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Early diagenetic geochemical homogenization of fine-grained carbonate sediments

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Fine-grained carbonates, carbonate ooze and their lithified counterpart (micrite), form a major constituent of limestones throughout much of Earth's history. Numerous workers exploit these materials as archives of for example past seawater properties, or for perturbations of the carbon cycle but data obtained range from promising to ambiguous. This diversity results from the often unknown origin of the mineralogically heterogeneous components forming these carbonate sediments and their corresponding rocks as well as their commonly poorly constrained diagenetic pathways. These problems become particularly obvious when comparing proxy data from what are considered ancient "well-preserved" bulk carbonates to such from recent (commonly (sub)tropical) fine-grained carbonates. The problem lies in the fact that previous workers report significant inter-grain variability of modern carbonate $\delta^{13}\text{C}$ (ranging from -1.6 to +5.3‰) and $\delta^{18}\text{O}$ (ranging from -3.2 to +2.3‰) signatures from coeval sediments in for example Belize, the Maldives, or Kuwait. This geochemical variability of individual components in fine-grained carbonates is due to a complex interplay of different carbonate mineralogies, mineralogical controls on $\Delta^{13}\text{C}_{\text{fluid-mineral}}$, differential metabolism of carbonate-secreting marine organisms, local environmental patterns, and many other factors. This primary variability, is at least in part, homogenized in bulk sediment data sets but the observation of a high level of primary variability remains in nearby sections that represent geologically very short, overlapping time intervals (10^3 yrs). On the other hand, low levels of bulk geochemical variability in fossil carbonate rocks are often taken as evidence for the "well-preserved" nature of these archives. Two questions result: (i) When (which diagenetic domain) do "noisy" environmental data sets transform into "low variability", homogenized bulk carbon isotope data? (ii) To which degree does geochemical homogenization affect the environmental information contained in these carbonates? Two possible answers offer themselves: Diagenetic homogenization takes place at an early stage and in the presence of only moderately modified marine porewaters. Obviously, the question is to which degree the porewater chemistry, pH, Eh etc. differ from that of the overlying seawater? If this early diagenetic stabilization is pervasive, then subsequent burial alteration of the diagenetically stabilized carbonates will be less significant due to their reduced diagenetic reactivity. An increase of geochemical heterogeneity is expected when reaching deeper burial environments, where renewed dissolution and reprecipitation adds additional phases. The second scenario suggests that diagenetic "marine" porewater stabilization is incomplete and alteration continues into increasing burial depths in the presence of non-marine aqueous fluids (brines). These observations are significant and require attention. In order to test these hypotheses; we present data from experimental approaches exposing natural, fine-grained marine carbonate sediments to dissolution-precipitation cycles under controlled experimental conditions. Work shown here aims at a better understanding of stabilization and homogenisation of diagenetically reactive, fine-grained carbonate sediments.

