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Natural laboratories document increasing diagenetic overprint on carbonate proxy data

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Carbonate archives record a brief snapshot of the ambient Earth's surface conditions at their deposition. When these materials form (also via amorphous precursors), they record a complex interplay of equilibrium and non-equilibrium processes. Fluid geochemistry, temperature, salinity, alkalinity and pH, mineralogy-dependent fractionation, and vital and/or kinetic effects all interact in an often stochastic (but not non-deterministic) manner. Consequently, the geologically reasonable extraction and interpretation of geochemical proxy data from ancient, diagenetically altered rock archives is fraught with problems. Three issues stand out: (i) the dichotomy between petrographic and geochemical alteration, (ii) the lack of quantitative age constraints for specific diagenetic phases resulting in a poorly constrained admixture of local, basin-wide and over-regional (far-field) features, and (iii) an often-insufficient understanding of the temperatures and compositions of diagenetic fluids. The challenge of the carbonate geoscientist is to separate a meaningful environmental signal from one that is modified by later diagenetic or metamorphic alteration and, hence, to reliably assess the integrity and robustness of the extracted proxy data as indicators of their paleo-environment. Laboratory alteration experiments of natural samples, performed under simplified but controlled conditions, provide insight into the response of proxy data under increasing degrees of alteration. Natural systems, however, are exceedingly more complex, and experiments are no substitute for field studies. That said, natural case examples offering access to gradually increasing alteration of comparable carbonate materials are rare and often extremely complex. These include diagenetic to regional- and contact metamorphic overprint in regional to supra-regional fault zones dissecting otherwise undisturbed carbonate units. Here, we present (isotope)geochemical and petrographic data from natural alteration gradients in their spatial and temporal context. Rocks exposed to regional tectonism and fluid flow, exposed to low to high degrees of overprint, are placed in their geological context. The main learning points for proxy research are summarised in a conceptual and process-oriented manner.