Carbonate porosity creation by mesogenetic dissolution: Reality or illusion?

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ABSTRACT

Many authors have proposed that significant volumes of porosity are created by deep-burial dissolution in carbonate reservoirs. We argue, however, that this model is unsupported by empirical data and violates important chemical constraints on mass transport. Because of the ubiquitous presence and rapid kinetics of dissolution of carbonate minerals, the mesogenetic pore waters in sedimentary basins can be expected to be always saturated and buffered by carbonates, providing little opportunity for the preservation of significantly undersaturated water chemistry during upward flow, even if the initial generation of such undersaturated pore water could occur. A review of the literature where this model has been advanced reveals a consistent lack of quantitative treatment. In consequence, the presumption of mesogenetic dissolution producing a net increase in secondary porosity should not be used in the prediction of carbonate reservoir quality.

INTRODUCTION

This article was stimulated by the recent reappraisal of sandstone diagenesis by Taylor et al. (2010, p. 1125), in particular, their conclusion that porosity creation by mesogenetic dissolution in sandstone petroleum reservoirs is mostly insignificant ("represents a relatively minor proportion of total porosity in most cases"), both in their worldwide data set and probably in general. Of particular relevance to carbonate

reservoirs is the conclusion of Taylor et al. (2010) that sandstone porosity creation by burial dissolution of earlier calcite cements can occur, but only very rarely. Although these conclusions are certainly not new (Bjørlykke, 1984; Bjørlykke et al., 1989), the retrospective nature of their new presentation is striking.

We point out (1) that the process of mesogenetic carbonate dissolution appears to be almost entirely unconstrained by quantitative evidence; (2) that geochemical constraints, as well as corollaries from the recent conclusions of Taylor et al. (2010) regarding sandstone reservoirs, indicate that the proposed causes of mesogenetic carbonate dissolution are likely to be insufficient; and (3) that Occam's Razor can be used to more simply explain our existing heritage of carbonate reservoir information in terms of rather minimal late porosity enhancement on a background of overwhelming porosity destruction during the course of progressive burial diagenesis. We wish to emphasize from the beginning that we are not arguing against the possibility of relatively small amounts of porosity being formed by late-burial dissolution, which may occur along fracture surfaces and thus increase bulk permeability. We also acknowledge that porosity may be created during burial dolomitization involving circulation of surface-derived water along deep fault zones, but we maintain that this has been documented in only a few cases. The terms "mesogenetic," "eogenetic," and "telogenetic" are used in this article following their original definitions in Choquette and Pray (1970).

In the areas of sedimentology, sequence stratigraphy, and especially diagenesis, sandstones and carbonates are commonly regarded as separate worlds, having different rules and requiring different approaches, different textbooks, and different experts. Scientifically, the siliciclastic paradigms tend to become established first, and then the carbonate treatment follows, generally with an introductory statement to the effect that carbonates are in fact completely different. Both lithologies must, however, ultimately obey the same principles of physics, chemistry, and geology.

Therefore, the conclusions of Taylor et al. (2010) regarding porosity controls in sandstone reservoirs should also have direct implications, although perhaps not direct quantitative applicability, for carbonate reservoirs. Certainly, the important differences in reactivity and solubility between the dominant minerals present (quartz in sandstones and low-magnesium calcite or dolomite in carbonates) result in important differences in diagenetic response. However, if the generation of acidic fluids by kerogen maturation or other burial processes is judged to be of too small magnitude to have significantly affected most petroleum-filled sandstone reservoirs, then it seems problematic that this same phenomenon should be of major magnitude with regard to carbonate reservoirs. We contend that burial and creation of carbonate porosity is laden with unwarranted complexity and that existing knowledge is best represented by the model of progressive destruction of porosity as a consequence of chemical compaction and associated cementation responding to increasing thermal exposure and effective stress during burial (Figure 1).

EVIDENCE FROM THE RESERVOIRS

Petrography

Distinguishing between shallow (eogenetic + telogenetic) dissolution and mesogenetic dissolution is important. Most authors seem to define the onset of mesogenesis by the beginning of stylolite formation, but chemical compaction can begin in carbonates at very shallow depths (Choquette and James, 1987) (Figure 2). Surface-driven processes such as seepage-reflux dolomitization and the circulation of seawater through permeable carbonate edifices of relatively young geologic age can extend well below 1 km (0.6 mi) depth but should be excluded from the present definition of mesogenetic porosity generation, although Choquette and Pray (1970) were purposfully vague on this question.

Recognizing that petrographic observations commonly cannot prove that the pore spaces in a deeply buried reservoir formed after burial and were not in large part already present is also important. Many articles reporting examples of mesogenetic porosity creation show photomicrographs of thin
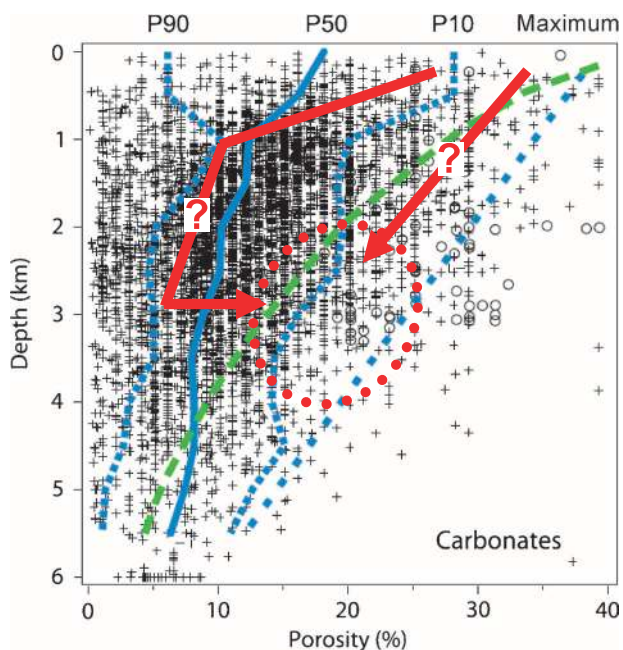
Figure 1. A plot of top reservoir depth versus average porosity for 10,481 carbonate petroleum reservoirs covering all petroleum-producing countries except Canada (from Ehrenberg and Nadeau, 2005; used with permission of AAPG). Small black circles represent chalk reservoirs. Blue lines are statistical values calculated excluding chalk values (black circles) for porosity at given depth (solid line = P50; close-spaced dashed lines = P10 and P90; wide-spaced dashed line = approximate maximum). Green dashed line is the south Florida carbonate trend of Schmoker and Halley (1982). Many reservoirs in the central and upper ranges of the data cloud have undergone uplift following maximum burial (Ehrenberg et al., 2008). For the range of better porosity at 2- to 4-km (1.2- to 2.8-mi) depth (dotted red oval), however, there are two end-member styles of interpretation (red arrows): burial dissolution versus porosity destruction. We contend that the former is both unsupported by evidence and awkward in design.

has not been created in the deep subsurface, but merely redistributed (Giles and de Boer, 1990).

It is well established that scientific data are in general strongly influenced by the expectations of those collecting the data. Therefore, it should not be surprising that what a geologist sees in a rock depends greatly on what is expected. Furthermore, the possibility that petrographic observations are affected by the creation of artifact pores during thin-section preparation (Pittman, 1992) is virually never considered in these articles, although this problem is most certainly not restricted to sandstones.

The presence in vugs of saddle dolomite and other burial cements, commonly containing fluid inclusions with oil and with high temperatures of homogenization, is commonly cited as evidence that the vugs formed mesogenetically. As expressed so succinctly by the rubber duck axiom of Loucks (2003; quoted from his oral presentation), however, "What is in a hole might not have anything to do with the origin of the hole." In other words, the above cements may have been precipitated in pores that were already present and which had formed from processes unrelated to the cementing waters.
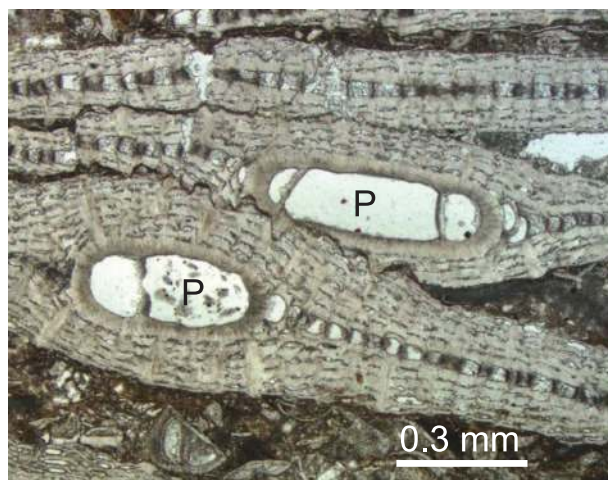
Figure 2. A photomicrograph of sample 194_1198_33R_1_097b cored by Ocean Drilling Program Leg 194 in site 1198. The present depth of 504 m (1654 ft) below the sea floor is the maximum burial depth that this Miocene (Burdigalian) rock has experienced. Large benthic foraminifers (*Lepidocyclina*) are separated by clay-lined microstylolites. Internal chambers (P) contain only traces of calcite cement.

sections as evidence, but alternative interpretations of the same textures are nearly always possible or likely. Mazzullo and Harris (1992, p. 617) state, "Mesogenetic pore types are similar to, and thus easily confused with, eogenetic pore types." In addition, the total pore volume in any given sample may be partly early and partly mesogenetic. Early pores can be enlarged by late dissolution, resulting in pore surfaces that crosscut earlier burial-formed fabric elements, such as cements, compaction features, and fractures. Such indications show that some but not necessarily all of the pore volume is late. The possibility also exists that pore volume

Corrosion along fractures is commonly observed and provides solid evidence of late (or at least post-fracture) dissolution, however fracture porosity typically comprises a small proportion of total reservoir porosity, although fractures can be very important for enhancing bulk permeability.

Porosity-Depth Data

As is also the case for sandstone reservoirs (Taylor et al., 2010), published porosity-depth and porosity-temperature trends for carbonate reservoirs (Figure 3) are consistent with progressive burial destruction of early porosity by chemical compaction and associated cementation. Such compilations always display considerable scatter, and it is impossible to disprove that the higher porosity values at any given depth may reflect mesogenetic dissolution. But systematic trends of porosity increase below a certain depth have never been reported.

Some of the arguments in this paper have already been stated in general terms by Ehrenberg and Nadeau (2005), with reference to their global compilation of average porosity-depth values for carbonate reservoirs (Figure 1). These values show enormous variability at all depths, which can be explained as the result of wide variations in uplift histories after maximum burial combined with widely varying lithologies and eogenetic porosity evolution. Median and especially maximum porosity values do, however, steadily decrease with increasing depth, and thus provide no positive support for mesogenetic porosity creation. Furthermore, subsets of these global carbonate data from basins having simple burial histories with no significant uplift follow overall trends of porosity destruction with increasing burial, but again having major scatter because of lithologic and eogenetic diversity (Ehrenberg et al., 2007; 2008).

Because effective stress correlates with thermal exposure in first cycle basins, it remains unclear whether overburden stress or temperature is in fact the ultimate driving factor for carbonate porosity loss during burial (Brown, 1985). The results of Schmoker (1984) show that carbonates clearly do not have one total porosity value associated with any given degree of thermal exposure,
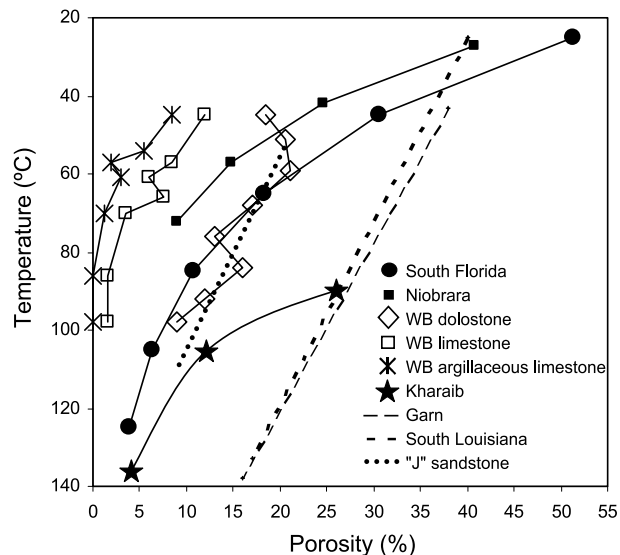

Figure 3. Temperature-porosity trends for carbonates (solid lines) and sandstones (dashed lines). These trends could alternatively be expressed as depth versus porosity, as it remains unknown to what degree porosity loss in carbonates and sandstones depends on effective stress as opposed to temperature. In any case, the available data show systematic porosity decline as burial increases, despite large variations apparently caused by lithology. South Florida (U.S.A.) limestone (25°C surface temperature; 20°C/km) and Niobrara chalk (Colorado and Kansas, U.S.A.) trends (12°C surface; 30°C/km) from Schmoker (1984). Williston Basin (WB) trends from Brown (1997; 12°C surface; 28°C/km). Kharaib Formation (Abu Dhabi, United Arab Emirates) trend from water-leg data of Neilson et al. (1998; figure 12a; 30°C surface; 27°C/km; corrected for assumed land surface elevation 130 m (427 ft) above sea level). Garn Formation (offshore Norway) trend from Ehrenberg (1990; 5°C surface; 38°C/km). South Louisiana Neogene trend from Atwater and Miller (1965; from data plotted in Blatt et al., 1980, p. 419; 25°C surface; 18°C/km). "J" sandstone (Colorado, U.S.A.) trend from Schmoker and Higley (1991; 12°C surface; assuming 30°C/km for shallow end; 40°C for deep end).

as expressed by the widely varying values of his multiplying coefficient, *a*.

AGGRESSIVE FLUIDS: WATER VOLUMES AND SOURCES OF ACIDITY IN THE BURIAL REALM

To dissolve carbonate minerals and transport the products out of a reservoir volume, there must be a supply of water that has the properties of being sufficiently undersaturated with carbonate and of sufficiently large volume to effect a proposed porosity

change. The first of these properties is commonly imagined to be of especially large magnitude because of the addition of chemical species that reduce pH during burial diagenesis. We argue here, however, that severe limitations on accomplishing this exist. Taylor et al. (2010) came to similar conclusions with regard to sources of aggressive fluids for causing late dissolution in sandstones.

With regard to the volumes of water required to create significant amounts of porosity by calcite dissolution, the problem is essentially the inverse of the mass-balance constraints that were pointed out long ago regarding derivation of dissolved calcium carbonate from external sources to effect porosity loss in limestones by calcite cementation (Dunham, 1969; Bathurst, 1975; Scholle and Halley, 1985; Morse and Mackenzie, 1993). For example, to increase the porosity of a 100-m (328-ft)-thick limestone bed by 1%, 1 m^3 (35 ft^3) of calcite must be dissolved for each square meter of bedding surface. For pore water that is undersaturated by 100 ppm, about 27,000 volumes of water are required to dissolve one volume of calcite. Increasing the porosity by 1% in a 100-m (328-ft)-thick limestone therefore requires 27,000 m^3 (953,496 ft^3) of water per square meter. However, even if the limestone was underlain by 5 km (3.1 mi) of sediments where an average porosity loss of 10% of total rock volume occurs, the pore water that is released from the underlying sediments is not more than 500 m^3/m^2. This is less than 2% of the necessary volume (Figure 4). For a porosity increase of 10% in the 100-m (328-ft)-thick limestone, the fluid flow from the underlying 5-km (3.1-mi)-thick sediment package would be less than 0.2% of the required volume.

The argument might be made that highly acidic pore waters could carry away larger amounts of dissolved carbonate than the near-equilibrium waters considered to be involved in causing cementation, but as discussed below, the concept of introducing highly undersaturated waters into reservoir strata is fundamentally unrealistic. Even if calcite-undersaturated pore water did flow through a limestone bed, dissolution would be localized at the points of influx because of high reaction rates (described below). It is, therefore, implausible to
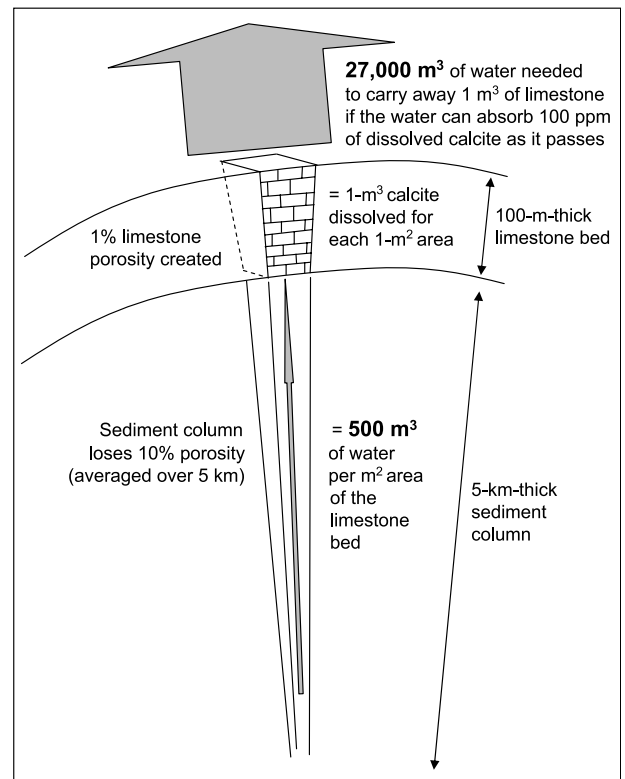

Figure 4. An illustration of water volume required to create 1% porosity by mesogenetic dissolution in a limestone bed.

envisage net dissolution distributed throughout the interior of the limestone bed. The following paragraphs discuss seven potential sources for aggressive fluids that have been used to explain burial porosity creation in carbonates.

1. Carbon dioxide and organic acids from kerogen. As with sandstones (Smith and Ehrenberg, 1989; Hutcheon et al., 1993), subsurface carbonate strata are necessarily rock buffered. Although profiles of p(CO_2) versus temperature have not yet been compiled from carbonate-dominated basins as are available for siliciclastic sections, the results are likely to be similar because of the presence of abundant siliciclastic material throughout virtually all petroleum-producing basins. In any case, acidity generated by kerogen maturation is likely to be neutralized within source rocks if they contain carbonate minerals or along migration pathways, well before reaching reservoirs where useful secondary porosity can be created (Barth and Bjørlykke, 1993; Heydari

and Wade, 2002). This is because the kinetics of calcite dissolution are very fast relative to plausible rates of flow of subsurface pore waters, such that waters necessarily maintain near equilibrium with the rocks they move through (Berner and Morse, 1974; Sjöberg and Rickard, 1984; Walter and Morse, 1984; Chou et al., 1989). Additional relevant arguments and references are listed by Taylor et al. (2010).

2. High CO_2 abundances from presumed metamorphic or igneous sources. Some basins contain waters and petroleum fluids with unusually high contents of CO_2, which are generally interpreted as reflecting either metamorphism of carbonate strata or igneous exhalations. Examples are the Sleipner-Brae area along the Norwegian–United Kingdom boundary in the North Sea (Ranaweera, 1987), offshore Tunisia (Beavington-Penney et al., 2008), and the Gulf of Thailand (Trevena and Clark, 1986). Water with high CO_2 contents could indeed dissolve substantial carbonate to create deep secondary porosity, but such occurrences are likely to be limited to a few specific areas.

3. Biodegradation. This is a potentially important cause of dissolution in shallow oil zones because bacteria can consume large volumes of oil and produce both CO_2 and organic acids as products of metabolism (Jaffe and Gallardo, 1993; Mackenzie et al., 1983; Behar and Albrecht, 1984). Nevertheless, only two examples of diagenesis linked to this cause are known to the authors: Gullfaks field sandstones (Ehrenberg and Jakobsen, 2001) and Liuhua field carbonates (Story et al., 2000; Heubeck et al., 2004; Sattler et al., 2004).

4. Hydrogen sulfide oxidation. As the example of Carlsbad Caverns testifies, major dissolution can occur in shallow carbonate strata that are supplied with both H_2S and O_2 (Hill, 1990; 1995). This process, however, can only occur where abundant oxygen is present, which is generally not the case under burial conditions.

5. Mixing corrosion. Although proposed by Hill (1995) as an important cause of burial dissolution, the actual volume of solid material that can be dissolved per unit of formation water is miniscule. For example, figure 1 of Hill (1995) shows that if the different waters are mixed in just the right proportion along the H_2S mixing curve, the resulting mixture gains the capacity to dissolve an additional amount of calcite equal to 0.007 cm^3/L (~19 ppm by weight). This is much too little to result in any perceptible porosity change even assuming unreasonably huge water rock ratios. In addition, undersaturation could not be preserved during flow, so mixing would need to occur at the exact site of dissolution. These limitations are reminiscent of the analogous failings of the meteoric-marine mixing model for the origin of dolomite (as debunked by Hardie, 1987). Morse et al. (1997) mentioned the concept of deep secondary porosity creation by mixing corrosion, but all of the calculations reported and all their figures in fact show calcite supersaturation instead of undersaturation resulting from mixing.

6. Thermochemical sulfate reduction. Although this process has the theoretical potential to create porosity on a very local reaction-front scale, relevant case studies show that this is in fact negligible (Machel, 2001).

7. Thermal convection. Because of the retrograde solubility of carbonate minerals, warm water moving upward will be undersaturated when it enters a cooler reservoir and could cause dissolution, whereas cool water moving downward is likely to precipitate carbonate cement (Giles and de Boer, 1989). Such effects are likely to be insignificant in any given stratum, however, because of the rapid kinetics of calcite-water equilibration noted above; the upward-moving waters will continuously maintain near equilibrium with the carbonate minerals of the rocks they are moving through. Furthermore, because of the constraints on thermal circulation in heterogeneous strata (Bjørlykke et al., 1988), these effects are likely to occur mainly in fractures. In basins having gradients in pore-water salinity (Ehrenberg et al., 2002), vertical circulation is prevented by density stratification.

A process that we believe could actually create significant porosity during burial, but which seems

to have received almost no consideration (exceptions include Luo and Machel, 1995, and Bouch et al., 2004), is late dissolution of calcium sulfate, which is abundant in arid-climate carbonates and is 100 times as soluble as calcite (Warren, 2006). Its late precipitation commonly involves the consumption of adjacent carbonate grains and cements, resulting in corroded carbonate surfaces. Friedman (1995) notes that Ca sulfate dissolution is also commonly overlooked as a mechanism of eogenetic porosity development in carbonate strata, and Warren (2006) points out how the effects of evaporite loss on stratal architecture may be difficult to recognize. Settings where late anhydrite removal can be expected are the postorogenic and collision-margin realms defined by Heydari (1997).

THE LITERATURE OF BURIAL-DISSOLUTION POROSITY IN CARBONATES

Choquette and James (1987) published the first general diagram describing deep-burial porosity creation in carbonates. The supporting examples were few (two), but the concept had already been successfully advanced for sandstones. Mazzullo and Harris (1991) then provided a more comprehensive general treatment, with examples from four fields in the Permian Basin of west Texas and New Mexico. All the evidence presented for mesogenetic timing of the porosity is, however, simply personal opinion. For example, the Chapman Deep field, the first case cited by Mazzullo and Harris (1991), consists of shallow-water limestone (reef and ooid sand facies). Most or all primary and eogenetic porosity is stated to have been lost before deep burial, and the present 3 to 14% porosity was formed by dissolution along fractures and stylolites at 3- to 4-km (1.9- to 2.5-mi) depth. The supporting article (Mazzullo, 1981) shows photomicrographs of oomoldic porosity, which could just as likely be of eogenetic origin. No evidence is shown that oomolds are in fact concentrated mainly along stylolite swarms as stated, although the possible significance of such a distribution is itself highly uncertain with regard to early versus late timing. Mazzullo and Harris (1991) state that po-

rosity postdates saddle dolomite, but this is nowhere mentioned in Mazzullo (1981). The other three cases are similarly documented with opinions and highly ambiguous information.

Mazzullo and Harris (1992) then published essentially the same message but with new figures and an appendix listing 29 case studies where mesogenetic dissolution had been invoked previously. In nine of these 29 studies, the deep porosity is listed as "minor," and for these, no complaint can be made, as insignificant deep porosity creation is no issue. The remaining 20 cases, however, are universal in lacking any form of compelling evidence for the interpretation of significant deep porosity creation. Although six of these 20 are conference abstracts (where presentation of actual evidence cannot be expected because of brevity), in all cases the authors' opinions serve as the sole basis for the interpretation of major to considerable deep porosity. Where photomicrographs are presented to show deep porosity creation, these appear open to equally plausible alternative interpretation in nearly all cases. The exceptions are porosity along stylolites and fractures (as in figures 4 and 5 of Mazzullo and Harris, 1992). Such porosity certainly formed after these features, but the critical issue is the total amount of such porosity, which may be very small.

The Appendix lists other articles that report major mesogenetic porosity creation but that were not cited in Mazzullo and Harris (1991, 1992). We feel that the interpretations of burial timing of porosity in these articles also fundamentally lack compelling evidence. Note that we cannot offer any proof about the origin of the porosity in these many case histories (the basic data being, in general, unavailable for analysis). Our point is that the previous authors do not have evidence, and therefore the porosity discussed may just as well be primary or eogenetic, which we feel to be the more plausible alternative in view of the geochemical arguments in the previous section.

Many of the above cited articles consist of comprehensive case studies focused on sedimentology and stratigraphy, where diagenesis and porosity evolution is part of an overall evaluation, but not the main focus. In such a context, the data regarding

porosity genesis must necessarily be summarized briefly, and opinions about how porosity might have formed are offered for the sake of giving a holistic picture of the reservoir. These reports are nevertheless listed by subsequent authors like votes in a roll call to show that mesogenetic porosity creation in carbonates is a solidly documented and worldwide phenomenon.

Burial Dissolution of Micrite in Middle East Carbonates

A striking exception to the above general condemnation is Lambert et al. (2006), who present convincing evidence that burial dissolution has enhanced chalky microporosity in the crestal zones of three Middle East oil fields. They show that early formed microrhombic micrite (aggraded micrite particles of low-Mg calcite overgrown with euhedral microspar cement) was dissolved to form rounded micrite morphology, thus increasing porosity either shortly before or after oil accumulated. Stylolitic dissolution and associated calcite cementation then proceeded to reduce microporosity on the water-filled flanks of the same fields. Inhibition of porosity loss by early oil charge is a well-documented phenomenon in this type of reservoir (Oswald et al., 1995; Neilson et al., 1998; Melville et al., 2004).

The rounded micrite samples are mainly located in the upper half of the oil column in each field studied, whereas microrhombic micrite samples occur in the lower part of the oil column and in the water zone. Porosity creation during dissolution is indicated by (1) average values of 8 to 13% (absolute) higher total porosity in rounded micrites than in microrhombic micrites in four sets of measured samples and (2) a linear trend of decreasing average crystal diameter with increasing porosity in the one sample set where diameters were measured.

Despite their clear observations, several aspects of the Lambert et al. (2006) interpretations stimulate comment and suggest that highly specialized circumstances may be required for even modest amounts of burial dissolution to occur. Insofar as this article is by far the most credible example of burial dissolution that we know of, these issues are discussed here in some detail, and an alternative (purely speculative, but plausible) explanation for their data is proposed. The crystal-diameter versus porosity trend (figure 8 of Lambert et al., 2006) extends from 4.5 μm at 2% porosity to 3 μm at 23% porosity. Extrapolated, this trend reaches 64% porosity at zero crystal diameter, so there must be plenty of larger crystals in these samples that are not included. This trend must reflect cementation as much as dissolution because the lowest porosity samples have compact anhedral texture and very low porosity. Also, if 4.5-μm-diameter spheres (48 μm^3 volume) are dissolved down to 3-μm diameter (14 μm^3 volume), then 71% of the solid rock is removed, which seems implausible. Even if dissolution were to begin with intermediate diameter spheres (3.75 μm), dissolution down to 3-μm diameter represents an increase of porosity by 39%, which is much more than the 11% increase suggested by the trend. So perhaps this set of measurements, although providing a valuable general indication of relationships, cannot be interpreted too literally.

The 8 to 13% porosity value that Lambert et al. (2006) calculate to have formed by dissolution (the average porosity difference between the rounded and the microrhombic micrite samples) is certainly too large. A significant proportion of this difference must be caused by continuing calcite cementation in the then water-filled lower part of the reservoir as the oil accumulated. After all, the products of micrite dissolution had to go somewhere. Also, some of the microrhombic samples included in the porosity averages used to get the 8 to 13% difference are taken from the present water zone (as shown by figure 9 of Lambert et al., 2006).

Another aspect requiring comment is the significance of the rounded micrite texture being confined to the upper part of the oil zone in each oil field studied. Lambert et al. (2006) suggest that dissolution was caused by acidic components that were released by kerogen maturation and entered the reservoir just before or at the same time as oil filled the structure. This process is implausible, however, because any excess acidity transported in the water phase would be neutralized by reaction in the conduit long before arriving in the reservoir and
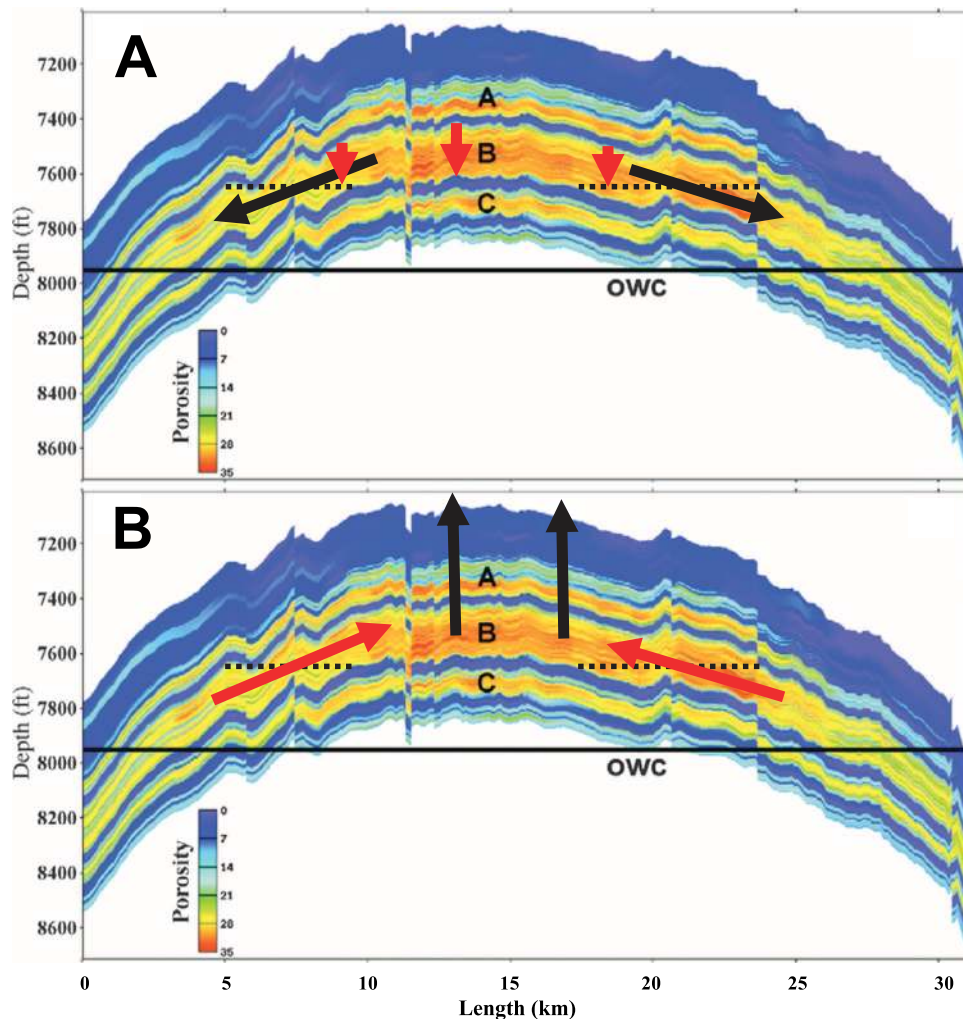
Figure 5. Alternative models for dissolution of microporous micritic calcite in the Middle East oil fields studied by Lambert et al. (2006). The alternatives are displayed using a cross section of a reservoir model showing porosity variation by colors (from figure 3 of Melville et al., 2004; used with permission of AAPG). Note that porosity in each reservoir zone decreases from crest to flank. Considering only the B reservoir zone for this example (middle porous layer), the Lambert et al. (2006) results would suggest burial dissolution to have occurred in the upper half of the oil column (above the black horizontal dotted line) and precipitation of calcite microcement below this level. Dissolution could have occurred either (A) during initial oil accumulation, with acidic components moving downward with the advancing oil-water contact (OWC) (red arrows) and dissolved calcite being transported downward into the water-filled part of the reservoir (black arrows) or (B) after partial filling, as acidic components were released from the oil to the residual water saturation. In this case, upward flow of the residual water (red arrows) would have transported dissolved calcite upward through the shale seal (black arrows).

would in any case cause dissolution throughout the entire column height instead of only near the crest. For the acid components to have been delivered mainly to the top of the structure, they must have been transported within the migrating oil and then released to affect dissolution as the first oil accumulated at the crest. Giles (1997, p. 393) notes that "polar molecules present in the hydrocarbon phase will, given sufficient amounts of time, become partitioned between the two fluid phases

and thus modify the composition of the water phase." Possibly, the dissolved calcite was removed by diffusion and was precipitated as cement in the underlying part of the reservoir (Figure 5A). It seems difficult to explain, however, why only the first oil to accumulate should have been acidic and why filling of the lower part of the reservoir then proceeded with no further dissolution.

An alternative to this scenario is that dissolution was focused at the top of the dome by upward flow

within the residual water saturation after the oil had accumulated (Figure 5B). Bjørkum et al. (1998) showed that such flow is possible in a water-wet reservoir. Presently, however, many Middle East reservoirs with chalky porosity have very low water saturation (<10%) and are regarded as being mixed oil–water wet, which would prevent upward flow of residual water. Even so, these reservoirs must have been water wet to begin with. As the oil first accumulated, capillary pressure would have increased as the column filled, and the oil would have begun to both (1) release any entrained acidic components to the residual water and (2) interact with the pore surfaces to wet them. As this process proceeded, water saturation would gradually decrease and the upward flow of the residual water through the caprock shale would stop, thus confining dissolution to the top part of the oil column. By this means, the dissolved calcite could have escaped upward instead of downward, and an upward-increasing gradient in burial dissolution would be produced.

Burial Dolomitization

Dolomitization requires very high water/rock ratios and therefore commonly involves major mass transport both into and out of the affected intervals. Although severe limitations for supplying sufficient magnesium from basinal sources (Warren, 2000) exist, numerous studies indicate that dolomitization of large limestone volumes can occur by thermally driven circulation of seawater or evaporatively concentrated seawater to depths of several kilometers (Machel, 2004). For example, Wendte et al. (1998) proposed a combination of seepage reflux and convective circulation to dolomitize Devonian carbonates of western Canada. Wilson et al. (1990) and Cervato (1990) proposed dolomitization of small platforms in the Italian Alps by hydrothermal circulation of normal seawater driven by heat from magmatic intrusions and Zempolich and Hardie (1997) proposed dolomitization of Jurassic limestones by seawater that circulated to depths of 5 to 10 km (3.1–6.2 mi) along high-angle faults during Alpine compressional tectonics.

As the above systems depend on the supply of magnesium from seawater at the earth's surface,

porosity creation is not driven by acidic components produced by burial diagenesis. In most such cases, it is also difficult or impossible to know whether the pore volumes in the dolostone actually formed deep in the subsurface or were mainly inherited from the earlier rock, and the same question applies to the dolomite itself.

In many cases of apparent post stylolite dolomitization, the possibility should be considered that the main proportion of the dolomite present was initially formed in near-surface settings and was then recrystallized at greater depth, as proposed, for example, by Montañez (1994) and Kupecz and Land (1994), and outlined in general by Warren (2000).

Fault-localized hydrothermal dolostones could potentially involve mesogenetic porosity creation, but many such examples formed at very shallow depths, where voids may be created mainly by extension rather than dissolution. For example the Albion-Scipio fields of the Michigan Basin are thought to have formed during the Silurian to the Devonian when overburden was less than 0.7 km (<0.4 mi) (Hurley and Budros, 1990; Yoo et al., 2000). Similar cases are described by Smith (2006). At greater depths, the alternative of massive porosity destruction instead of creation is the more likely effect of hydrothermal activity, as documented by Katz et al. (2006) in Madison carbonates (Mississippian) of Montana and Wyoming. Most studies of hydrothermal dolomitization, however, contain little or no information about porosity.

CONCLUSIONS

Like the Emperor's new clothes, the model of mesogenetic carbonate porosity creation is supported by personal opinion and reference to the many who have believed it before. Petrographic relationships have been described as evidence for carbonate porosity creation by burial dissolution, but it is only very rarely if ever possible to show from petrography that net porosity has been created. Available porosity-depth-temperature data show no sign of late porosity increase, and the waters

proposed for this purpose are mostly inadequate in both degree of undersaturation and volume. Possible exceptions are burial dissolution of evaporite minerals and burial dolomitization involving deep circulation of seawater or hypersaline brine along high-permeability conduits connected to the surface. Credible examples documenting actual porosity creation by these means are, however, rare.

Because it is very difficult to quantify what has been dissolved relative to the volumes of cements precipitated, diagenetic reactions must be constrained geochemically. The pore water in sedimentary basins is nearly always saturated and buffered by carbonates even when the pH is low, also in the presence of organic acids. The theory that dissolution by acid pore water has produced significant net increases in bulk porosity has not been supported by quantitative data or models of mineral solubility and fluid flow. In contrast, near-surface meteoric diagenesis involves high fluid fluxes of initially undersaturated water capable of generating net increases in porosity.

At greater depth, burial diagenetic reactions are controlled by the solid phases and very little solids can be held as ions in solution. The kinetics of carbonate dissolution are so fast that pore water undersaturated with respect to calcite will readily become neutralized. Undersaturated pore water from shales would therefore only be able to dissolve limestones immediately adjacent to the shale contacts. As no rational mechanism can explain the formation of mesogenetic secondary porosity, the occurrence of such porosity cannot be predicted or modeled.

RECOMMENDATIONS

To end on a positive and constructive note, we list here a few suggestions for how the present appraisal should be implemented in future studies of carbonate reservoir quality.

Despite our criticism that previous petrographic studies have been mostly ambiguous with regard to the timing of porosity genesis, we emphasize that petrographic characterization of pore types, rock fabric, and paragenesis provide unique and essential information for many aspects of reservoir characterization. Petrographic relationships, however, cannot be expected to uniquely constrain the relative timing when pores formed, except under special fortunate circumstances, as for example when bitumen coatings provide a marker horizon separating premigration and postmigration pores. In any case, however, authors should actively consider and discuss the possibility that much or all of the pore space in any deeply buried carbonate reservoir was inherited from earlier times instead of created at depth. Consideration should also be given to the possibility that observed pores, especially along sites of mechanical weakness like fractures or clay-lined stylolites, are in part artifacts of coring or thin-section preparation.

Studies addressing porosity timing and origin should make use of mass-balance calculations to constrain assumptions arising from apparent relationships.

Studies addressing reservoir potential resulting from dolomitization should strive to determine the time when the bulk rock initially became enriched in magnesium, acknowledging that this can in many cases be much earlier than the time when the existing dolomite crystals formed. Efforts should be expended on measuring the volumes of pore space present in dolostone outcrops and realistically evaluating the available constraints on the time of initial porosity creation.

APPENDIX: LITERATURE REPORTING MAJOR MESOGENETIC POROSITY CREATION IN CARBONATE RESERVOIRS

Articles cited in Mazzullo and Harris (1991; 1992) are covered in the text.

Elliott (1982) reported that carbonate shoal (margin) and lagoon–tidal-flat facies of the Mission Canyon Formation (Mississippian), North Dakota, contain dominantly solution-enlarged fenestral, moldic, and vuggy pore types. Various points of evidence are listed, supporting the conclusion that most of the dissolution that created these pores occurred during deep burial (after stylolites formed), including localization of vugs along stylolites, non–fabric-selective dissolution, anomalous variations in packing, anomalous distributions of early cements, anomalous distribution of porosity. None of these points are documented in any detail, however, and quantitative values of

pore volumes are not cited. We feel that this type of qualitative listing does not constitute compelling evidence but is subject to alternative interpretations of timing.

Dravis (1989) reported porosities of 8 to 15% in Jurassic ooid grainstones at 3- to 4-km (1.9- to 2.5-mi) depth in onshore Texas. The porosity consists mainly of micropores (1–10 μm) in concentrically laminated ooid cortices, whereas macromoldic pores are rare, and intergranular volumes are filled by coarse calcite cement. Most of the arguments listed for a late-burial timing of porosity creation are of questionable significance, including the presence of microporosity instead of macroporosity, dissolution of low-Mg calcite bioclasts, the occurrence of pore spaces in proximity to stylolites, and the lack of evidence for meteoric diagenesis. One observation that supports burial timing of the microporosity is the occurrence in at least one sample of undissolved ooids encased in bitumen, but it is not clear whether microporous ooids that are similarly bitumen coated do not occur. Furthermore, it appears likely that many ooid grainstones without bitumen also lack microporosity because it is stated that microporosity has been lost by cementation along the tops and bottoms of thicker grainstone beds in response to pressure solution in adjacent micritic facies.

Jameson (1994) determined that roughly 60% of total porosity in Pennsylvanian limestones of Lisburne field, Alaska, formed by burial dissolution in the latest Cretaceous to the Paleogene. We find the evidence presented for this figure, however, to be highly questionable and inconclusive. Certainly pores that crosscut burial fabrics indicate some degree of late dissolution, but, as previously explained, the relative amounts of late versus early pores in even a single rock sample, let alone an entire reservoir, are subject to extremes of conjecture depending on the inclination of the observer much more than on objective observation. The figure of 60% could therefore just as plausibly be set much lower by an observer with other expectations. Jameson (1994) argues that because most of the late pores are micropores and commonly occur within low-Mg calcite bioclasts, the waters involved were only slightly undersaturated with calcite and therefore likely to be of deep-burial origin. This inference is, however, entirely undocumented by experimental evidence. Jameson (1994) argues that the spatial association of most microporosity with a Lower Cretaceous unconformity and the occurrence of this porosity mainly above the oil-water contact indicate burial timing of dissolution. We feel, however, that these arguments involve many unsubstantiated assumptions and that the distribution of pore types and abundances as described are compatible with numerous other possible explanations.

Heward et al. (2000) propose that karst-like porosity at about 3-km (~1.9-mi) depth formed by deep-burial dissolution in offshore oil wells of the western Gulf of Thailand, where gas accumulations commonly have high CO_2. They report a formation water sample that was nearly saturated with gas consisting of 76% CO_2. Although the proposed mechanism of dissolution by hydrothermal circulation is indeed plausible and thought provoking, the supporting evidence is circumstantial: (1) presence of vuggy porosity in strata both above and below a major unconformity; (2) production flow higher than might be expected from karst caverns observed in adjacent mainland outcrops of the same strata; (3) high-temperature cements and high geotherms within some occurrences;

(4) staining of vugs with oil and pyrite, and (5) lack of speleothems in the cores recovered.

Heasley et al. (2000) argue that microporosity was created by burial dissolution, possibly caused by acidic components associated with oil accumulation, in Jurassic ooilitic grainstones of an onshore oil reservoir south of London. In the one photomicrograph showing this microporosity, however (their figure 5C), microporous particles fill intergranular volumes between ooids. If it is the presence or absence of this intergranular matrix-like material that accounts for the reported increase in microporosity that their argument is based on, then it would appear more plausible to relate this to depositional texture instead of diagenesis. Furthermore, their contention that microporosity is more abundant below a supposed paleo-oil–water contact is subject to serious doubt because it is based on an overall difference in log-calculated residual water saturation values, instead of petrographic observations. Higher residual water saturation suggests that a higher proportion of the pore system exists behind small pore throats in the deeper interval, but it does not alone say anything about the absolute abundance of the pores. Finally, we question the logic as to why greater microporosity in the lower part of the oil column (even accepting this to be the case) should necessarily indicate late dissolution. For example, the argument that absence of localized occlusion of microporosity adjacent to stylolites indicates formation of microporosity after the stylolites is clearly contentious. Many factors can influence the relative spatial relationships of pore spaces and stylolites, and these spatial relationships are in any case undocumented by data.

Esteban and Taberner (2003) simply restate the ideas of Mazzullo and Harris (1991; 1992), showing no supporting data or examples.

Pöppelreiter et al. (2005) report deep-burial porosity in fractured Cretaceous limestones of the Cogollo Group, Venezuela. Supporting evidence is not part of the presentation, other than citation of personal communications and the information that vuggy pores are commonly partly filled by burial cements containing high-temperature fluid inclusions. Previous publications report scant details about the late porosity in these reservoirs, including Reijers and Bartok (1985), where late leaching is listed as "common" in only one of the six wells studied. Pöppelreiter et al. (2005) use proximity to faults supplying aggressive fluids as one of three main parameters in a reservoir model designed to produce a 3-D map of predicted porosity in a selected oil field. If the assumption is wrong about significant burial porosity creation by aggressive fluids entering the reservoir from faults, however, then the porosity grid generated by the model will have a proportional component of systematic error.

Wierzbicki et al. (2006) argue for burial creation of up to 15% porosity in Jurassic limestones and dolostones presently at 3.4- to 4-km (2.1- to 2.5-mi) depth in offshore Nova Scotia. These gas reservoirs occur within the high-energy margin of a platform that formed during opening of the Atlantic Ocean. Dominantly moldic macropores are interpreted to be of deep burial origin based on evidence such as crosscutting relationships with stylolites, occurrence of pores next to stylolites, dissolution of low-Mg-calcite bioclasts, and high temperatures of precipitation of pore-filling cements. We would point out, however, that virtually all of these evidences appear equally

consistent with partial rearrangement, enlargement, and cementation of preexisting pore spaces in depositionally favorable porous predecessor lithologies. Another possible factor not considered is dissolution of earlier anhydrite cements.

Beavington-Penney et al. (2008) interpret major burial-dissolution porosity to be present in Eocene carbonates at about 3-km (~1.9-mi) depth in offshore Tunisia, where gases have mainly 3 to 14 mol. % CO_2 (one field with 65%). However, the pores in the photomicrographs shown (and also those in a previous article on these carbonates, Racey et al., 2001) appear to be combinations of primary intrachamber (nummulite) and intergranular macropores, in some cases augmented by molds of possible eogenetic origin. The argument given by Racey et al. (2001) for late dissolution is simply that the two largest oil fields in the group are located basinward of the others and therefore would be well placed to receive acidic pore waters associated with a migrating hydrocarbon front.

Jin et al. (2009) report "well-developed" and "very important" mesogenetic dissolution porosity in Ordovician limestone from an oil field in China. They do not say how much of the total porosity is thought to have been created mesogenetically, but total porosity in the one well example shown ranges from less than 1 to 5% in two intervals that are 6 and 8 m (19.7 and 26.2 ft) thick. The arguments for why this porosity is thought to be mesogenetic are not articulated, and the photomicrographs and core photographs seem equally consistent with eogenetic timing of porosity formation.

Story et al. (2000), Heubeck et al. (2004), and Sattler et al. (2004) describe a case in which biodegradation of oil at shallow depth may be related to massive reservoir dissolution in Miocene carbonates of the Liuhua oil field, a few hundred kilometers offshore from Hong Kong. This isolated platform contains late dissolution fabrics and seismically visible karst-collapse features (dolines) that formed after deposition of the overlying shale section. The shallow depth of this reservoir (890 m 2920 ft below sea floor), the highly biodegraded composition of the heavy Liuhua oil, and the presence of gas chimneys streaming from the dolines are consistent with dissolution driven by the acidic products of biodegradation. Alternatively (or in addition), dissolution may be driven by active circulation of cold seawater through the permeable carbonate platform (Heubeck et al., 2004).

Zampetti (2011) studied one of the many isolated carbonate platforms of Miocene age in the Luconia province, offshore Sarawak. Most of the reservoir porosity is found to result from deep-burial dissolution, probably caused by mixing corrosion involving hydrothermal waters rising from depth. The burial depth is shown to be only 300 to 800 m (984–2625 ft); however, and no evidence is presented for anomalously high temperatures. The evidence cited, including solution-enlarged fractures, dissolution pores preferentially located along stylolites, and pores not lined by blocky calcite cement crystals, is inconclusive because the (1) timing of fracture formation is not addressed, (2) occurrence of pores near stylolites does not indicate a causal relationship, and (3) heterogeneous distribution of calcite cement is a typical characteristic of limestones that, in general, proves nothing about relative timing. Previously, Luconia studies ascribe extensive dissolution pores to meteoric diagenesis (Epting, 1980; Vahrenkamp et al., 2004), illustrating the importance of personal expectations for observational results.

Warrlich et al. (2011, p. 112) compare two Miocene-isolated carbonate platforms of Southeast Asia. They report no significant burial dissolution in the Malampaya platform, but in the E11 gas field of Luconia province, the best reservoir quality is interpreted to reflect preferential dolomitization and associated dissolution of mud-dominated facies following stylolite formation. Evidence cited includes the occurrences of stylolites in porous dolostones, similarity between dolomite fluid inclusion measurements and present formation-water salinities and temperatures (108°C at 1.75 km below sea floor), and negative oxgyen isotope values of dolomites. While consistent with the proposed post-stylolite timing of porosity creation, none of these evidences is compelling, and there are no indications at all for the suggested "hot fluids channeled upward along faults" (p. 111). Although not addressed by Warrlich et al. (2011), limitations for both delivery of magnesium and removal of dissolved calcite are likely to be problematic if dolomitization and dissolution must have taken place after the E11 platform was buried beneath its overlying shale section.

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