluids in sample T0702–14. Across a ~500 µm transect with 12 elemental spot analyses (10–20 µm diameter; Figure 1), we identified two populations: 1) a primary trend of increasing Mg/Ca and Fe/Ca away from the vein-mudstone interface on both sides, and 2) consistently low Mn/Ca and Sr/Ca that later overprinted via dissolution-precipitation. This is seen in a spike in Sr/Ca paired with a relative decrease in Mg/Ca and Fe/Ca along the central axis of the vein. We suspect that interaction with a subsurface brine caused Sr/Ca enrichment in the second alteration event because saline burial fluids typically carry significantly higher Sr concentrations than seawater (Banner, 1995).

The clumped isotope-derived temperatures ranged from ~80 to 10 °C (Ingalls, 2019), reflecting the complex water-rock and solid-state alteration history. Ingalls (2019) assessed the potential extent of solid-state reordering using thermochronologic data from the Xigaze forearc (Orme, 2017) in an exchange-diffusion model (Lloyd, 2020) partnered with fabric-specific analyses. The model results suggest that late-stage, low-temperature, fluid-based alteration superseded partial solid-state reordering in the Jialazi Formation, overprinting the deep burial history with alteration superseded partial solid-state reordering in the Jialazi Formation, overprinting the deep burial history with late-stage, low-temperature, fluid-based alteration that resulted in domains of preserved primary carbonate.

To demonstrate the magnitude of error that can arise from misinterpretation of altered δ18O values, we performed Δ(δ18Ow)–δ18Ow-based calculations using the endmember Jialazi Fm δ18Ow values for sea level estimates (~19.1, ~12.8‰ VSMOW, noting that seawater δ18Ow, recorded by marine carbonate, is typically higher than meteoric δ18Ow), and both Paleocene (~13.6‰; Ingalls et al., 2017) and modern compositions (~18.1‰; Bershaw et al., 2012) from the high-altitude margin of Tibet (see Supplement). Using Jialazi Fm δ18Ow values with modern precipitation yielded elevations of ~755 and 2,874 m. a.s.l. for a land surface currently >4,000 m. a.s.l. Therefore, incorrectly using altered δ18O values as an estimate for low elevation meteoric water in paleoaltimetry calculations can underestimate elevations by several kilometers (Supplementary Table S1). By the same logic, alteration of high-altitude samples can result in inaccurate paleo-elevations by similar magnitudes.

**SUMMARY**

We present a hierarchical framework for assessing alteration in carbonates used for environmental and tectonic reconstructions. As an example, we built on the exchange-diffusion modeling and texture-specific isotopic measurements of Ingalls (2019) to construct a more detailed alteration history for the Jialazi Formation. We demonstrated that apparent textural preservation can coincide with differential alteration of primary isotopic values, which can lead to significant errors in paleoaltimetric reconstructions. Had the Jialazi Formation been nonmarine, the application of the full suite of screening techniques and consideration of thermal history would have been essential to ruling out the use of δ18O and ΔT for paleoaltimetry. The adoption of this hierarchical framework for assessing carbonate alteration could improve our understanding of the carbonate record and processes of carbonate isotopic alteration, as well as resolve previously unsolvable tectonic problems by enabling access to finite domains of preserved primary carbonate.

**DATA AVAILABILITY STATEMENT**

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession numbers can be found below: https://osf.io/34k8y doi: 10.17605/OSF.IO/34K8Y.

**AUTHOR CONTRIBUTIONS**

MI conceived of the hierarchical assessment framework, performed analyses, interpreted data and wrote the manuscript. KS contributed to the conception of the alteration
framework, and contributed writing and feedback on the manuscript.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2021.623982/full#supplementary-material.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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