Diagenetic pathways linked to labile Mg-clays in lacustrine carbonate reservoirs: A model for the origin of secondary porosity in the Cretaceous Pre-Salt Barra Velha Formation, offshore Brazil

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Abstract

The lacustrine carbonate reservoirs of the South Atlantic host significant accumulations of chemically-reactive and Al-free Mg-silicate minerals (e.g., stevensite, kerolite and talc). Petrographic data from units such as the Cretaceous Barra Velha Formation in the Santos Basin suggest that Mg-silicate minerals strongly influenced, and perhaps created, much of the observed secondary porosity. The diagenetic interactions between reactive Mg-silicate minerals and carbonate sediments are, however, poorly known. Here we develop a conceptual model for the origin of secondary porosity in the Barra Velha Formation guided by first principles considerations of the chemistry that triggers Mg-silicate crystallisation, as well as the geochemical and mineralogical factors that act as prerequisites for rapid Mg-silicate dissolution during early and late diagenesis. We conclude that sub-littoral zones of volcanically-influenced rift lakes would have acted as the locus for widespread Mg-silicate accumulation and preservation. Organic rich profundal sediments, however, would be especially prone to Mg-silicate dissolution and secondary porosity development. Here, organic matter diagenesis (especially methanogenesis), plays a major role in modifying the dissolved inorganic carbon budget and, pH of sediment pore waters which preferentially destabilises and then dissolves Mg-silicates. Together, the sedimentological, stratigraphic and geochemical predictions of the model explain many enigmatic features of the Barra Velha Formation, providing a novel framework for understanding how Mg-silicate-carbonate interactions might generate secondary porosity more broadly in other lacustrine carbonate reservoirs across the South Atlantic.

39 Introduction

40 The proposal that carbonate-hosted porosity in the large oil fields in the Barra Velha
41 Formation of the Santos Basin, offshore Brazil, is a result of the dissolution of Mg-silicates
42 such as stevensite (Wright and Barnett 2014), raises the possibility that an unstudied
43 diagenetic system strongly influences the properties of lacustrine carbonates. To address
44 this issue this paper reviews the distribution and diagenetic behaviour of Mg-silicates,
45 especially those associated with rift basins such as those currently the focus of intense
46 exploration in the south Atlantic. Based on these considerations we develop a model for
47 understanding how Mg-silicate-carbonate interactions lead to the generation of secondary
48 porosity in lacustrine reservoirs such as the Barra Velha Formation.

49 Lake systems developed on rifted margins, specifically those that are volcanically
50 influenced, produce a wide variety of carbonate sediments (Renaut et al. 2002; Wright
51 2012; Gierlowski-Kordesch 2010). In these settings the lithology of the surrounding
52 catchment influences lake water chemistry which, in turn, controls the style of carbonate
53 production (Wright, 2012; Jones and Bowser 1978). Lakes developed on volcanic
54 catchments tend to feature waters rich in Ca, Mg, $\text{SiO}_2(\text{aq})$, and HCO_3^- , commonly
55 reaching alkaline pH values (Cerling 1994; Yuretich and Cerling 1983). This frequent
56 combination of dissolved $\text{SiO}_2(\text{aq})$ and Mg^{2+} at high pH triggers the formation of Mg-rich
57 clay minerals (here collectively referred to as Mg-silicates), abundant products of alkaline
58 lake systems, but products that have received little attention from the standpoint of
59 carbonate reservoir properties.

60 Mg-silicates are the most geochemically reactive of all of the clay mineral groups;
61 they form very early during peri-marine and lacustrine sediment diagenesis and are known
62 to precipitate directly (and very rapidly) from the water column, setting them apart from
63 other clay minerals (Jones 1986; Millot 1970). Because they exhibit marked variation in
64 response to changes in pH, cation chemistry, salinity and the presence/absence of Al-
65 bearing detrital material, Mg-rich clays have long been recognised as valuable tools in
66 developing facies models for lacustrine environments. Most notably, Millot (1970)
67 developed a facies model for the distribution of Mg-rich clays in close basin settings that
68 has largely withstood the test of time. The model places the most Al- and Fe-rich clay
69 minerals at the basin margins as aluminosilicate detritus becomes more important, with
70 clay mineral chemistry progressively becoming more Mg- and Si-rich (and Al-poor) toward
71 the basin centre. Eventually, clays formed in the centre of the basin are dominated by Mg-
72 rich smectite (i.e., stevensite), kerolite and sepiolite. This model, and the decades of
73 subsequent work refining it (see more expanded discussions in Calvo et al. 1999; Jones

1986; Deocampo et al. 2009; Tosca 2014), places lacustrine clay mineral formation and Mg-silicates within an easily understood depositional framework. Nevertheless, predicting the distribution of Mg-rich clays on a thermodynamic basis has been hindered by gaps in understanding the Mg-silicate crystallisation process (Jones 1986; Galán and Pozo 2011; Tosca 2014).

Although the formation of lacustrine Mg-silicates has received considerable attention, the diagenesis of Mg-silicate clay minerals and the processes that drive dissolution and generate porosity in lacustrine carbonates have received very little. In the following sections we explore this process from a number of perspectives. We start by introducing the major structural characteristics of the most common lacustrine Mg-rich clay minerals and examine the processes that lead to their formation. This background makes it easier to understand why Mg-silicates are so susceptible to destruction during early and later diagenesis of lacustrine carbonates, as we discuss below.

Structural factors influencing Mg-silicate formation and diagenesis

Although there are a number of Mg-rich silicate phases which are known to occur in lacustrine carbonates (Bristow et al. 2012; Galán and Pozo 2011; Pozo and Casas 1999), they all share many structural characteristics and have nearly identical chemical compositions. The most common Mg-silicates deposited with lacustrine carbonates are composed almost exclusively of Mg and Si, with only stevensite containing additional cations, most commonly Na. As a consequence, the crystal structures of these phases are closely related but differ significantly in detail (Bailey 1980; Brindley et al. 1977; Guggenheim and Krekeler 2011; Guggenheim and Eggleton 1987). On the one hand, this overall structural similarity offers a possible explanation for the common co-occurrence and broadly similar geochemical affinity of Mg-silicates for saline alkaline environments. On the other hand, however, the subtle structural details that distinguish one phase from another mean that each Mg-silicate has specific genetic significance that lends detailed insight into the sedimentary and geochemical environment of deposition.

The lacustrine Mg-silicates are all built loosely on permutations of the talc structure. The crystal structure of talc is composed of a “TOT” (also referred to as a 2:1 type) structure whereby layers of Mg octahedra (“O” layers) are effectively sandwiched by two layers of Si tetrahedra (“T” layers), attached at the top and bottom of the octahedral layer (Figure 1). Because talc contains an octahedral sheet composed only of Mg with no substitution in the tetrahedral or octahedral layer, the layers have no permanent charge and therefore no expandability or interlayer cations can be accommodated (Drits et al.

2012; Evans and Guggenheim 1988; Bailey 1980). Kerolite, a common lacustrine Mg-silicate, is most intuitively viewed as a hydrated variety of the talc structure. Here, interlayer and surface adsorbed H₂O lead to a slightly larger interlayer repeat distance (Figure 1), although the details of how this is accommodated are not well known (Brindley et al. 1977; Miller et al. 1991). Because of these close similarities, kerolite in practice is commonly mistaken for talc (and vice versa), but in most sedimentary environments that give rise to Mg-silicates, kerolite precipitates initially and talc (*sensu stricto*) formation usually results from prolonged dehydration for example upon burial diagenesis (Mitsuda and Taguchi 1977; Noack et al. 1989; Tosca et al. 2011). Stevensite, yet another common lacustrine Mg-silicate, is broadly similar to talc and kerolite except that the Mg-octahedral layer contains a number of cation vacancies which impart a low but permanent negative charge to the structure; this must be accommodated by positively-charged interlayer cations (Figure 1; Faust and Murata 1953; Faust et al. 1959; Wilson 2013). This classifies stevensite as an expandable clay and member of the smectite group, but overall its structure still shares many structural similarities with talc and kerolite. Finally, sepiolite is composed of "TOT ribbons" of Mg-octahedra and Si tetrahedra (Guggenheim & Krekeler, 2011). These ribbons run parallel with the crystallographic x-axis and, when linked together at their corners, form voids or channels that accommodate molecular H₂O (Figure 1).

From the standpoint of reservoir quality, the lacustrine Mg-silicate minerals discussed above share one critical feature that sets them apart from the rest of the clay mineral family: they do not contain appreciable levels of Al³⁺. The lack of Al³⁺ allows these phases to be precipitated with relative ease directly from most natural waters (because Al³⁺ is normally insoluble under the chemical conditions of most surface waters). Also, the absence of Al³⁺ has direct consequences for Mg-silicate dissolution rates and mechanisms, which in turn places strict limits on the range of secondary products that might be formed upon their destruction.

Without Al³⁺, the structures of the lacustrine Mg-silicates are composed entirely of Mg-O and Si-O bonds, and this strongly influences their dissolution kinetics compared to Al-bearing counterparts (Oelkers 2001; Saldi et al. 2007). The dissolution of silicate minerals typically proceeds through the breaking of metal-oxygen bonds, which can occur at different rates depending on the bond types present (Oelkers 2001). Thus, as a silicate mineral dissolves, metals are extracted from the structure in the relative order of their bond disruption rates. Of course, to maintain charge balance within the structure, proton (H⁺)

143 exchange necessarily accompanies metal release, causing H-O bonds to be formed to
144 replace broken metal-O bonds (Oelkers 2001).

145 One consequence of the structures discussed above is that Mg-O bonds are
146 destroyed faster than both Al-O and Fe(III)-O bonds, both of which tend to be common in
147 other aluminosilicates such as illite or montmorillonite (Oelkers 2001; Casey and Westrich
148 1992). Mg-O bonds are also destroyed faster than Si-O bonds. There is abundant
149 evidence to support these trends, including more rapid Mg release from serpentine,
150 forsterite, enstatite (Casey and Ludwig 1995; Oelkers 2001; Oelkers and Schott 2001) as
151 well as antigorite, talc and phlogopite dissolution (Saldi et al. 2007; Brantley 2008). In
152 drawing analogies to silicate mineral dissolution and ligand exchange reactions that occur
153 around a particular cation, Casey & Ludwig (1995) noted that bond destruction rates
154 strongly correlate with H₂O exchange rates around a given cation (which also correlate
155 with bond strength). Indeed, H₂O exchange rates for Mg²⁺ are orders of magnitude faster
156 than for Al³⁺ and Fe³⁺ providing a mechanistic basis for observed differences in dissolution
157 rates among silicates.

158 Given the variation in metal-O bond disruption rates, it follows that the slowest
159 metal-oxygen bond to break that holds the mineral structure together therefore becomes
160 rate-limiting (Oelkers 2001; Saldi et al. 2007). The overall mineral dissolution rate is then a
161 function of whether this bond disruption rate is accelerated or decelerated under specific
162 conditions. Importantly, however, not all bonds need to be broken to completely destroy a
163 mineral structure. For example in the Mg-olivine mineral forsterite, Mg-O bonds are the
164 rate limiting step simply because their destruction liberates silica tetrahedra without
165 needing to break Si-O bonds (because the SiO₄ tetrahedra are isolated from one another;
166 Oelkers 1999; 2001).

167 Mg-rich clay minerals appear to dissolve in a similar fashion, with a mechanism
168 dictated by the specifics of the crystal structures discussed above. For example, under
169 acidic conditions the rates of proton exchange for Mg²⁺ in the octahedral sheet are so
170 rapid that as this proceeds inward from the edges, partially detached silica species are
171 liberated in the process, in turn leading to increased surface area and further accelerated
172 rates of dissolution (Saldi et al. 2007).

173 Together, the distinctly Al-free composition and similar structures of the Mg-rich
174 silicates leads to dissolution rates that are much more rapid than the other aluminosilicate
175 minerals. Most importantly, Al-free compositions lead to congruent dissolution insofar as
176 all mineral components are liberated into solution without the formation of secondary
177 aluminosilicates. This makes specific predictions for the range of possible products

178 produced once Mg-silicates dissolve. However, predicting the occurrence of secondary
179 porosity resulting from Mg-rich clay dissolution logically involves understanding the
180 processes responsible for their original distribution within lacustrine facies.

181

182 **Chemical controls on Mg-silicate formation in lacustrine sediments**

183 A brief inspection of the chemical formulas of the Al-free Mg-silicates indicates that
184 their stabilities will be affected by dissolved Mg^{2+} , $\text{SiO}_2(\text{aq})$, pH and salinity. Indeed,
185 natural occurrences of Al-free Mg-silicates in saline alkaline lake settings, combined with
186 laboratory synthesis studies, indicate that these variables are responsible for the formation
187 of one particular phase over another in most environments (Jones 1986; Jones and Galan
188 1988; Jones and Conko 2011; Galán and Pozo 2011). However, although the most
189 important chemical variables in driving Mg-rich clay formation have long been recognised,
190 predicting the occurrence of Mg-silicates from natural waters has historically been difficult
191 and difficulties are often attributed sluggish precipitation kinetics.

192 The chemical and physical processes that lead to Mg-rich clay formation are easier
193 to understand if placed within the broader context of mineral nucleation and crystal growth
194 kinetics. Like most other minerals, clay precipitation first involves nucleation (the *de novo*
195 generation of crystal nuclei) and then crystal growth. Mg-silicates may nucleate directly
196 from water (termed homogeneous nucleation) or on the surface of a pre-existing solid
197 (termed heterogeneous nucleation; Tosca 2014; Stumm 1992). Classical nucleation theory
198 states that the homogeneous nucleation of Mg-silicates from water necessarily requires
199 overcoming a critical level of supersaturation (Stumm 1992). This critical supersaturation
200 boundary predicts that spontaneous nucleation will not occur unless a given water is many
201 times more supersaturated than equilibrium solubility predicts.

202 Until recently, the critical supersaturation boundary that triggers Mg-silicate
203 nucleation from water was not well known, but a recent review of experimental synthesis
204 data (Tosca 2014) de-lineated a clear boundary in more quantitative terms. This boundary
205 can be expressed in terms of a “Mg-silicate solubility diagram” which captures the three
206 major chemical controls on Mg-silicate formation (i.e., $a_{\text{SiO}_2(\text{aq})}$, $a_{\text{Mg}^{2+}}$ and pH, or a_{H^+})
207 (Jones 1986; Jones and Galan 1988; Figure 2). Figure 2 shows that this nucleation
208 boundary lies well above the equilibrium solubilities for Mg-silicate minerals, implying
209 significant supersaturation is required to initiate nucleation. Figure 2 also shows that a
210 number of different combinations of pH, Mg^{2+} and $\text{SiO}_2(\text{aq})$ may result in the formation of
211 Mg-silicates directly from water, but the individual phase that grows from such nuclei (e.g.,

stevensite, kerolite or sepiolite) is dependent on the kinetics of subsequent crystal growth (Jones 1986; Tosca 2014; Tosca and Masterson 2014).

Most importantly, the nucleation boundary on Figure 2 indicates why the evaporative concentration of some lake waters leads to the formation of Mg-silicates from solution and some do not. Unless this boundary is crossed, Mg-silicates will not precipitate directly from water, regardless of the phase. As Figure 2 shows, at higher $\text{SiO}_2(\text{aq})$ concentrations (or activities), lower Mg and/or pH is required to overcome the nucleation boundary. This boundary also provides further support for why the most common formation pathway for stevensite is now widely recognised as authigenic precipitation from lake water (Wilson 2013). Critically, any process which results in a rapid or sudden supersaturation above this boundary will result in Mg-silicate precipitation directly from water. Such a process could include pore water modification by biological activity, mixing of water sources (e.g., hot spring input), or, much more commonly, evaporative concentration. The type of Mg-silicate formed is sensitive to the pH, Mg/Si ratio, salinity, $\text{SiO}_2(\text{aq})$ input and temperature under which crystal growth occurs.

The nucleation boundary discussed above also agrees with geochemical and mineralogical analyses of evaporating saline lakes. Combined mineralogical and lake water analyses reported in Gac et al. (1977) and Darragi & Tardy (1987) offers a clear example. These authors showed that in Lake Yoa of Northern Chad, authigenic stevensite precipitates with aragonite. Although aragonite is commonly formed from the Lake Yoa waters, the authigenic carbonate phase associated with Mg-silicate mineralization may vary even within the Lake Chad system), illustrating the varying impact of Mg-silicates on the resulting Ca/Mg ratio of solution (e.g., Gac et al., 1977; Eugster & Jones, 1979; Darragi & Tardy, 1987). For example, authigenic low-Mg calcite has been observed to crystallise with Mg-silicates in the Pantanal wetlands of Brazil (Barbiero et al., 2002), and, indeed, Mg-silicates and low-Mg calcitic spherules both crystallised early in the history of the Barra Velha precursor sediment (Wright and Barnett, 2014). Regardless of the identify of the main carbonate phase, however, the chemical evolution of the evaporating water in Lake Yoa follows a pathway illustrated in Figure 2. This pathway agrees with the supersaturation levels predicted from synthesis studies and represents an important step in understanding when and where Mg-silicates are likely to form. This also provides some of the most convincing evidence that the main genetic pathway for widespread stevensite formation is through evaporative concentration.

The relationships discussed above can be used to make predictions regarding the distribution of Mg-silicates in lacustrine systems. Clearly, homogeneous nucleation of Mg-

silicates directly from water is one of the only mechanisms that will result in the most laterally extensive accumulations of Mg-silicates. This is simply because climatic controls (e.g., evaporative hydrologic regimes) act over regionally-extensive areas. In contrast, the nucleation of Mg-silicates on pre-existing surfaces (e.g., heterogeneous nucleation, which requires lower levels of supersaturation) is critically dependent on the nature and distribution of the substrate itself (Tosca 2014). A number of substrates may act as favourable surfaces which cause Mg-silicate nucleation (e.g., amorphous silica, detrital certain clay minerals and biological materials such as EPS), but this process is arguably most important when favourable chemistry and favourable surface properties (e.g., binding properties that decrease Mg-silicate-solution interfacial energy; Tosca 2014) coincide in more locally confined environments such as microbial mats (Bontognali et al. 2010; Leveille et al. 2002; Souza-Egipsy et al. 2005). For example Arp et al. (2003) noted, some biofilm laminae in sub-fossil microstromatolites from a marine influenced crater lake in Indonesia, had undergone replacement by Mg-Si. Bontognali et al. (2010) identified the potential for Mg and silica to be concentrated in EPS in microbial mats in recent microbial mats from Abu Dhabi. Burne et al. (2014) record Mg-silicates (stevensite) in modern thrombolites from Lake Clifton in Western Australia, which provides the structural rigidity for thrombolite growth, produced by biofilm mineralization, with aragonite growing in the stevensite matrix. In a more ancient example, Tosca et al. (2011) have explained the association of microbialites and early talc in Neoproterozoic carbonates as potentially reflecting microbial activity in influencing pore water chemistry. Wright & Barnett (2014) have identified multi-metre scale cyclothems in the Barra Velha Formation of the Santos Basin, offshore Brazil, in which stevensite was a common matrix, but direct evidence for a microbial influence is certainly absent from the associated carbonates; these authors invoked evaporation as the likely trigger for large scale stevensite precipitation.

272

273 **Sedimentological implications of Mg-silicate nucleation and gel formation**

274 Once the nucleation boundary is crossed, nucleation of Mg-silicates from water
275 does not immediately produce a crystalline clay mineral, but instead produces a Mg-
276 silicate “gel”. This precipitation pathway undoubtedly influences early and later diagenetic
277 reactions and sedimentary textures in many non-marine carbonates.

278 There is abundant experimental and field-based evidence to support this pathway.
279 For example, in their experimental study of Mg-silicate (including stevensite) precipitation
280 from water at 25°C, Tosca & Masterson (2014) showed that the initial stages of stevensite
281 precipitation occur rapidly (e.g., minutes to hours) upon crossing the critical

282 supersaturation, producing a "gel-phase" characterised by stevensite crystallites that
283 exhibit limited stacking order and a high degree of hydration (e.g., between 20-30 wt. %
284 H₂O). The "gel" phase then, is simply defined as a hydrated aggregate of Mg-silicate
285 nanoparticles and is evidently persistent through the early diagenetic stages of lacustrine
286 and peri-marine sediments. For example, a number of authors have reported the
287 observation of Mg-silicate "gels", "poorly developed clays" or "poorly crystalline silicates"
288 (Millot 1970; Jeans 1971; Brindley et al. 1977; Gac et al. 1977; Calvo et al. 1999; Pozo &
289 Casas 1999; Leveille et al. 2000; 2002; Polyak & Guven 2000; De Santiago Buey et al.
290 2000; Miller & James 2012). The environments in which these gel phases are most often
291 found commonly involve fluids at high solute concentration (i.e., strongly supersaturated
292 with respect to Mg-silicates), high salinity and pH, and most often include speleothems,
293 evaporitic lacustrine environments and saline pore water. The results reported in these
294 studies are in general agreement with those of Tosca & Masterson (2014) in terms of
295 structural aspects detectable from X-ray diffraction, FT-IR and thermal analysis. Indeed,
296 the precipitation of a hydrated "poorly crystalline" precursor appears to be a common
297 pathway involved in the *de novo* formation of Mg-silicates from supersaturated solutions
298 thereby providing a link between experimental results and numerous occurrences of Mg-
299 silicate "gel". In fact, because of the viscous nature of the gel and because of its role in
300 removing Mg²⁺ from water (especially if the Mg/Si ratio in the fluid is less than that of
301 stevensite), Wright (2012) suggested that stevensite gel might act as an ideal substrate for
302 spherulitic calcite precipitation, explaining some of the unusual textures observed in
303 Santos Basin carbonates. [Because the gel phase has been reported in lacustrine and peri-](#)
304 [marine subsurface sediments in addition to those exposed to overlying bottom water \(e.g.,](#)
305 [Pozo & Casas 1999; Leveille et al. 2000; 2002; Polyak & Guven 2000; De Santiago Buey](#)
306 [et al. 2000; Miller & James 2012\), the gel phase evidently persists in the subsurface with](#)
307 [the kinetics of dehydration dependent on the factors discussed above. Thus, Mg-silicate](#)
308 [gels provide an important source of late diagenetic water to buried sediment as well as a](#)
309 [unique chemical and physical substrate to mediate further diagenetic reactions upon](#)
310 [burial.](#)

311 This Mg-silicate precipitation pathway predicts that a number of diagenetic reactions
312 will take place between the initially-precipitated gel and surrounding sediments. For
313 example, dehydration will ultimately take place upon the deposition of Mg-silicate gel, and
314 this may occur in response to wetting-drying cycles, prolonged exposure to high salinity
315 solutions (i.e., low $a_{\text{H}_2\text{O}}$) or upon even shallow burial and mild heating (as most H₂O is
316 released at very low temperatures during thermal analysis; see Tosca & Masterson 2014).

317 Indeed, “gel-dehydration” has been invoked by a number of authors as an important driver
318 to explain the development of Mg-silicate minerals in evaporative environments and during
319 sediment diagenesis (Darragi & Tardy 1987; Gac et al. 1977; Pozo & Casas 1999;
320 Stoessell & Hay 1978). Gel dehydration was invoked as a main driver for the formation of
321 kerolite associated with microbial mats in speleothems in basaltic caves found in Hawaii
322 (Leveille et al. 2000; 2002). A similar dehydration pathway was suggested to explain
323 stevensite associated with evaporitic deposits from saline lakes (Darragi & Tardy 1987;
324 Gac et al. 1977; Pozo & Casas 1999; Stoessell & Hay 1978; De Santiago Buey et al.
325 2000). Indeed, gel dehydration has also been implicated in explaining sedimentary
326 textures associated with palygorskite and sepiolite-bearing ooids formed in palustrine
327 settings influenced by wetting-drying cycles (Miller & James 2012). The common feature of
328 all of these environments involves initially high supersaturation states with respect to Mg-
329 silicate minerals and environments driving the prolonged and perhaps cyclic dehydration
330 of initially formed products. Importantly, because the initial gel phase may incorporate
331 between 20 and 30 et. % H₂O by weight even after drying at room temperature (Tosca &
332 Masterson 2014), this may represent an important basinal fluid source to drive the de-
333 stabilisation of other minerals upon burial.

334 The sedimentological aspects of gel formation require additional consideration.
335 Such gels are likely to accumulate in specific low energy settings and where they will not
336 be exposed to desiccation. They are unlikely to accumulate around lake margins where
337 exposure and wave reworking will occur, so should be more characteristic of deeper sub-
338 littoral areas, although as discussed below, not necessarily in organic-rich profundal
339 settings. In small lakes or ponds with limited fetch Mg-silicate gels have the potential to
340 accumulate in relatively shallow settings, although would then be prone to exposure.

341

342 **Early diagenesis, Mg-silicate dissolution and porosity formation**

343 Once Mg-silicates are deposited, there are a number of factors that can lead to their
344 de-stabilisation and subsequent dissolution during diagenesis. However, evidence for Mg-
345 silicate (e.g., stevensite) dissolution, as documented from field settings, and the underlying
346 reasons for this rather unusual phenomenon have not received much attention in the
347 literature. From first principles, a simple shift in the saturation state of a given pore water
348 with respect to Mg-silicates will establish a thermodynamic drive toward dissolution. Once
349 this drive is established, dissolution and removal will take place at rapidly, controlled in
350 part by the structure and bonding characteristics discussed above, and also by the
351 extremely high specific surface area inherent to Mg-silicates. Under what conditions would

352 such a drive for dissolution be established? Once this happens, how long would Mg-
353 silicates persist in lacustrine sediments, and would this process affect surrounding
354 carbonate sediments?

355 Lake Turkana, a brackish Na-HCO₃ lake of the East African rift system, offers
356 important insight into how a thermodynamic drive for Mg-silicate dissolution could be
357 established and also how labile Mg-silicate phases can be under certain chemical
358 conditions. Stevensite, is an important early precipitate from the lake water at Turkana, as
359 demonstrated by cation mass balance and mineralogical analyses (Cerling 1979; 1996;
360 Yuretich and Cerling 1983). Stevensite forms directly from evaporating lake water, which in
361 turn exerts a strong control on Mg²⁺ depletion of the overall basin (Cerling 1996; Yuretich
362 and Cerling 1983). In a detailed study of pore water chemistry at Lake Turkana, Cerling
363 (1996) found that a number of sediment cores showed chemical variations with depth,
364 indicating a diagenetic process not previously identified in lacustrine sediments.
365 Specifically, Cerling (1996) observed increases in excess alkalinity with depth (mostly
366 dominated by carbonate alkalinity), and further showed that these alkalinity increases were
367 accompanied by releases in both Mg²⁺ and SiO₂(aq) corresponding to a Mg/Si ratio
368 stoichiometrically equivalent to stevensite. Because dissolved SO₄ is depleted in the
369 Turkana pore waters and the δ¹³C composition of the dissolved inorganic carbon from
370 these waters progressively increases with depth, Cerling (1996) argued that
371 methanogenesis (only efficient in the near absence of dissolved sulfate; Hoehler et al.
372 2010) triggered these changes. Methanogenesis, or the microbial generation of methane,
373 typically occurs via one of two possible pathways (Canfield et al. 2005): (1) the reduction
374 of CO₂ by H₂, or (2) the fermentation of organic matter, specifically acetate or other
375 organic substrates, to produce methane and dissolved inorganic carbon. The second
376 pathway is typically more important in non-marine sediments (Canfield et al. 2005) and
377 results in CH₄ that is highly enriched in ¹²C, and DIC that is highly enriched in ¹³C. In
378 addition to down-core increases in carbonate alkalinity (from organic matter fermentation),
379 Mg²⁺ and SiO₂(aq), Cerling (1996) also observed a significant increase in the δ¹³C of
380 dissolved inorganic carbon, supporting the idea that methanogenesis drove stevensite
381 dissolution in lake Turkana sediments with depth.

382 The latter observation suggests that the carbon isotope composition of lacustrine
383 carbonates may in fact be a useful guide in identifying processes that may have influenced
384 the alkalinity budget of sediments during early diagenesis, perhaps initiating the corrosion
385 of Mg-silicates (e.g., methanogenesis). However, the δ¹³C composition of lacustrine
386 carbonates may be influenced by a number of factors, including the composition of input

387 waters, atmospheric CO₂ exchange, mixing of gas sources from produced by microbial
388 respiration (e.g., Gierlowski-Kordesch, 2010). Particularly relevant to Mg-silicate-rich
389 systems, though, are changes in the relative amounts of authigenic dolomite and calcite
390 which may be driven by changes in Ca and Mg availability (among many other factors).
391 This may in turn affect the bulk $\delta^{13}\text{C}$ composition because the mineral specific
392 fractionation factors for dolomite and calcite are offset from one another (e.g., Bristow et
393 al., 2012). These caveats indicate that an integrated mineralogical, geochemical and
394 isotopic approach is needed to establish reliable fingerprints of early diagenetic Mg-silicate
395 corrosion. Nevertheless, the basic observation from Lake Turkana that a silicate mineral
396 such as stevensite shows rapid dissolution behaviour in preference to calcium carbonate
397 sediments is, at first glance, a rather unusual one; it raises the broader question of why
398 such a phenomenon might occur in lacustrine sediments and whether it might be a more
399 general process to which Mg-silicates are particularly susceptible.

400 To illustrate why stevensite dissolution should occur in the Lake Turkana
401 sediments, we have constructed a simple thermodynamic model exploring how pore water
402 chemistry is modified by methanogenesis. Here, we use a thermodynamic model detailed
403 in Tosca & Masterson (2014) that uses the Pitzer ion interaction model for calculating ion
404 activity coefficients and therefore mineral saturation states in high ionic strength waters.

405 As a starting point, our calculations begin with the initial chemical composition of
406 Lake Turkana water as reported in Cerling (1996). Here the water has a pH of ~9.2 and is
407 initially supersaturated with respect to stevensite, despite being somewhat depleted in
408 Mg²⁺ (from widespread stevensite formation as discussed above). The most important
409 chemical change occurring in response to methanogenesis is the addition of excess
410 dissolved inorganic carbon (DIC) from the fermentation of organic substrates. These
411 changes can be very simply modelled by adding dissolved inorganic carbon to the system
412 as HCO₃⁻. In the model, this is also equivalent to adding CO₂ in dissolved form (Figure
413 3A), because regardless of the form of DIC added to the water (e.g., CO₂(aq), HCO₃⁻ or
414 CO₃²⁻), the distribution of carbonate species is dictated both by equilibrium
415 thermodynamics and the prevailing pH of the lake Turkana system.

416 As HCO₃⁻ is added to the Lake Turkana water, the increase in carbonate alkalinity
417 rapidly shifts the pH from 9.2 to ~8.5 as ~60 mmol/kg HCO₃⁻ is added. At this endpoint in
418 our calculations, the pH and alkalinity values of the simulated pore water are nearly
419 identical to those compositions reported in Cerling (1996). This simple change has marked
420 effects on the saturation state of Mg-silicate minerals. Because Mg-silicate phases display
421 a thermodynamic and kinetic sensitivity to pH, the decrease from pH 9.2 to 8.5 causes

422 stevensite to shift from supersaturated (in the initial Lake Turkana water) to undersaturated
423 (in the pore water once methanogenesis is established) (Figure 3B). At the same time,
424 because pore water chemistry is effectively buffered by the carbonate system, the
425 saturation states with respect to carbonate minerals actually show slight increases in
426 saturation state and therefore remain unsusceptible to dissolution. This provides
427 convincing evidence that small changes in carbonate alkalinity, driven for example by the
428 microbial diagenesis of organic matter, are effective in pushing Mg-silicates outside of their
429 thermodynamic stability windows, establishing a thermodynamic drive for dissolution.

430 At first glance, it is somewhat unexpected that the pH values associated with
431 stevensite dissolution in the Lake Turkana cores reach a minimum of ~8.5, yet are able to
432 dissolve stevensite. This indicates that acidic conditions are not necessarily required to
433 dissolve stevensite, so long as thermodynamic undersaturation is established. A related
434 question, however, is why stevensite appears to dissolve so rapidly in the Lake Turkana
435 cores once this undersaturation is established. We can understand this better by returning
436 to the effects of the stevensite crystal structure and particle size on dissolution rate and
437 the lifetime of stevensite in undersaturated sediment pore water.

438 Aside from the bonding types and crystal structure of stevensite as outlined above,
439 one additional factor causing rapid dissolution lies in its high specific surface area. Like
440 most clay minerals that form under Earth surface conditions, stevensite occurs in a variety
441 of morphological crystal forms that are, at a maximum, on the order of 100's of nm in size
442 (Wilson 2013). In fact, neoformed stevensite has been shown to occur as distinctive
443 spheres ranging from 50-1000 Å in diameter (or 100 nm maximum; De Santiago Buey et
444 al. 2000; Benhammou et al. 2009). As a consequence, the specific surface area of
445 stevensite has been reported to lie between 150-400 m²/g, roughly equivalent to the area
446 of a tennis court contained in one gram. Freshly precipitated stevensite, expected upon
447 initial precipitation from evaporating lake water, undoubtedly lies at the upper end of this
448 range and perhaps beyond. Regardless of exact values, the very small size of discrete
449 stevensite particles means that in the presence of a thermodynamic drive for dissolution,
450 the lifetime of these particles within a sediment might be expected to be far lower than
451 many other minerals. This can be quantitatively illustrated if we assume a dissolution rate
452 for stevensite using laboratory dissolution rates measured for crystalline talc as a structural
453 analog (Saldi et al. 2007). If we assume far-from-equilibrium dissolution rates for talc at pH
454 8.5 (from Saldi et al. 2007) and a discrete spherical particle size of 100 nm (e.g., De
455 Santiago Buey 2000), then by using the molar volume of stevensite and a simple kinetic
456 relationship between dissolution rate and mineral lifetime (Lasaga, 1998) we estimate that

under the Lake Turkana pore water conditions, individual stevensite particles would not last longer than ~70 years. Although there are large uncertainties inherent in this calculation, this is broadly consistent with the indications of rapid stevensite dissolution from the Lake Turkana cores (Cerling, 1996), and also with reports of near instantaneous Mg-silicate scale removal at circum-neutral pH (e.g., Gunnlaugsson & Einarsson 1989). Indeed, these calculations show that once a thermodynamic undersaturation for stevensite exists, complete dissolution occurs in a geological instant.

Mg-silicates may also be prone to destabilisation during later diagenetic reactions initiated upon burial. For example, the thermal energy supplied upon burial often leads to the migration of cations from interlayer (exchangeable) positions to vacant octahedral sites (Jaynes & Bigham 1987; Jaynes et al. 1992; Komadel et al. 2005; Petit et al. 2008). This process, known as the Hofmann-Klemen effect, occurs mainly in montmorillonite-group clay minerals, to which stevensite belongs. Stevensite itself would be particularly vulnerable to this process because its structure demands that at least 10% of octahedral sites are vacant (Faust & Murata 1953). Univalent cations (e.g., Na⁺ and Li⁺) are most susceptible to migration in the stevensite structure, and divalent cations may migrate as well (Jaynes & Bigham 1987; Jaynes et al. 1992; Komadel et al. 2005; Petit et al. 2008). Importantly, the migration of cations within the structure produces a loss of layer charge and expandability, and the generation of “talc-like” species. Along with these changes, the loss of a proton from structural hydroxyl (-OH) groups occurs (Jaynes et al. 1992; Komadel et al. 2005; Petit et al. 2008), which would produce acidic pore water. In this way, stevensite may initiate its own self-destruction and dissolution resulting from cation migration driven by shallow burial.

Discussion and Summary

Based on the considerations above Mg-silicates formed in lacustrine settings should display a series of what might be termed “behaviours” which can help understand and predict their distribution and subsequent diagenesis. In terms of distribution they not only require highly alkaline conditions, commonly met by the carbonate alkalinity provided in rifts with high volcanic activity, but also a specific chemistry. [As discussed above, this chemistry may be generated through a number of means, but the most rapid and laterally extensive mechanism is through evaporative concentration.](#) In the case of the Barra Velha Formation of Brazil, the abundance of calcite and Mg-silicates and the absence of the more typical evaporite minerals such as chlorides and sulphates, supports the view that the catchment areas were draining basic volcanic terrains. Wright (2012) also highlighted

492 these controls, following the proposal from Cerling (1994) that lakes where volcanic
493 terrains predominate tend to produce calcite, tri-octahedral smectite, analcime and various
494 bicarbonate–carbonate minerals. What remains unclear is whether a sufficient source of
495 both Mg and $\text{SiO}_2(\text{aq})$ was available to fuel the extensive precipitation of Mg-silicates in
496 these Cretaceous lakes. An unusual and alternative source of solutes might be
497 serpentinisation of the mantle. Zalan et al. (2011) have shown that the Santos, Campos
498 and Espírito Santo basins are all expressions of a magma-poor passive margin, and argue
499 for the presence of a continuous belt of exhumed mantle at the transition between
500 continental and oceanic crusts that flanks all three basins. They infer that serpentinization
501 of exhumed mantle, deduced from the gravimetric modelling, occurred to 6-8 kms depth.
502 This suggestion notwithstanding, direct evidence for serpentinisation and/or the presence
503 of exhumed mantle in the offshore Brazilian basins has remained elusive.

504 In total, given suitable geochemical conditions Mg-silicate gels are predicted to
505 accumulate in lower energy settings below wave base and not prone to exposure,
506 desiccation and reworking (Figure 4). However, the effects of methanogenesis in profundal
507 areas where organic matter could be concentrated implies that Mg-silicates would be more
508 prone to destabilisation and dissolution, reducing the likelihood of accumulating in such
509 settings. Although methanogenesis is demonstrably effective in tipping the pore water
510 alkalinity balance in favour of Mg-silicate dissolution and carbonate precipitation, any
511 process which disrupts this balance (i.e., decreases pH and Mg-silicate saturation but
512 increases carbonate alkalinity) will produce the same effect. In total, from a facies model
513 standpoint, we are left with a “Goldilocks” situation where Mg-silicates would not
514 accumulate in sediments deposited in waters which were too shallow or potentially too
515 deep. Shallow closed-system lakes are, in reality, characteristically dynamic and so the
516 actual distribution of Mg-silicates is expected to exhibit more complexity with controls on
517 chemistry and also with accommodation space playing a critical role. In rift settings the up-
518 dip regions of half-grabens are prone to both differential tilting and footwall uplift and so
519 these might be seen as poor sites for Mg-silicate gel accumulation, whereas deeper
520 settings (for example in lows adjacent to main faults) are expected to result in the highest
521 levels of organic matter accumulation in profundal zones, promoting, for example,
522 methanogenesis (Figure 4; Bosence 1998).

523 The congruent dissolution of Mg-silicates, leaving no direct *in situ* product, is likely
524 to produce porosity. Wright & Barnett (2014) have identified petrographic criteria for
525 identifying porosity formed after the dissolution of stevensite in the Barra Velha Formation
526 of the Santos Basin. One of the most distinctive manifestations of this effect is seen in the

widespread pseudo-fenestral porosity seen in the spherulitic facies. The resulting pore systems are illustrated by Terra et al. (2010) (their Figures 20 & 21, especially Fig. 20b).

Complete decay of the Mg-silicates would result in the release of Mg (30%), silica (60%) and minor Na (3%), in addition to bound water (Figure 5). Thus expected diagenetic products would include replacement dolomites (as the Mg^{2+} cannibalised any existing calcite), extensive silica cementation and replacement, and Na-silicates. The release of bound water might contribute to local overpressure which would limit physical and chemical compaction. These products all fit with anecdotal evidence that the Barra Velha shows replacement dolomitization, extensive silicification, the presence of cryolite (although the source of Al is unresolved) and the survival of open-packed pore systems and rarity of stylolites.

Jones and Xiao (2013) have proposed that geothermal convection linked to localized conduits might also be a critical factor in enhancing porosity and permeability in lacustrine carbonates sealed by salt as in the specific case of the Barra Velha Formation in the Santos Basin. The study implies an awareness that late stage corrosion has affected these carbonates (as is also our experience), but an alternative process which could cause later stage dissolution could also reflect an inherent property of the decay on Mg-silicates, specifically the production of protons by the Hofmann-Klemen effect discussed above. If this operated in the Barra Velha Formation it would produce a more widespread dissolution effect and not one linked to major fluid conduits such as faults, a testable alternative model if and when more data becomes available from the region.

In summary, although both the occurrence and diagenetic consequences of Mg-silicates in carbonate reservoirs are somewhat unfamiliar from the standpoint of petroleum geology, many enigmatic features can be understood from first-principles considerations rooted in geochemistry, mineralogy and sedimentology. The model presented here provides a novel framework for understanding and predicting Mg-silicate-carbonate interactions and their geological consequences, and should provide a fertile starting point to develop and test new hypotheses for porosity evolution as data continue to emerge.

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758

759 **Figures:**

760 **Figure 1.** A comparison of major structural features of common lacustrine Mg-silicate
 761 minerals, showing that all of the minerals under consideration are built from permutations
 762 of a 2:1 arrangement of Si-tetrahedra and Mg-octahedra, and are nominally free of Al.

763

764 **Figure 2. (A)** Solubility diagram for the Mg-SiO₂-H₂O system at 25°C. The diagram
 765 illustrates the solubility of Mg-silicates for water compositions that have increasing Mg²⁺
 766 concentrations and/or pH (larger y-axis values) or increasing SiO₂(aq) concentrations

767 (larger x-values). Water compositions plotting on or above a given boundary indicate
768 supersaturation with respect to the Mg-silicate phase of interest. Note that the “critical
769 supersaturation” boundary delineated by experimental studies (Tosca 2014) corresponds
770 to the point at which nucleation of Mg-silicates will occur directly from water with no
771 available substrate. Modern seawater is plotted for reference, and shows why nucleation
772 of Mg-silicates does not occur. Vertical dashed lines indicate solubilities for quartz and
773 amorphous silica. **(B)** Chemical evolution of waters from Lake Yoa indicating the effects of
774 evaporative concentration (data from Darragi & Tardy 1987). Waters from which stevensite
775 has precipitated are plotted as blue circles. Sources of thermodynamic data are detailed in
776 Tosca (2014).

777

778 **Figure 3.** Thermodynamic model calculations illustrating the effect of methanogenesis on
779 Lake Turkana pore water chemistry. **(A)** Evolution of pore water pH (left axis) and
780 dissolved CO₂ (right axis) during methanogenesis. As methanogenesis produces dissolved
781 inorganic carbon (DIC), the pH of the original water (corresponding to Lake Turkana water
782 reported in Cerling (1996)) decreases from 9.2 to less than 8.5, closely corresponding to
783 porewater chemistry reported by Cerling (1996). **(B)** Calculated saturation states of
784 stevensite, calcite and aragonite during methanogenesis in Lake Turkana pore water. The
785 resulting pH decreases and DIC increases result in negligible effects on carbonate mineral
786 stability, but result in pore waters that are undersaturated with respect to stevensite,
787 enabling dissolution to proceed.

788

789 **Figure 4.** Modelled distribution of Mg-silicates in an idealized rift basin setting. Shallower
790 but sub-littoral waters prone to evaporative concentration commonly cross the
791 supersaturation boundary required for nucleation directly from water, and are less prone to
792 reworking and exposure which results in the largest and most widespread accumulations.
793 Sediments deposited in deeper profundal settings are strongly influenced by organic
794 matter diagenesis. Here methanogenesis, for example, would result in higher DIC (and
795 dissolved P_{CO2}) conditions where Mg-silicates would commonly destabilise and dissolve,
796 imparting heavy $\delta^{13}\text{C}$ compositions to DIC which may be transferred to the carbonate
797 sediments.

798

799 **Figure 5.** Schematic showing the relative proportions of chemical components released
800 from stevensite dissolution and their primary diagenetic products.

801