

A Tale of Three Fluids

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Targeting both the fluid and solid earth, fluid-rock (mineral) interaction is one of the widest and most actively investigated topics in sedimentary research and includes a plethora of fundamental and applied aspects from atom to reservoir scale. Carbonates nucleate and precipitate from either marine, meteoric, or formation waters; biominerals are secreted from body fluids. Following formation and deposition of carbonates, these interact with ambient pore fluids that may change in their properties with time resulting in dissolution and reprecipitation, mass transport, and diffusion processes. From a conceptual viewpoint, fluid-rock interaction of natural carbonates can be categorized into two end-member settings: (i) exchange between a fixed amount of (stagnant) pore fluid and a polyphase carbonate hostrock (closed system, $\text{Volume}_{\text{rock}} \gg \text{Volume}_{\text{fluid}}$). This system is dominated by the geochemical and mineralogical properties of the hostrock. When altered, processes include micro-scale dissolution and precipitation mainly via diffusion. (ii) Exchange between a significant volume of pore fluid that is continuously passing through the pore space and fracture network of a given carbonate rock in an open system behavior ($\text{Volume}_{\text{rock}} \ll \text{Volume}_{\text{fluid}}$ dominated by mass transport). The majority of studies published focus on examples of at least in part fluid-controlled (open system) diagenesis and mass transport commonly leading to one or several cycles of partial to full replacement of initial geochemical and petrographic properties of carbonate rocks. Conventionally, authors marshal various types of aquifer waters to argue for processes taking place during meteoric and marine diagenesis and subsequent burial as manifested in the mineralogy and geochemistry of the newly formed (diagenetic phases). In contrast, the principles of closed-system diagenesis are less well understood and some of the mechanisms found are counter-intuitive. I suggest that the view of a dominant aquifer-water system represents an oversimplification of the complex chain of processes taking place from rock to sub-crystal scale. The alternative suggestion brought forward here is that during burial, many carbonates experience interaction with three different fluid reservoirs that may display variable degrees of isolation: (i) the above-mentioned pore-filling aquifer water including fluids circulating through open fracture networks; (ii) the thin fluid film at the boundary of crystals and in intraparticle porosity; (iii) and 'water' (H_2O and OH) bound to inter- and intra-crystalline organic matter (between less than one and three percent by weight in for example biogenic carbonates) and water contained in fluid inclusions. Evidence is provided that the significance of aquifer water is perhaps overrated. In contrast, it is suggested, that the intercrystalline and intracrystalline fluid reservoir, being volumetrically several orders of magnitude smaller compared to aquifer waters, may be dominant depending on the case study investigated. These considerations may explain some of the paradoxical observations in carbonate research including decoupled petrographic and geochemical overprint.

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