

Assessing the Impact of Initial Carbonate Diagenetic Reactivity on Reservoir Properties*

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Abstract

Here I critically evaluate the question of the spatial and temporal distribution of carbonate mineralogies, characterized by their different diagenetic reactivity at the time of deposition, as a fundamental factor controlling the subsequent evolution of carbonate reservoir properties. If this were the case, then a wide range of “depositional facies architectures” could be grouped into a smaller number of “diagenetic facies architectures”. The concepts presented here represent a progress report.

I propose that these general considerations are significant. This is because most reservoir models are built on a case-by-case basis and as a result, the more general patterns and similarities in diagenetic facies evolution between reservoirs with different depositional architectures will not be obvious. The hypothesis tested here relies on the substantially different thermodynamic properties (solubility) of the four dominant marine carbonate mineralogies at deposition: calcite and low-Mg calcite (<4 mole%) being the more stable/less reactive phases, and aragonite and magnesian calcite (4 to >20 mol% Mg) being the more reactive/less stable carbonate ones (Figure 1; Böttcher and Dietzel, 2010). Differences in stability depend on crystallographic properties with Mg²⁺ having a smaller ionic radius compared to Ca²⁺. Substitution of Ca²⁺ with Mg²⁺ has a significant impact on the crystal lattice (Zhang et al., 2010), and the shift in the (104) d-spacing, i.e. the unit cell parameter, is roughly proportional to the amount of the Mg in the crystal structure. Dolomite, in contrast, is built by an ordered structure of alternating Ca-rich and Mg-rich layers and is thus stable (Warren, 2000).

Carbonate Mineralogies Controls

Three main factors control the spatial and temporal distribution of carbonate mineralogies in marine depositional environments throughout Earth history: (i) seawater geochemistry; (ii) climate and bathymetry, and (iii) evolutionary changes of carbonate secreting marine organisms: (i) Stable, (low-)Mg calcite precipitation (organic, inorganic and organomineralic) dominates during time intervals with seawater Mg/Ca ratio of less than 2 (Figure 2; calcite seas; Cambrian to Mississippian and Late Jurassic to Paleogene). Conversely, time intervals with seawater Mg/Ca ratios of above 2 (Pennsylvanian to Mid-Jurassic and Neogene to Recent), induced mainly metastable aragonite and high-Mg calcite carbonate precipitation (Hardie, 1996). (ii) Tropical and subtropical carbonate depositional settings (the T-Factory of Schlager, 2005) favor Mg-calcite and aragonite precipitation whilst coolwater carbonate depositional environments (the C-Factory of Schlager (2005) are the sites of mainly (Mg-)calcite precipitation. Hemi-pelagic chalk reservoirs are typified by low-porosity calcite mineralogies but aragonite mineralogy such as ammonite shell material is present too. The mineralogy of the carbonate sediment at deposition directly affects marine cement precipitation. An aragonite substratum triggers – in many cases – the precipitation of aragonite cements, whilst a calcite substratum will induce calcite cement precipitation. (iii) The evolution of carbonate secreting organisms through time is of relevance, for example the Paleozoic corals had a calcite skeleton, whilst the Triassic to Holocene (scleractinian) corals have aragonite skeletons (Flügel, 2004). Therefore, a Paleozoic coral-dominated reef (calcite) edifice is expected to enter the burial realm with an overall lower diagenetic reactivity compared to a Lower Jurassic (aragonite) one.

Consequently, the question is raised if for example Pennsylvanian carbonate facies (aragonite sea mode) should form better reservoir rocks than those deposited during the Cretaceous (calcite sea mode)? A possible verification comes from statistics listing reservoir facies in the Middle East (Ehrenberg et al., 2008). The Middle East statistics exemplify that there is not a simple relation between reservoir properties and calcite *versus* aragonite sea modes. This is because calcite sea mode Cretaceous strata in the Middle East contain about 50% of the recoverable oil and about 13% of the recoverable gas. Of the more than 1800 Middle East reservoirs, only about 20% fall into the Permo-Triassic time interval representing an aragonite sea mode (Ehrenberg et al., 2008).

Does this imply that the initial carbonate mineralogy at deposition has no impact on reservoir facies? Probably not. This is because the compilation shown in Ehrenberg et al. (2008) does not differentiate between fracture-controlled and porosity-controlled reservoir end members. Fractured reservoirs may exhibit high permeability at comparably low porosity (see discussion in Ahr, 2008). In addition, the compilation shown in Ehrenberg et al. (2008) lists both sandstone and carbonate reservoir lithologies. Finally, in order to contain commercial amounts of oil or gas, a carbonate storage rock body must interact with a trap, a seal and a source rock. All of these factors are independent of the initial carbonate mineralogy.

Carbonate Porosity Controls

Another factor that requires attention is the aspect of rock property statistics versus rock spatial statistics. Two different carbonate facies types might have very similar porosity and permeability properties. In the sense of descriptive statistics, these carbonate facies are then near-identical, even if they differ from the viewpoint of carbonate facies terminology. In contrast, the same carbonate facies, organized spatially in different manners in different carbonate rock bodies, might have significantly different flow characteristics. These issues severely complicate the assessment of carbonate mineralogy and its impact on reservoir properties. Therefore, a more detailed discussion of carbonate diagenetic pathways is required.

Newly-deposited carbonates are generally highly porous and polymineralic, i.e. composed of mixtures of aragonite, high- and low-magnesian calcite (Mazzullo, 2004). The eogenetic exposure of these sediments to meteoric or marine porewater results in the formation of cemented limestones with varying porosity and a stable low-Mg calcite mineralogy (notwithstanding dolomitization). Unlike siliciclastic reservoirs, carbonate deposits with high abundances of aragonite and Mg-calcite are subject to extreme variations in porosity loss and/or porosity formation in the shallow (eogenetic) diagenetic environment, whilst (low-)Mg calcite dominated facies are expectedly less reactive. Typically, dissolution of metastable carbonates forms vuggy and cavernous porosity. Solutes are transported in pore fluids and may re-precipitate at a later stage and a different site (Ehrenberg, 2006). Precipitation will occlude pore space and reduce permeability (Immenhauser et al., 2004). The subaerial diagenetic freshwater model, promoting the formation of extensive secondary pore networks beneath exposure surfaces, is now questioned in the literature (Mazzullo, 2004). Dissolution of already stabilized limestones can also result in the formation of mineralogy-selective porosity because of subtle changes in diagenetic reactivity, particle size or micro-structural arrangement. In contrast, late eogenetic and mesogenetic exposure to freshwater or marine and burial porewater is not driven by such differences in the relative solubility of aragonite, high-Mg and low-Mg calcite. Further dissolution takes place only if reactive fluids are strongly undersaturated with the least soluble form of carbonate, calcite. Subsurface hypogenic karsting takes place where aggressive burial fluids rise in limestone bodies and become trapped beneath seals (Immenhauser and Rameil, 2011).

Carbonate Diagenetic Controls

It has been argued that post-depositional diagenetic overprint, rather than following depositional boundaries, may crosscut facies boundaries and outline for example ancient water tables or follow fracture systems. Moreover, most reservoir rocks were affected by more than one episode of diagenesis during their near surface to burial pathways leading to the formation of complex hybrid pore systems (Moore, 1989; Mazzullo, 2004). These statements are clearly valid but others (Ehrenberg et al., unpublished) proposed that the model of porosity creation in carbonate reservoirs during deep burial (mesogenetic) stages is both unsupported by quantitative evidence and theoretically implausible. If this were the case, then the spatial organization of carbonate phases with differential

diagenetic reactivity, from the viewpoint of reservoir models, is equally important - or even more important - than depositional facies architecture. Examples of comparably inert carbonate facies include sediments such as crinoid-rich Mississippian limestones that typically have low porosities. Examples of reactive carbonates include Neogene scleractinian coral facies, Cretaceous aragonite/calcite-shell dominated rudist limestones or Lower Jurassic Ammonitico Rosso facies characterized by early diagenetic nodulation (Coimbra et al., 2009). Early diagenetic seafloor lithification in the latter case example is due to dissolution of aragonite and reprecipitation of calcite as marine cement phase.

Sedimentation rate (burial rate) interacts with carbonate reactive mineralogy. Under slow sedimentation rates, common for hemipelagic settings, metastable carbonate mineralogies will stabilize to low-Mg calcite in a near-seafloor, shallow burial marine porewater (eodiagenetic) environment. This diagenetic facies will enter the deeper burial domain as a relatively inert phase, whilst compaction and stylolithization will still affect pore volumes. The early diagenetic porosity and permeability will significantly affect subsequent pathways of burial fluids. Under high sedimentation rates, typical for shoalwater settings, a significant proportion of the metastable carbonate might enter the mesogenetic burial domain as aragonite and magnesian calcite-dominated reactive facies.

Conclusions

Considering the above discussion, what are the preliminary conclusions?

- 1) The conceptual label “diagenetic facies architectures” is intermediate between the two end members of depositional and diagenetic (Ahr, 2008) carbonate reservoirs. This is because the spatial distribution of different carbonate mineralogies is a depositional feature, whilst the post-depositional diagenetic pathways are driven by the respective reactivity of the diagenetic facies architecture.
- 2) Initial mineralogy and reactivity is but one factor that controls carbonate reservoir characteristics. Chalk carbonate bodies in the North Sea, comparably inert due to their low-Mg calcite mineralogy, are economically important as fractured reservoirs. High-porosity, high-permeability carbonate facies without sealing facies has very limited economic significance. Rock porosity statistics may be as important as rock spatial statistics.
- 3) Reactive carbonate mineralogies at deposition may undergo extreme changes during the eogenetic stage. In contrast, mesogenetic (burial) pathways may be driven by fluids with physico-chemical properties that differ considerably from sea water, shallow burial porewater or meteoric fluids. Burial dolomitization and de-dolomitization, compaction and stylolithization as well as hypogenic karsting may affect formerly stable carbonate mineralogies.

Nevertheless, this considerable level of complexity might be less formidable than expected due to the overriding importance of a limited number of the controlling factors. Carbonate mineralogy at deposition is amongst them. Carbonate reservoir models are commonly designed around the available data density and quality and are guided by a specific business purpose. If the model purpose is the prediction of in-place hydrocarbon volumes without regard for flow characteristics, a simplistic and low-resolution model will suffice and less conceptual input parameters are required. If the model is to predict flow characteristics in a given reservoir, the level of detail required is considerably higher.

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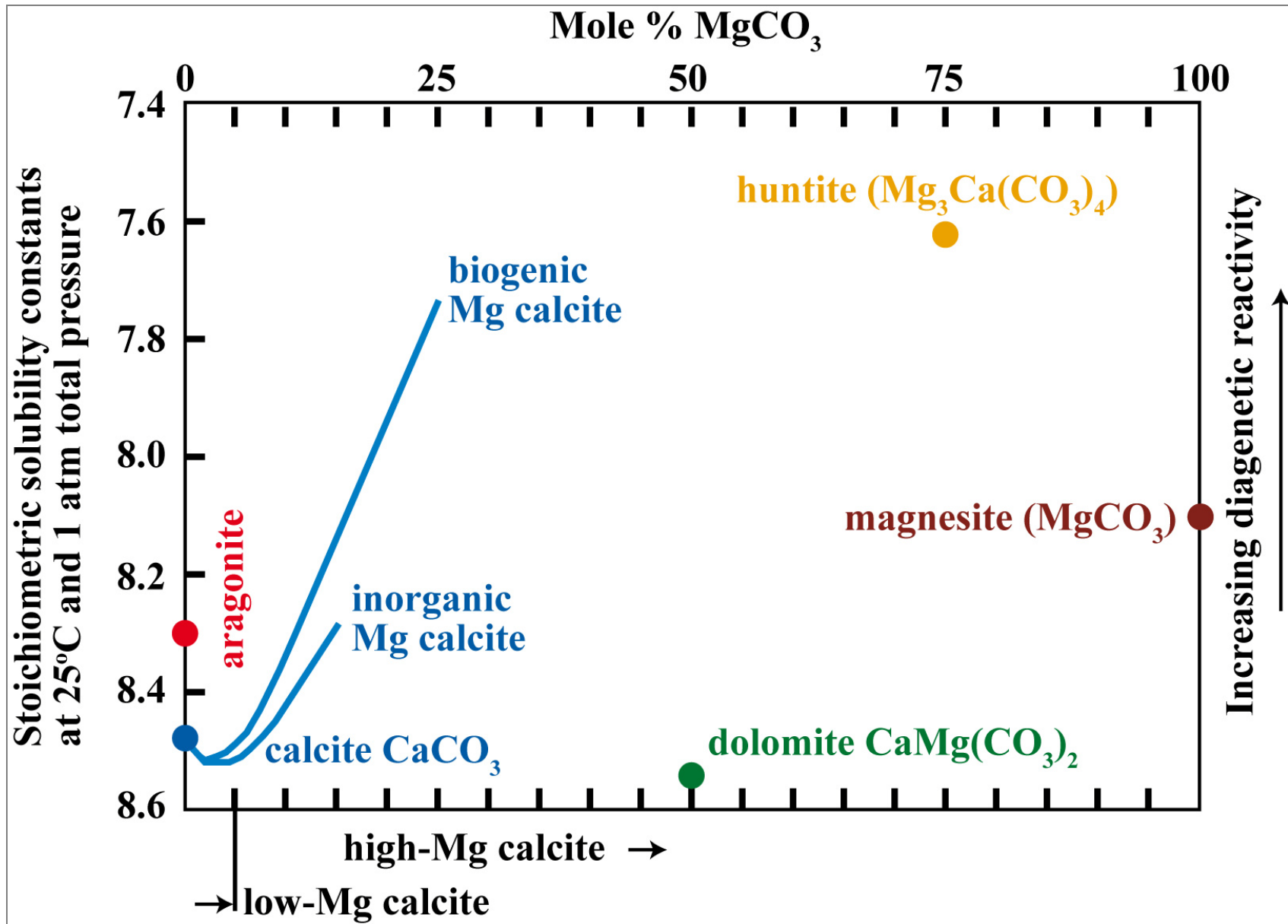


Figure 1. Solubility values of different carbonates at 25°C and 1 atm total pressure for stoichiometric calcite, inorganic and organic Mg calcite, aragonite, dolomite, huntite and magnesite as a function of Mg content. Solubility is roughly proportional to diagenetic reactivity of different carbonate minerals in reservoir rock (modified after Böttcher and Dietzel, 2010).

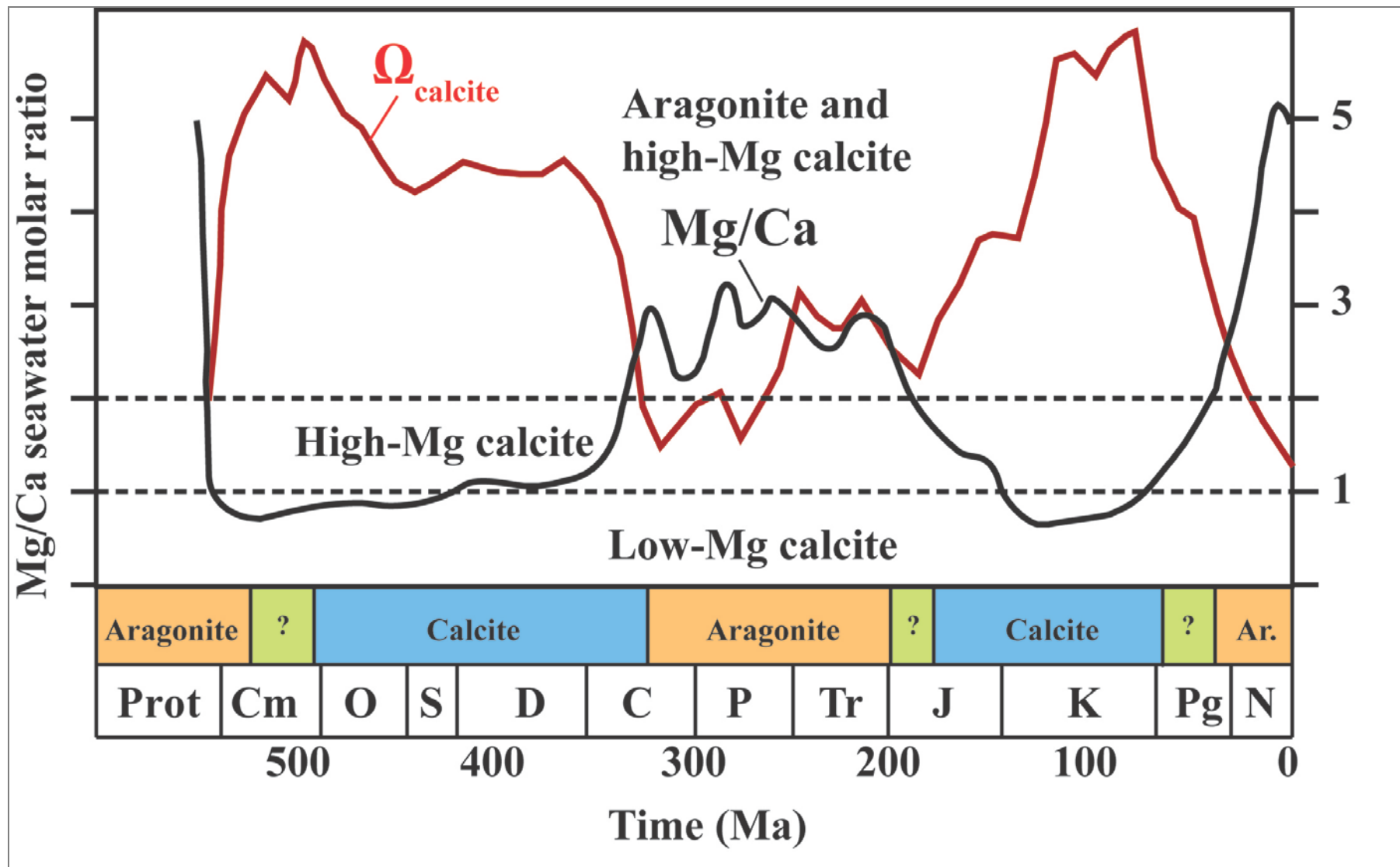


Figure 2. Magnesium/Calcium molar ratio variability of seawater through Earth history. Note, time intervals characterized by Mg/Ca values below 1 are typified by diagenetically inert low-Mg calcite, values below 2 triggered high-Mg calcite precipitation and oceans with Mg/Ca seawater ratios of more than 2 favor aragonite and high-Mg calcite precipitation (modified after Stanley, 2006).