



Why magnesite, talc, and MVT ore deposits are associated with burial dolostones: Serpentinization provides the magnesium

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Abstract. Magnesite, talc, and MVT ore deposits are hosted in burial dolomites in several districts because they all form from the same deep hot Mg-rich brines that first drive replacement of limestone by dolomite. Then talc and magnesite replace the dolomite. These replacements are Mg-driven and happen by precipitation/pressure-dissolution, which is why mineral volume is preserved, which warrants adjusting replacement mass balances on volume. The dolomite-for-calcite replacement is self-accelerating via the Ca^{2+} released and affects huge volumes of limestone. Continued infiltration of the dolostone by the Mg-rich brine causes its replacement by magnesite and talc. The talc, magnesite, and MVT ores, and dedolomitization too, are part and parcel of the dolomitization process.

We propose that the huge amount of Mg needed to dolomitize limestones and form associated magnesite and talc ores, comes most likely from another huge process, the serpentinization of peridotites, which – only if we adjust the serpentine-for-olivine mass balance on volume – is seen to release much $\text{Mg}^{2+}(\text{aq})$ and $\text{SiO}_2(\text{aq})$. The release of these two ingredients makes the replacement self-accelerating, which in turn, through a rheological-kinetic feedback, accounts for the typical mesh and/or zebra displacive veining of serpentinites, and for the fact that even huge peridotite massifs are serpentinized completely.

1 Introduction

Burial dolomites around the world are host to Mississippi-Valley-type ore deposits (Zn-Pb sulphides or carbonates, barite, celestite, fluorite), and also to magnesite (MgCO_3) and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) ores. One such association of burial dolomites hosting MVT, magnesite, and talc ores occurs across the northern Iberian Peninsula (e.g., Velasco et al. 1987; Tornos and Spiro 2000). Another example is the set of MVT, talc, and magnesite ore deposits hosted in dolomites of southeastern British Columbia (e.g., Powell et al. 2006; Paradis and Simandl 2018).

Why are those ores typically hosted in burial dolomites? To drive dolomitization as well as magnesite and talc mineralization, magnesium is needed. The minerals involved form by replacement: dolomite replaces entire limestones. Magnesite replaces dolomite (Velasco et al. 1987; Lugli et al. 2000). Talc replaces

dolomite and may also replace quartz in quartzites (Tornos and Spiro 2000).

However, saying that Mg is needed to make magnesite and talc does not make it clear which are the mineral reactions involved, or what are their driving forces, or how to account for the fact that all the ores and the dolomite that hosts them occur as replacements, or where the necessary magnesium comes from. Our approach below is to adjust replacement mass balances on volume (as required by the conservation of volume shown in Figures 1-3), and to take account of the new replacement physics (Merino and Dewers 1998; Merino and Canals 2011), by which replacement forms not by dissolution-precipitation as widely assumed, but by its opposite, precipitation/pressure-solution.

We very briefly discuss below the dynamic model of dolomitization and MVT mineralization by deep hot Mg-rich brines also rich in Sr, Ba, Zn and Pb (Merino and Canals 2011). The model shows how the brines drive the dolomite-for-calcite replacement essential to dolomitization, along with associated MVT ores, and how the same brines – if they continue infiltrating the dolostone – can drive the replacement of (some of) the dolomite formed by magnesite and talc.

The second question raised is: What is the source of the colossal amount of aqueous Mg^{2+} needed to make burial dolomites and their associated magnesium ores, magnesite and talc? Again, it is by studying the serpentine-for-olivine replacement according to the new physics of replacement that we realize that the serpentinization of peridotites releases much magnesium and can provide the Mg needed by dolomitization.

2 Replacement and self-accelerating dolomitization

The phenomenon of replacement is essential in all types of metasomatism. (Please refer in detail to Merino and Canals (2011) and Merino et al. (2006).) Replacement is characterized by its spatial property of pseudomorphism - that the new mineral preserves both the volume and some 'ghosts' of the host. That double preservation implies two kinetic properties already grasped by Bastin et al. (1931, p.603): that the two 'half-reactions' of any replacement must be simultaneous and equal-rate. The pseudomorphism and the kinetic properties it implies



can be produced only by precipitation/pressure dissolution, not by dissolution-precipitation as generally assumed.

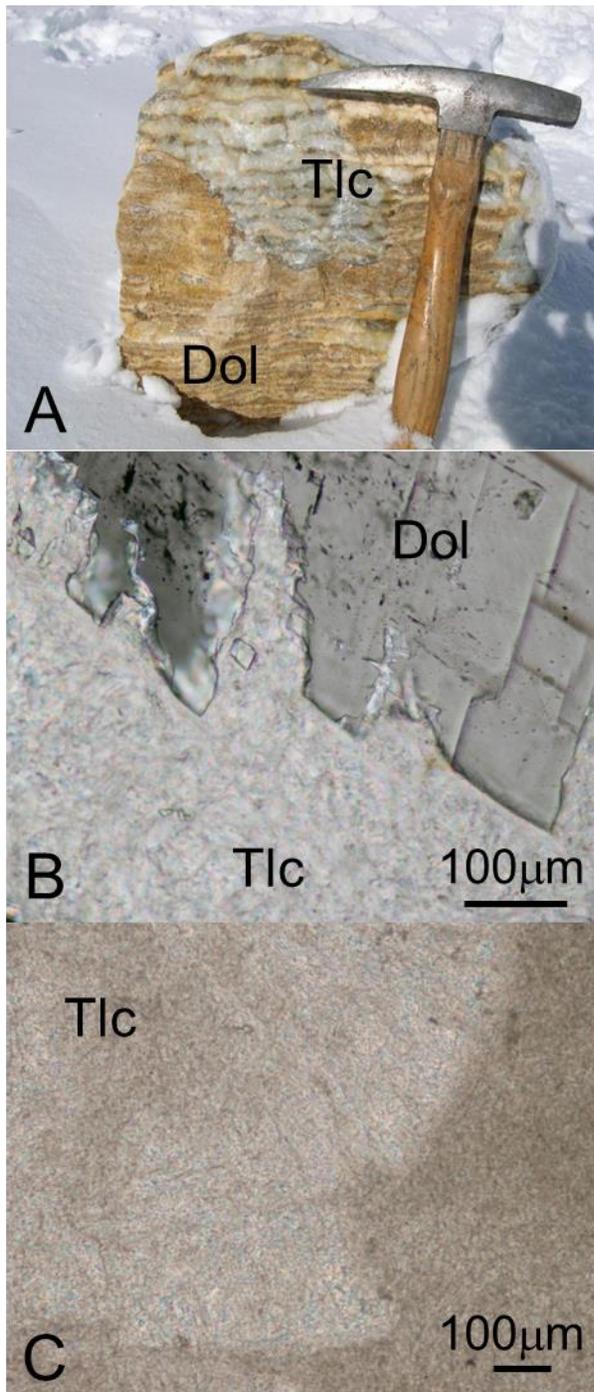
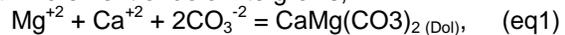


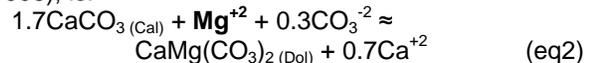
Figure 1. A) Zebra dolomite texture (Dol) is partly replaced by talc (Tlc). B) Talc replaces saddle dolomite from the central part of a zebra vein. C) Photomicrograph XP. Talc completely replaces two large saddle dolomite crystals, preserving their curved outlines. Samples from the Respina Mine, Spain.

Merino and Canals's (2011) comprehensive model of dolomitization dynamics rests on that view of replacement. Dolomite grows within a rigid limestone

from a Mg-rich brine, exerting a local induced stress on the adjacent calcite and on itself. The stress pressure-dissolves the calcite and automatically equalizes the rates of calcite dissolution and dolomite growth (Nahon and Merino 1997), thus preserving mineral volume. As an increment of dolomite grows,



it pressure dissolves an equal volume of calcite. The mass balance, adjusted on volume (Merino and Dewers 1998), is:

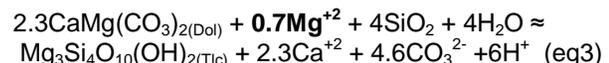


The Ca^{+2} released drives the growth of a new increment of dolomite by eq1, which will pressure dissolve more calcite, releasing more Ca^{+2} , and so on. This replacement is thus self-accelerating via Ca^{+2} . Numerous predicted consequences of this self-acceleration are all confirmed by independent observations (Merino and Canals 2011). One prediction is that, when the dolomite-for-calcite replacement becomes fast enough, it lowers the local rock viscosity (because crystalline carbonate aggregates are strain-rate softening), and it should convert itself into a late minor phase of displacive growth, and indeed displacive is precisely what the characteristic zebra and breccia-like dolomitic veins are (Merino et al. 2006). Also, the self-acceleration makes it easier to understand why burial dolostones are so large and why they replace the original limestone completely. Another prediction of the model is that, because of the positive feedback between Ca^{+2} concentration and replacement rate, when the fast dolomite growth shuts itself down by using up all local $\text{Mg}^{+2}(\text{aq})$, the huge Ca^{+2} concentration in the local brine immediately drives precipitation of calcite as so-called late-stage calcite and as calcite-for-dolomite replacement, or dedolomitization.

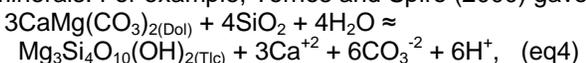
3 Mass balances for the dolomite replacements

If the Mg-rich brine continues to infiltrate the dolostone, it can then drive the replacement of the dolomite by talc (Fig. 1) and/or by magnesite (Fig.2) according to the following mass balances:

3.1 Talc-for-dolomite, Figure 1:



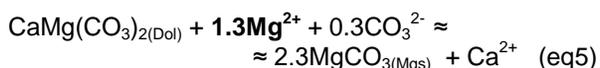
where 2.3 (=145/64 or quotient of formula volumes) equalizes mineral volume. This replacement is not self-accelerating, since it does not release Mg or SiO_2 that would reinforce further talc growth. Note that published replacement reactions for the talc-for-dolomite replacement are adjusted to conserve Mg among the minerals. For example, Tornos and Spiro (2000) gave:



which has the unintended consequences of hiding that Mg^{+2} drives the phenomenon and of violating the petrographically observed volume conservation.



3.2 Magnesite-for-dolomite, Figure 2:



where the 2.3 factor ($\approx 64.5/28.1$) equalizes mineral volume, as required by petrography (Fig. 2). This mass balance tells us that when magnesite grows (from Mg^{2+} and CO_3^{2-}) and pressure dissolves an equal volume of dolomite, only Ca^{2+} is released, which does not reinforce the growth of more magnesite. Thus magnesite-for-dolomite is not self-accelerating.

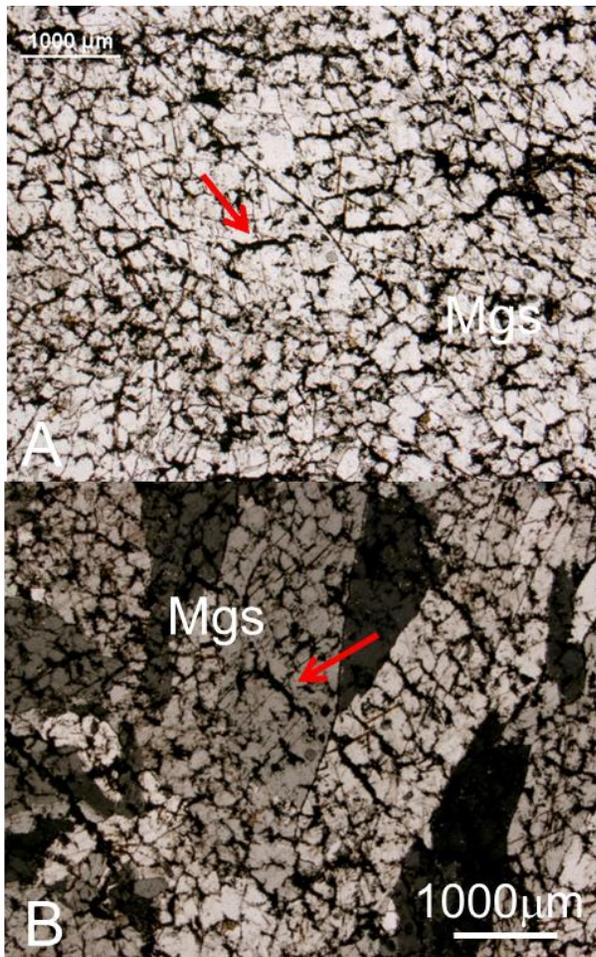
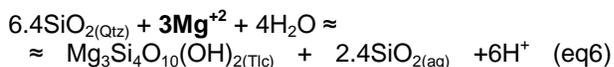


Figure 2. (A) Large porphyroblasts of magnesite (only visible in frame B) have completely replaced many sparry dolomite crystals, perfectly preserving their outlines and volumes, under PP. (B) Same area as in frame (A), rotated 50° clockwise around tip of red arrow, under XP. The magnesite porphyroblasts are distinguishable only by their uniform birefringence. Sample from the magnesite mine at Eugui, Spain.

3.3 Talc-for-quartz:



where the 6.4 factor ($\approx 145/22.7$) equalizes volumes. The mass balance releases $\text{SiO}_2(\text{aq})$ which does make this replacement self-accelerating, and which could help talc

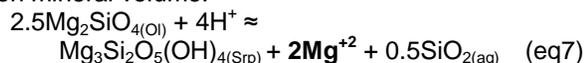
to replace dolomite by providing silica (eq3) especially if the site of talc-for-dolomite was downflow from the site of the talc-for-quartz replacement.

All texturally correct mass balances, eqs 2, 3, 5 and 6, explicitly have Mg^{+2} on the left side, confirming that these replacements are driven by Mg-rich brines.

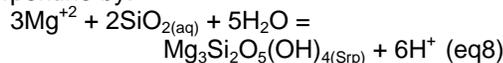
4 Serpentinization: Mg source for dolomitization and its magnesium ores

Burial dolomites and the associated magnesite and/or talc deposits require huge amounts of hot Mg-rich brines that rise from deep sedimentary basins. Where does the Mg come to those basins from?

We propose that the Mg^{2+} needed comes from the serpentinization of peridotites and dunites, which consists primarily of the replacement of Mg-rich olivine by serpentine. Again, because the replacement preserves volume (Fig. 3B), we adjust its mass balance on mineral volume:

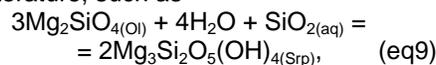


where a round factor of 2.5 ($\approx 106.6/43.7$) on olivine equalizes volumes. Thus, every increment of serpentine growth pressure dissolves olivine and releases Mg and silica, which reinforce growth of the next increment of serpentine by:



replacing more olivine, releasing yet more Mg and silica, and so on. Thus, the serpentine-for-olivine replacement is self-accelerating. Once each olivine crystal starts to be replaced by serpentine, it propels its own replacement faster and faster, simultaneously with all the others, until completion – unless water runs out first. That's probably why “Incompletely serpentinized peridotite and the nearby co-occurrence of little-altered and highly altered peridotite are both commonly observed” (Evans 2013, p.103). That serpentinization, if it starts, always tends to go to completion is significant for geophysical model calculations in gravity and magnetic surveys (e.g., Pedrera et al. 2017). The combination of self-accelerating feedback with the known strain-rate-softening rheology of olivine-rich rocks (Faul et al. 2011), leads – exactly as for dolomite-for-calcite replacement (Merino and Canals 2011) – to driving the conversion of replacive serpentine growth into displacive veins of serpentine, zebra-like (Fig. 3A).

The dynamics just described – the release of Mg^{+2} plus silica, the self-accelerating replacement, and the kinetic-rheological feedback producing veins – has remained hidden from geochemists and petrologists because serpentinization reactions proposed in the literature, such as



and others (Deer et al. 2009, p.213), are routinely adjusted conserving Mg between the minerals involved, which unintendedly violates petrographic evidence of volume conservation and makes it impossible to realize that Mg is actually lost to the pore fluid.



The fact that the serpentine-for-olivine replacement is self-accelerating means that serpentinization of an ultramafic body takes place roughly simultaneously everywhere, not at a travelling hydration front.

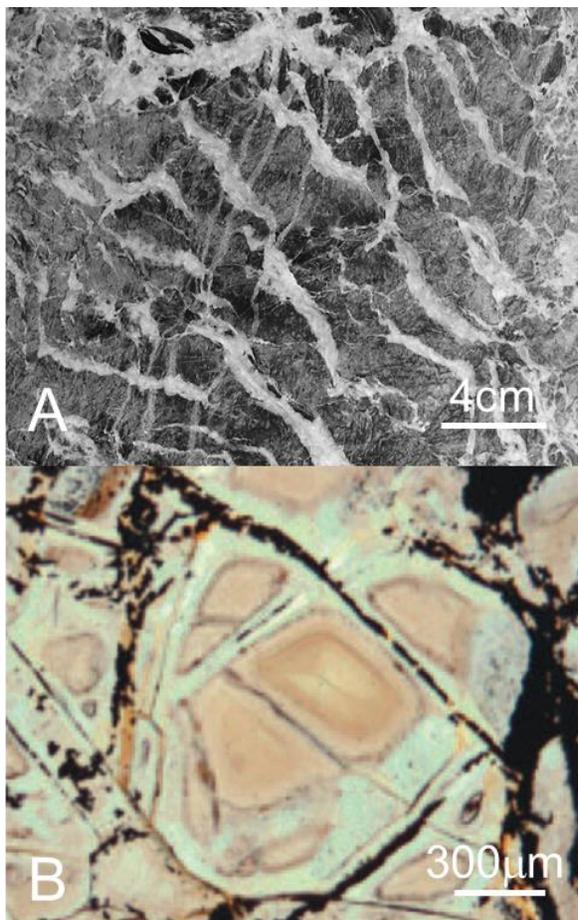


Figure 3. A) Zebra serpentine veins in ophiolite, Val d'Aosta, from Merino et al. (2006). **B)** The serpentine lizardite completely replaces an olivine crystal with hourglass and mesh textures. PP light. Northern Serpentine Belt, Dominican Republic. Courtesy of Benoit Saumur. The zebra veins in frame **A** are displacive and result from the fact that the serpentine-for-olivine replacement is self-accelerating. The rheological-kinetic feedback involved is the same that produces zebra and breccia-like displacive veins in dolostones (Merino et al. 2006; Merino and Canals 20011)

5 Conclusions

Magnesite and talc ore deposits are hosted by burial dolostones because they are actually – along with MVT ores and dedolomitization – part and parcel of the burial dolomitization process, and are driven by the same deep Mg-rich brines that drive the dolomitization itself. This is seen when mass balances are adjusted on volume (eq 2-5), not on Mg.

The huge amount of Mg^{2+} needed to make burial dolomites and their associated magnesium ores is most likely provided by serpentinization of peridotites and dunites, among the largest alteration process in the crust (Evans et al. 2013), which releases up to 40 percent of the Mg in olivine upon its replacement by

serpentine.

Volume-adjusted mass balances combined with replacement-by-precipitation/pressure-solution leads to the discovery that some replacements are self-accelerating. Two of these, both huge, are dolomite-for-calcite in dolomitization and serpentine-for-olivine in serpentinization of peridotites. The former requires Mg, the latter releases it.

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