

REPLY

(Reply to the Comment by David W. Morrow on “Self-accelerating dolomite-for-calcite replacement: Self-organized dynamics of burial dolomitization and associated mineralization”, v. 311, n. 7, p. 573–607.)

ENRIQUE MERINO*[†] and ÀNGELS CANALS**

We welcome David W. Morrow’s Comment to our article Merino and Canals (2011) (MC-2011 hereafter), in which we presented a new model of burial dolomitization. Morrow raises several questions and sees conflicts of some of the model’s parts with published experiments.

THE NEW MODEL

Morrow points out that our model is “significantly different from prevailing views . . .” Indeed, the fundamental strength of the new dolomitization paradigm we present in MC-2011 is that – based on two postulates – it predicts a multitude of associated properties of burial dolostones that are independently confirmed by observations. The first postulate is that dolomitizing brines must be Mg-rich but undersaturated with respect to both calcite and dolomite. According to the second postulate, replacement, a phenomenon dominant in dolomitization and all other types of metasomatism, happens not by “dissolution-precipitation” as assumed by geochemists since the 1960s, but by precipitation/pressure-dissolution within a rigid rock via the induced stress. To summarize: the new paradigm differs from prevailing views in that (a) it proceeds *forward* from the two basic postulates; (b) both postulates are contrary to prevailing wisdom; (c) it involves no *ad-hoc* assumptions; (d) it includes feedbacks – especially a crucial self-accelerating feedback – ignored by traditional models; and finally, as noted, (e) it makes “a multitude of associated predictions” – lithological, paragenetic, textural, rheological, geochemical, petrophysical – which are independently confirmed by observations.

PULSES OF REPLACEMENT

In the model, the dolomitizing brine infiltrates a limestone continuously but the dolomite growth and its replacement of calcite happen in discrete pulses. The precipitation-and-replacement in pulses results from the exponentially self-accelerating kinetics of the dolomite-for-calcite replacement within a rigid limestone. Each pulse of dolomite precipitation is discrete in time because, being self-accelerating, it shuts itself off in a time T when all available local Mg^{2+} (aq) abruptly runs out.

Figures 5A and 5B in MC-2011 describe the dynamics of just one “pulse” of dolomite precipitation and how it is kicked off by a fast initial calcite dissolution by the incoming calcite-undersaturated brine. That pulse is indeed the first step “. . . of massive dolomitization of limestones,” as Morrow says, but because the precipitation-dissolution replacement is self-accelerating and therefore abruptly self-shutting, and because each pulse of precipitation makes only < 1 percent by volume of dolomite, hundreds of similar dolomite-for-calcite steps (each triggered by its own fast initial calcite dissolution) automatically take place until an L length of limestone thickness is

* Department of Earth and Atmospheric Sciences, Indiana University, Bloomington, Indiana 47405, USA, merino@indiana.edu

** Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona, c/ Martí i Franquès s/n, 08028 Barcelona, Spain, angelscanals@ub.edu

[†] Corresponding author: merino@indiana.edu

completely replaced, and only then does the whole process starts with the next L length, or slice, of limestone (see fig. 6 of MC-2011). The precipitation of each pulse of dolomite takes place over the whole length (L) of one segment of limestone, not “at the far end of each limestone segment and then . . . successive pulses progressively backfill”. Morrow’s reading confuses the evolution versus *time* of one pulse of precipitation as per figure 5A, for the evolution versus *distance* as per figure 5B. Plausible values of T , L , and N , the number of precipitation-and-replacement pulses needed to fully dolomitize one slice of thickness L of limestone, are calculated in the Appendices of MC-2011. The whole process in the model is open, but in the last stages of each pulse transport becomes negligible in relation to the now-very-fast dolomite growth; that is why the growth shuts itself down abruptly. Pulses of precipitation are not pulses of brine; the dolomitizing brine infiltrates the limestone continuously.

REPLACEMENT MASS BALANCE

Merino and Canals (2011) wrote the volume-adjusted mass balance for the dolomite-for-calcite replacement as “ $1.74\text{calcite} + \text{Mg}^{+2} + 0.26\text{CO}_3^{-2} = \text{dolomite} + 0.74 \text{Ca}^{+2}$,” and explained that the 1.74 factor on calcite results from dividing the formula volume for dolomite, 64.3 cm^3 , by that of calcite, 36.9 cm^3 . Morrow notes that this mass balance “was given without citation.” It did not occur to us that implementing volume conservation needed citing sources. Merino (1975) had the idea of adjusting the mass balance for a replacement *on volume*. Merino and others (1993), Merino and Dewers (1998), Li and others (2004), and Banerjee and Merino (2011) have applied the same volume-based adjustment to various replacements.

THE MECHANISM OF REPLACEMENT

In several paragraphs Morrow questions the mechanism of replacement that we adopted as the second postulate of our model – that replacement be understood to happen not by dissolution-precipitation but by its opposite, *precipitation-dissolution*.

1. Morrow’s statement,

“Merino and Canals (2011) cite the occurrence of extremely texturally-preservative examples of dolomitization to support their case for induced stress dissolution of calcite by growing dolomite . . .”

is inaccurate. The case for the growth induced stress and for replacement by pressure solution was made by Maliva and Siever (1988). The induced stress is not hypothetical. Our case for the existence, evidence for, and crucial role of the induced stress was made by Merino and others (2006), and Fletcher and Merino (2001). In Section III, “Replacement Physics”, of MC-2011, we summarized from previous articles how the mechanism of precipitation-dissolution was discovered, and how it works. Maliva and Siever (1988) had the idea that the *force of crystallization* generated by the growth of the new mineral within a rigid rock pressure dissolves the host. The empirical force of crystallization was conceptually upgraded to the *induced stress*, and the induced stress was calculated by Fletcher and Merino (2001). Nahon and Merino (1997) showed how the induced stress self-adjusts to always equalize the growth rate of the new mineral and the dissolution rate of the host, explaining why volume is characteristically preserved by replacement – as reproduced in figure 3 of MC-2011. Note that the equalization of rates by the induced stress works equally well in explaining replacements involving a host and a guest with *no* components in common, as in the dolomite-for-sphalerite replacement of our figure 7A of MC-2011. Furthermore, not only does the stress induced by dolomite growth within a limestone drive the replacement of the host calcite by pressure solution. Because the dolomite-for-calcite replacement is self-accelerating and “softens” the rheology of carbonate aggregates (see fig. 8A), the

induced stress also ends up driving *displacive* zebra veins and their self-organization by *trriage* leaving the survivors regularly spaced, as shown in detail in Merino, Canals and Fletcher (2006).

2. Morrow dismisses the evidence of preservation of volume and spatial details (and therefore of the implied simultaneity and equal-rate of the two half-reactions of any replacement) shown in our figures 1A and 7A and in many others in the literature (notably, fig. 12 in Bastin and others, 1931), treating them as exceptions or outliers that apply only on “a nanometer scale”. He bases his preference for dolomitization by dissolution-precipitation on the *absence* of textural preservation, and describes burial dolostones as “. . . even without exception fabric-destructive.” He uses that assumed absence of preservation (a) as an argument to dismiss the existence of the growth induced stress; and (b) assuming that volume is not preserved, either, and that dolomitization proceeds by dissolution-precipitation and generates a lot of porosity. Morrow argues that dissolution-precipitation also can preserve morphological details citing the mimetic lab experiments of Zempolich and Baker (1993). But these experiments were made in a fluid-dominated system and this is quite different from growth within a solid rock – a distinction pointed out by Harker (1950, p. 25).

Also, it must be pointed out that the “fabric-destructiveness” of dolostones, or “absence of fabric preservation,” which Morrow takes as evidence supporting the dissolution-precipitation theory of dolomitization, is actually another prediction of our model. It results from the precipitation “storm” caused by the self-accelerating nature of the precipitation/pressure dissolution dolomite-for-calcite replacement when it reaches its highest growth rates between times t_4 and T in MC-2011 Figure 5A. The dolomite growth increments then may become as large as morphological details in the limestone, or larger, and can therefore erase or half-erase them for the same reason that a painting of a country house rendered by Cézanne with large brush strokes (see fig. 4B in MC-2011) makes it difficult even to tell that the house has windows.

3. Morrow criticizes the model because it does not generate sufficient porosity. The model produces considerable dissolution porosity, as each pulse of dolomite precipitation like the one pictured in figures 5(A,B) is triggered by a fast initial dissolution of calcite, and hundreds of such pulses take place automatically in each meter or so of limestone thickness that is completely dolomitized, as shown in figure 6 of MC-2011.

4. The conventional mechanism of dissolution-precipitation dear to geochemists cannot account for the kinetic properties of replacement already discovered by Bastin and others (1931, their fig. 12 and p. 603), namely, simultaneity and equal rate of the two half-reactions of any replacement. But dissolution-precipitation is also precluded texturally. Figure 1A of MC-2011, showing a euhedral dolomite partly replacing several *öolites*, contains three independent bits of spatial/textural evidence, each precluding dissolution-precipitation, but only one of the three is the preservation of *öolite* inclusions by the new dolomite that Morrow discards. The other two have to do with the fact that the new dolomite crystal is euhedral: (1) If this situation had been reached by dissolution-precipitation we would have to admit that the dissolution of the host “knew” how to open vugs having the internal crystallographic growth form (that is, rhombohedral) preferred by the future of dolomite crystal, which is impossible. (2) There is still another evidence in figure 1A precluding dissolution-precipitation, given on p. 579 of MC-2011: the central dolomite rhomb in figure 1A partly replaces *three* separate *öolites* at once. If this had happened by dissolution-precipitation, the three idiomorphic dissolution vugs would have had to be in close communication with each other to ensure they were oriented appropriately to be filled in by the one idiomorphic crystal that grew later.

5. Morrow gives another argument against dolomitization by precipitation/pressure-dissolution:

“Clearly, saddle dolomites and associated zebra fabrics are not *in themselves* indicative of an intercrystalline pressure-dissolution dolomitization process . . .” (our italics).

As Morrow points out, associated zebra veins and saddle crystals do not by themselves suggest any *ad-hoc* reason for their association. But our model contains no *ad hoc* hypotheses regarding the genesis of dolomitic zebra and breccia-like veins or regarding their association with saddle dolomite crystals. Here however lies the serendipity of our dynamic model: What happens is it *predicts why* saddle dolomite crystals and displacive zebra and breccia-like veins – *and* their characteristic continuous, gradational replacive/displacive contacts as seen under a microscope – do form *mutually associated* in burial dolostones from different ages and places. The model shows that they all result from the exponential rise in aqueous Ca^{2+} concentration that is coupled with the exponential rise in the rate of the dolomite-for-calcite replacement, combined with the strain-rate softening property of carbonate aggregates, and with the incorporation by fast growing dolomite crystals of tiny calcitic crystallites that deform the dolomite structure. (The calcitic crystallites are unable to defuse the self-accelerating feedback as feared by Morrow, see below.) The predicted rise in Ca^{2+} accounts still for more features that are also associated, namely the precipitation of the “late-stage calcite”, dedolomitization, and precipitation of other Ca-bearing minerals such as anhydrite and/or fluorite.

As for another comment by Morrow,

“Merino and Canals (2011) also cite the occurrence of zebra fabrics and saddle dolomites in hydrothermal dolomite masses as supportive of their hypothesized intercrystalline pressure-dissolution dolomitization process, arguing that the absence of porosity in some examples of saddle-dolomite-filled zebra fabrics is direct supportive evidence.”

we do not argue that “absence of porosity” supports anything or that it exists at all. On the contrary, our model predicts initial limestone dissolution porosity to trigger *each of* the hundreds of pulses of dolomite precipitation (like the one in fig. 5A) per meter of limestone thickness that is replaced by dolomite.

And we had shown previously (Merino and others, 2006), with field, petrographic and theoretical evidence, that the zebra and breccia-like veins are forcibly displacive via the induced stress, and how this stress drives a feedback through which zebra veins pressure dissolve too-close neighbors, with the survivors of this *triage* becoming more regularly spaced. But we did not find out until 2011 why the replacive dolomite of the walls passes continuously to displacive vein dolomite, or why the vein crystals are saddle shaped.

6. Morrow points out that the exponentially growing Ca^{2+} concentration shown in our figures 5A, 5B and 6 should drive calcite growth, which would defuse the self-accelerating dolomite-for-calcite feedback that produces it. There is indeed formation of tiny calcitic crystallites in the later times of each precipitation pulse, but these crystallites cannot form viable calcite nuclei in the middle of the storm of dolomite growth that takes place late in each pulse. They are instead immediately incorporated into the structure of very-fast-growing dolomite crystals, deforming them into their characteristic saddle shape. (They were detected by transmission electron microscopy, Barber and others, 1985.) The valuable kinetic experiments by Arvidson and Mackenzie (1999) do not throw light on the matter because they took place in a fluid-dominated system, thus they do not reproduce the real conditions under which dolomitization takes place in nature, namely, crystal growth “in the heart of a solid

rock” (Harker, 1950, p. 25). Therefore, the conflict with the experiment is only apparent.

CALCITE AND DOLOMITE SATURATION INDICES OF TWO SEDIMENTARY BRINES

Merino and Canals (2011) in table 1 cited two deep, hot, sedimentary brines rich in Mg and Ca and barren in carbonate, and having slightly negative saturation indices (calculated with SOLMINEQ) for both calcite and dolomite, as plausible examples of the dolomitizing brines required by the first postulate of the new model. They are also rich in Pb, Zn, Ba, Sr, and other elements typical of Mississippi-Valley-type ores so often associated with dolostones. Morrow reports that his aqueous speciation calculations with PHREEQC for brine 84-MS-11 (Kharaka and others, 1987) yield calcite saturation indices of +1.94 and +0.09, depending on databases used, and of +1.5 and -0.39 for the Smackover Fm Brine 55 (Moldovanyi and Walters, 1992). That is, all values (except the -0.39) indicate calcite supersaturation, leading Morrow to say that neither brine is a good candidate to trigger dolomitization according to the new model.

Morrow may be right, but there are several sources of uncertainty in his speciation calculations that warrant caution: (1) We believe PHREEQC does not calculate uncertainty brackets reflecting how (a) uncertainties in the input analyses and (b) uncertainties in the calculation of activity coefficients in superconcentrated brines, are propagated through the speciation calculations. Determining just such brackets was the aim of the Monte Carlo method of error propagation proposed by Merino (1979). (2) The two S.I.(calcite) values that Morrow calculates for each of the two brines are almost two log units apart just by using different databases. (3) Finally, the high-temperature pH (=5.0) reported for the two brines and included in the input for the speciation calculations was not an analytically measured value but one independently calculated by Kharaka and others (1987, p. 557) by estimating the amount of CO₂ degassed from the brine upon sampling at the oil well head, and “adding” it to the brine by a calculation prior to the speciation calculation. It is likely that that calculation did not include consideration of the fact that in these brines, being very rich in Mg, there would be considerable ion-pairing of Mg²⁺ with one or two OH⁻ s which would result in pHs < 5, which in turn would make SI for calcite (and for dolomite) lower.

CONCLUDING REMARK

We want to conclude stressing the fact that in the dolomitization model of Merino and Canals (2011) all the “moving parts” of the new dynamics work together to produce – without *ad hoc* assumptions – a chain of associated predictions that are all of a piece, and all confirmed by independent evidence. If any of the two postulates were wrong, or if the dolomite-for-calcite replacement were not self-accelerating via Ca²⁺, or if calcite dissolution were not inherently very fast, or if crystalline carbonate aggregates were not strain-rate-softening – the model would not work.

Because the many predictions of the model are all of a piece, it has been difficult for us to reply briefly to some of the Comments by D. Morrow addressing the causes of specific items of evidence. Such questions can only be well answered and clarified by presenting the whole self-accelerating and self-organized dynamics of which they are part.

REFERENCES CITED

- Arvidson, R. S., and Mackenzie, F. T., 1999, The dolomite problem: Control of precipitation kinetics by temperature and saturation state: *American Journal of Science*, v. 299, n. 4, p. 257–288, <https://doi.org/10.2475/ajs.299.4.257>
- Banerjee, A., and Merino, E., 2011, Terra rossa genesis by replacement of limestone by kaolinite. III. Dynamic quantitative model: *The Journal of Geology*, v. 119, n. 3, p. 259–274, <http://dx.doi.org/10.1086/659146>

- Barber, D. J., Reeder, R. J., and Smith, D. J., 1985, A tem microstructural study of dolomite with curved faces (saddle dolomite): *Contributions to Mineralogy and Petrology*, v. 91, n. 1, p. 82–92, <http://dx.doi.org/10.1007/BF00429430>
- Bastin, E. S., Graton, L. C., Lindgren, W., Newhouse, W. H., Schwartz, G. M., and Short, M. N., 1931, Criteria of age relations of minerals, with especial reference to polished sections of ores: *Economic Geology*, v. 26, n. 6, p. 561–610, <http://dx.doi.org/10.2113/gsecongeo.26.6.561>
- Fletcher, R. C., and Merino, E., 2001, Mineral growth in rocks: Kinetic-rheological models of replacement, vein formation, and syntectonic crystallization: *Geochimica et Cosmochimica Acta*, v. 65, n. 21, p. 3733–3748, [https://doi.org/10.1016/S0016-7037\(01\)00726-8](https://doi.org/10.1016/S0016-7037(01)00726-8)
- Harker, A., 1950, *Metamorphism*, 3rd edition: London, Methuen, 362 p.
- Kharaka, Y. K., Maest, A. S., Carothers, W. W., Law, L. M., Lamothe, P. J., and Fries, T. L., 1987, Geochemistry of metal-rich brines from central Mississippi Salt Dome basin, U.S.A.: *Applied Geochemistry*, v. 2, n. 5–6, p. 543–561, [http://dx.doi.org/10.1016/0883-2927\(87\)90008-4](http://dx.doi.org/10.1016/0883-2927(87)90008-4)
- Li, C., Ripley, E. M., Merino, E., and Maier, W. D., 2004, Replacement of base metal sulfides by actinolite, epidote, calcite, and magnetite in the UG2 and Merensky Reef of the Bushveld Complex, South Africa: *Economic Geology*, v. 99, n. 1, p. 173–184, <https://doi.org/10.2113/gsecongeo.99.1.0173>
- Maliva, R. G., and Siever, R., 1988, Diagenetic replacement controlled by force of crystallization: *Geology*, v. 16, n. 8, p. 688–691, [https://doi.org/10.1130/0091-7613\(1988\)016<0688:DRCBFO>2.3.CO;2](https://doi.org/10.1130/0091-7613(1988)016<0688:DRCBFO>2.3.CO;2)
- Merino E., 1975, Diagenesis in Tertiary sandstones from Kettleman North Dome, California. I. Diagenetic mineralogy: *Journal of Sedimentary Research*, v. 45, n. 1, p. 320–336, <https://doi.org/10.1306/212F6D52-2B24-11D7-8648000102C1865D>
- 1979, Internal consistency of a water analysis and uncertainty of the calculated distribution of species at 25 °C: *Geochimica et Cosmochimica Acta*, v. 43, n. 9, p. 1533–1542, [http://dx.doi.org/10.1016/0016-7037\(79\)90146-7](http://dx.doi.org/10.1016/0016-7037(79)90146-7)
- Merino, E., and Canals, À., 2011, Self-accelerating dolomite-for-calcite replacement: Self-organized dynamics of burial dolomitization and associated mineralization: *American Journal of Science*, v. 311, n. 7, p. 573–607, <https://doi.org/10.2475/07.2011.01>
- Merino, E., and Dewers, T., 1998, Implications of replacement for reaction-transport modeling: *Journal of Hydrology*, v. 209, n. 1–4, p. 137–146, [http://dx.doi.org/10.1016/S0022-1694\(98\)00150-4](http://dx.doi.org/10.1016/S0022-1694(98)00150-4)
- Merino, E., Nahon, D., and Wang, Y., 1993, Kinetics and mass transfer of pseudomorphic replacement: Application to replacement of parent minerals and kaolinite by Al, Fe, and Mn oxides during weathering: *American Journal Science*, v. 293, n. 2, p. 135–155, <http://dx.doi.org/10.2475/ajs.293.2.135>
- Merino, E., Canals, A., and Fletcher, R. C., 2006, Genesis of self-organized zebra textures in burial dolomites: Displacive veins, induced stress, and dolomitization: *Geologica Acta*, v. 4, n. 3, p. 383–393. <http://dx.doi.org/10.1344/105.000000352>
- Moldovanyi, E. P., and Walters, L. M., 1992, Regional trends in water chemistry, Smackover Formation, southwest Arkansas: *Geochemical and physical controls: AAPG (American Association of Petroleum Geologists) Bulletin*, v. 76, n. 6, p. 864–894.
- Morrow, D. R., 2018, Comment to article by Merino and Canals, 2011: *American Journal of Science*, v. 318, n. 7, p.
- Nahon, D., and Merino, E., 1997, Pseudomorphic replacement in tropical weathering: Evidence, geochemical consequences, and kinetic-rheological origin: *American Journal of Science*, v. 297, n. 4, p. 393–417. <http://dx.doi.org/10.2475/ajs.297.4.393>
- Zempolich, W. G., and Baker, P. A., 1993, Experimental and Natural Mimetic Dolomitization of Aragonite Ooids: *Journal Of Sedimentary Research*, v. 63, n. 4, p. 596–606, <https://doi.org/10.1306/D4267B86-2B26-11D7-8648000102C1865D>