1 The contribution of aqueous catechol-silica complexes to silicification

2 during carbonate diagenesis

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7 Abstract

8 Pore-filling and carbonate-replacing silica is exceedingly common in carbonates, but the
9 fundamental geochemical mechanisms that drive these silicification reactions during diagenesis
10 remain poorly understood. An existing model has proposed that carbonate silicification proceeds
11 through an interface-coupled dissolution-precipitation reaction, but it lacks a mechanism that enables
12 pore fluids to reach the requisite level of supersaturation with respect to silica to allow nucleation and
13 growth. Here, we present a sequence of batch experiments ranging in duration from 7 to 49 days
14 designed to test the hypothesis that these reactions are facilitated by the formation and destruction of
15 organo-silica complexes during diagenesis. Our results illustrate that the stability of organo-silica
16 complexes is dependent upon the concentration of organic molecules in solution, as well as pH,
17 salinity, and solution redox state. Together, these results allow us to present the following scheme for
18 organo-silica complex mediation of silicification reactions: Firstly, the breakdown of organic matter
19 in the presence of siliceous material creates organo-silica complexes, leading to silica-enriched pore
20 fluids, a process which is enhanced by the anoxic conditions accompanying sediment burial. Then, as
21 environmental conditions evolve (fO_2 , salinity, light, fCO_2 , pH...), the stability of the organo-silica
22 complexes diminishes, and the organo-silica complexes break down. Simultaneously, the pore fluids
23 become intensely silica-supersaturated, in direct proportion to the amount of organic material
24 remaining in solution. The resulting supersaturation drives carbonate silicification via the
25 precipitation of silica minerals, a process which is aided by the presence of silica “nuclei” (such as

sponge spicules). This study contributes new data and a conceptual model that will aid in the ongoing quest to understand carbonate silicification reactions and their potential applications in hydrocarbon exploitation and geologic CO₂ storage. Moreover, it helps to explain the common association between silica precipitates and organic mineral in the sedimentary rock record.

1. INTRODUCTION

Pore-filling and carbonate-replacing silica is exceedingly common in carbonate rocks (e.g., Maliva et al., 1989). This silica (e.g., quartz, chalcedony, Opal-A and/or Opal-CT) is interpreted to have been deposited by silica-rich solutions during a diagenetic process known as silicification. Because the silica fills porosity and reduces permeability, this process has significant implications for both hydrocarbon exploitation and efforts to inject anthropogenic CO₂ into carbonate reservoirs.

Over more than 30 years, scientists have attempted to understand this process (e.g., Butts and Briggs, 2010; Butts, 2014; Calvert, 1974; Maliva and Siever, 1988; Ehrlich et al., 2010; Hesse, 1989; Bustillo, 2010). An early model put forward by Schmitt and Boyd (1981) suggested that one possible replacement mechanism is bulk dissolution of carbonate and later precipitation of pore-filling silica in the resulting void. This void-filling process is commonly observed during the silicification of wood, for instance (Hesse, 1989; Götze et al., 2019). In contrast to this earlier model, Maliva and Siever (1988) presented numerous observations of silica minerals replacing primary carbonate minerals, rather than filling in pre-existing voids. Based on their petrographic evidence and thermodynamic calculations, Maliva and Siever (1988) postulated that carbonate replacement occurs via an interface-coupled dissolution-precipitation reaction (Putnis, 2002). According to this model, the force of crystallization of growing silica crystals results in increased pressure at silica-carbonate contacts, locally increasing the solubility of carbonate (e.g., calcite) through pressure-solution.

In the Maliva and Siever (1988) model, the solution film between the growing silica mineral and the primary carbonates must be supersaturated with respect to the precipitating silica phase and undersaturated with respect to the carbonate in order for the replacement reaction to proceed. Importantly, seawater itself has likely never had SiO₂ concentrations in excess of silica saturation,

52 even in deep time prior to the evolution of silica-secreting organisms (Siever, 1992; Fisher and Knoll,
53 2009, Stefurak et al., 2014). In the modern oceans, the dissolution of biogenic silica of SiO_2 -secreting
54 organisms (e.g., diatoms, radiolaria, and sponges) during diagenesis could be a source of
55 supersaturation of silica in pore fluids, but even these materials can only dissolve to the point of
56 equilibrium with respect to amorphous silica, and are therefore likely never more than a factor of 10
57 or so supersaturated with respect to the quartz, the least soluble low-temperature diagenetic silica
58 phase (Rimstidt, 1997). However, in the absence of SiO_2 -secreting organisms, Precambrian silica
59 must have largely been removed by chemical processes (Maliva et al., 1989), such as the direct
60 precipitation of silica gel on the seafloor (Stefurak et al. 2014) or interaction with basaltic weathering
61 products during low-temperature hydrothermal circulation (Siever 1992).

62 Because its silica concentration has likely never exceed equilibrium with respect to amorphous
63 (1.9 mmolal at 25°C, Gunnarsson and Arnórsson, 2000), seawater itself cannot ever have been the
64 strongly silica-supersaturated solution required to drive the silicification scheme proposed by Maliva
65 and Siever (1988). Some studies have hypothesized that in Late Proterozoic oceans with higher than
66 present day concentrations of dissolved silica, downward diffusion of silica from seawater into
67 sediments might fuel the growth of chert nodules nucleated on organic matter or some other attractant
68 (Siever, 1992), but, even in this case, the significant supersaturation required for silica growth and
69 carbonate pressure solution/replacement could not be achieved without additional silica being added
70 to solution.

71 Field and experimental observations have demonstrated that dissolved organic carbon (DOC) can
72 significantly enhance silica solubility through the formation of organo-silica complexes, such that
73 quartz rapidly dissolves into DOC-rich solutions far above even the thermodynamic solubility of
74 amorphous silica (e.g., Bennett and Siegel, 1987, Bennett, 1991, Pokrovski and Schott, 1998, Ohman
75 et al., 1991, Klein and Walter, 1995; Swanson, 1988). Biological growth of diatoms and plant
76 phytoliths also present enticing evidence for the ability of organic carbon molecules to selectively
77 control the solubility of silica (e.g., Ehrlich et al., 2010; Sangster et al., 2001; Hildebrand et al., 2018).

78 Nevertheless, the nature and stability of these organo-silica complexes, and their role in the diagenesis
79 of carbonate rocks, remains poorly constrained.

80 Based on the evidence that organic matter (e.g., catechol) can strongly enhance the solubility of
81 silica at relative high concentrations (~ 0.1 mol/kg) and pH ~ 8 (e.g., Pokrovski and Schott, 1998 and
82 Ohman et al., 1991), that dissolved organic matter exists in the oceans at 34 to ~ 80 $\mu\text{mol/kg}^{-1}$ (Hansell
83 et al., 2009), and that diagenetic silica are commonly found together in the rock record (Knoll, 1985),
84 we hypothesize a mechanism for producing the significant pore fluid silica supersaturation required
85 for carbonate silicification as follows: 1) organo-silica complexes create strongly silica-enriched pore
86 fluids during the earliest stages of organic matter decay and accumulation; 2) reservoir conditions
87 evolve, causing the organo-silica complexes become unstable; and 3) silica becomes strongly
88 supersaturated in pore fluids, with the degree of supersaturation being directly proportional to the
89 amount of relevant dissolved organic molecules remaining in solution. To test this hypothesis – in
90 particular the mechanisms by which organo-silica complexes form and destabilize – we performed a
91 series of batch experiments at ambient temperatures characteristic of the earliest stages of diagenesis
92 when silicification reactions are interpreted to occur (Bustillo, 2010; Berner, 1980; Hesse, 1989).
93 Using the results of these experiments, we are able to delineate the conditions which promote as well
94 as hinder the stability of organo-silica complexes. We then put these results into a geological context
95 and present a conceptual model for the conditions under which this organo-silica complexing
96 mechanism can lead to significant carbonate silicification.

97 2. METHODS

98 In order to constrain the interactions between organic compounds and silica minerals during
99 silicification of carbonates in diagenetic conditions, we have performed 12 batch experiments at 25°C.
100 These experiments were specifically designed to evaluate:

- 101 1) The stability of aqueous organo-silica complexes in variable physical and chemical
102 conditions. This group of experiments will be referred to as *organo-silica complexation*

experiments. Experiments were performed by reacting an organic-rich solution with amorphous silica gel in anaerobic and/or aerobic conditions.

2) The evolution of the carbonate silicification process during changes in the stability of the organo-silica complexes. This group of experiments will henceforth be referred to as *silicification experiments*. Experiments were performed by reacting an organic-rich solution calcite saturated and/or supersaturated with amorphous silica gel and/or calcite bearing minerals in anaerobic and/or aerobic conditions.

The experimental parameters for both groups of experiments are reported in Table 1.

2.1 Experimental design

2.1.1) Organo-silica complexation experiments

The organo-silica complexation experiments (labeled A to E) involved the reaction of 125 g of an organic-rich solution with amorphous silica gel (Baker Analyzed Reagent) over 1 to 49 days at room temperature (22°C). Experiments A and A' were duplicates. The solutions were prepared with nanopure (18 M $\cdot\Omega$) deionized water and with a concentration of 0.01 M of NaOH (Anachemia) and 0.1 M of catechol (C₆H₆O₂) (Acros organics). Catechol is representative of a class of organic compounds present in early diagenetic pore waters; they are found in numerous higher plants, lignin, humic acids, as well as arthropod cuticles (Swanson, 1988; Moussian, 2013), and was used here because it is easily obtained in quantity from chemical suppliers, has been previously shown to form complexes with aqueous silica (e.g., Bennett, 1991, Pokrovski and Schott, 1998, Ohman et al., 1991), and has reliable thermodynamic data for aqueous geochemical calculations. It is likely that numerous other aqueous organic compounds form strong complexes with silica in diagenetic pore waters (Kubicki and Heaney, 2003), although these species are not well described and therefore less amenable to study. To ensure silica gel would be in excess, amorphous silica gel (0.75 g) was added to the solutions, rendering a concentration of 10 mmol/kg. The solutions were continuously shaken throughout the duration of the experiments with a rotary or orbital shaker at 100-150 RPM (VWR). Solutions were prepared in polycarbonate (PC) bottles with lined septum closures. The bottles were

covered with aluminium foil throughout the experiments in order to prevent catechol photo-oxidation (Sato et al., 2017). The addition of catechol in solution triggers a decrease on the initial pH (Swanson, 1988). In order to obtain a basic pH near 8.5 (seawater pH) the solutions were adjusted by adding 1 M NaOH drop-wise into the solution. Additionally, to evaluate the effect of the ionic strength on the organo-silica complexation, Experiments C and D were prepared with a concentration of 0.5 M NaCl (Fisher chemical), which is approximately consistent with the salinity of seawater (~35 ‰, Millero et al. 2008).

Catechol is strongly sensitive to oxidation when in contact with the atmosphere (Baumann, 1965). To quantify the effects of oxidation on organo-silica complex stability, Experiments A - C were first conducted in a Coy anaerobic chamber under an anoxic atmosphere (<1 ppm O₂) composed dominantly of N₂ (~97.5%) and H₂ (~2.5%). After 5 or 15 days, the bottles were removed from the anaerobic chamber and the N₂ gas headspace in the bottles was removed with a syringe and replaced with pure compressed oxygen (Alphagaz) in order to simulate organic matter oxidation during early diagenesis at depths close to the sediment-water interface (e.g., Martin and Sayles, 2003; Hammond et al., 1996). In Experiment B, the solution was filtered after 5 days (before oxygen was introduced into the bottles) using 0.22 µm Nylon membrane syringe filter to remove silica seed particles > 0.22 µm before introducing O₂ into the bottles. Experiments D and E were exclusively run under pure oxygen atmosphere and not filtered.

2.1.2 Carbonate silicification experiments

Type I - Carbonate supersaturation

Type I experiments were designed to simulate pore waters enriched in organics and supersaturated with respect to primary calcite. Experiments F - G involved reacting 105 g of organic-rich solution with amorphous silica gel and pure ground Iceland spar calcite over a period of 9 days at room temperature (22°C), first in anaerobic conditions in the Coy anaerobic chamber (described above) and subsequently in aerobic conditions. The Iceland spar calcite used in our experiments was prepared by grinding a large, transparent crystal of Iceland spar and sieving it to obtain a size fraction

of 106 – 212 μm . This size fraction was then repeatedly sonicated in order to remove fine particles clinging to the mineral surfaces. In this experimental sequence, two duplicates (F' and G') were performed. The experimental solutions were prepared using nanopure deionized water matrix and concentrations of 0.01 M NaOH and 0.1 M catechol ($\text{C}_6\text{H}_6\text{O}_2$). The solutions contain Ca concentrations ~ 5 times higher than the calcite for a pH 7.5 solution equilibrated with atmospheric $\text{pCO}_2=10^{-3.5}$, rendering an initial saturation index (SI) of the solutions with respect to calcite of 2.1 – 1.7 and initial $\text{Ca}^{2+}:\text{CO}_3^{-2}$ ratio of 611-220 (Table 1). The saturation index of the fluid with respect to a mineral was calculated using Geochemist's Workbench (GWB, Bethke and Yeakel, 2015) (see section 2.3). In order to avoid complications associated with the sluggish rates of atmosphere-solution equilibration (Johnson, 1982), this pCO_2 was achieved through the addition of an appropriate amount of NaHCO_3 reagent to achieve a concentration calculated to be in equilibrium to atmospheric $\text{pCO}_2=10^{-3.5}$ at pH 7.5. The equilibrated solutions were prepared using CaCl_2 at 2.75% w/v (VWR chemical) and NaHCO_3 (Fisher chemical) reagents.

Amorphous silica gel (0.75 g) was introduced in the bottles immediately after the solution was made. Similar to the *organo-silica complexation experiments*, solutions were prepared in polycarbonate (PC) bottles with lined septum closures and covered with aluminium film to prevent catechol photo-oxidation. Once the silica was added to solution, the bottles were systematically shaken with a rotary (under anaerobic conditions) or orbital (under aerobic conditions) shaker. The experiments were first run in anaerobic atmosphere and then, after 3 days (i.e., once steady-state concentrations were expected to have been reached), the gas atmosphere was removed following the same protocol described above. Before oxygen was introduced in the bottles, solutions of experiments F and F' were filtered using 0.22 μm Nylon membrane syringe filters to remove silica seed particles $>0.22 \mu\text{m}$. Then, 0.5 g of calcite spar were introduced in the bottles of experiments F-F' and G-G'. The supersaturation of solutions with calcite prevents dissolution of the Iceland spar, but may result in secondary precipitation on the surface of the Iceland spar.

Type II – Carbonate saturation

Type II experiments simulate pore water enriched in organics (i.e., catechol) and *at equilibrium with respect to calcite*. Experiments H and I involved reacting 125 g of organic-rich solution with silica gel and Iceland spar calcite over a period of 18 days at room temperature (22°C) under anaerobic and aerobic conditions. The experimental solutions were prepared using nanopure deionized water and concentrations of 0.01 M NaOH and 0.1 M catechol (C₆H₆O₂). The solutions contain an amount of Ca calculated to be in equilibrium with calcite for a pH 7.5 and equilibrated with atmospheric pCO₂ = 10^{-3.5} following the same protocol described for *Type I* experiments. They were prepared using CaCl₂·2H₂O (VWR analytical) and NaHCO₃ (Fisher chemical) reagents. The initial saturation index (SI) of the solutions with respect to calcite was 0.7 and initial Ca²⁺:CO₃⁻² ratio was 398-354 (Table 1).

Silica gel (0.75 g) was introduced into the bottles following solution preparation. Solutions were prepared using the same method as *Type I*. The experiments were first run in anaerobic atmosphere and then, after 8 days to ensure steady-state concentrations had been reached in the carbonate saturation solutions, the N₂ gas atmosphere was removed following the same protocol described above. Before oxygen was introduced in the bottles, solution of Experiment I was filtered using 0.22 µm Nylon membrane syringe filters to remove substantial amount of amorphous silica seed. Then, 0.5 g of Iceland calcite spar was introduced in the bottles. The saturation of solutions with calcite limits dissolution of the calcite seed and may maintain unreacted surfaces.

2.2 Analytical procedures

Fluid samples (2 mL) were taken periodically throughout the experiments with a 5 mL syringe and filtered through 0.22 µm Whatman[®] PVDF syringe filters. Aliquots of 0.5 mL were acidified and diluted 20 times with 2% analytical reagent grade nitric acid (Anachemia) in order to prevent mineral precipitation during storage before fluid analysis. In addition, pH was measured on 1.5 mL non-acidified samples using a Thermo Scientific[™] Orion Dual Star[™] pH/SE meter outfitted with a Thermo Scientific[™] Orion[™] 8103BN ROSS[™] Combination Semi-micro pH Electrode, which was calibrated before each measurement using NIST-traceable pH 4, 7, and 10 buffers. The

reproducibility and accuracy of the pH measurements was assessed using the NIST-traceable pH 4, 7 and 10 buffers, and was better than ± 0.02 pH units. Concentrations of Si, Ca and Na were measured using a Varian 725-ES Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) at the University of Calgary. Individual samples were analysed in triplicate. The reproducibility and accuracy of the chemical analysis was assessed using certified standard SANGAMON-03 (NRC) and was better than 4 % and 8 %, respectively.

After experiments were finished, solids phases were prepared following the method described by Tutolo and Tosca (2018). First, materials were vacuum-filtered onto 0.22 μm Durapore[®] membrane filters and rinsed with at least 500 mL of deionized water. Second, solids were dried in air in a natural convection oven at 60°C. Solid phases from experiments F and G were not rinsed with deionized water prior to drying, and the potential effects of this are discussed below. Following drying, solid phases were characterized using scanning electron microscopy (SEM) imaging coupled to energy dispersive X-ray spectroscopy (EDS) for chemical analysis. Samples were prepared for SEM-EDS analyses by adhering well mixed disaggregated solids to conductive carbon tape. SEM imaging and measurement were performed using a FEI Quanta 250 FEG instrument at high vacuum mode at the University of Calgary. For the Everhart-Thornley Detector, an electron beam with 2.50 kV accelerating voltage was used, and on the Back Scattered Electron Detector with 7.50-15 kV accelerating voltage was used.

2.3 Geochemical calculations

Geochemical calculations were performed using the Geochemist's Workbench (GWB, Bethke and Yeakel, 2015) with a database modified after that presented by Tutolo and Tosca (2018) to include the stability constant at 25°C of the catechol aqueous species (Sillen and Martell, 1971) and Si complexes with catechol in saline (0.6 M NaCl) and saline-free solutions, $\log K_{25^\circ\text{C}} = -10.44$ (Ohman et al., 1991) and $\log K_{25^\circ\text{C}} = -11.5$ (Pokrovski and Schott, 1998) respectively. The saturation index (SI) of the initial solutions and samples extracted through the course of the experiments were calculated using the GWB software. The saturation index (SI) is defined as:

$$SI = \log\left(\frac{IAP}{K}\right)$$

Where IAP is the ion activity product and K is the equilibrium constant. When SI is negative for a given mineral ($SI < 0$), the solution is under saturated and can potentially dissolve this mineral. When it is positive ($SI > 0$), the solution is supersaturated and this mineral has the potential to precipitate, provided nucleation occurs and kinetics are favourable. The saturation index of the solutions are reported in Table 1, and for the fluid samples extracted throughout the course of the experiment SI are reported on Tables 2 and 3.

3. RESULTS

3.1 Fluid chemistry

3.1.1 Organo-silica complexation experiments (Expts. A - E)

Time-series measurements demonstrate the impact of solution chemistry on the variations of species in solution (Table 2 and Fig.1). In all experiments, the concentrations of Si in solution increase due to the dissolution of the silica gel in the presence of catechol (Fig. 1a, Table 2). In anaerobic conditions, silica concentration in solution achieves a steady state of 4.9 – 6.0 mmol/kg in only 1 day (Expts. A - C), which is almost 2.6 to 3.2 times more than the solubility of amorphous silica in dilute solutions (1.9 mmol/kg) (Gunnarsson and Arnórsson, 2000). However, during experiments run exclusively in aerobic conditions (Expts. D and E) the concentration of silica was lower (~3 mmol/kg) and attained steady state in 5 days. This result highlights the possible kinetic effect of the oxygen fugacity on organo-silica complexation reactions. In addition, NaCl solutions obtained lower concentration of silica (4.9 mmol/kg) at steady state compared to those in nanopure deionized water (6.0 mmol/kg). Once steady state was reached in anaerobic conditions, silica concentrations in solution remained almost constant, but then drastically decreased when O_2 (g) was introduced in the headspace of the bottles (Fig. 1a). Importantly, this decrease only occurs in unfiltered experimental solutions (i.e., those which were permitted to retain the remaining silica gel - Expts. A, A' and C). Expt. A and A' showed a Si depletion of 3 mmol/kg in 33 and 36 days at aerobic

conditions, respectively, and, in Expt. C, silica concentration decreased by 0.8 mmol/kg after 6 days at aerobic conditions.

The initial pH (8.3 - 8.5) of the solutions decreased in ~1 day to lower values (7.2 -7.5), which remain almost constant until the end of the experiments. Measured pH increased slightly when O₂ was introduced into the headspace of Expts. A', B and C, but slightly decreased when the same was done to Expt. A. In addition, experiments run with NaCl in solutions (Expts. D and E) maintained generally lower pH when compared to solutions run with nanopure water (e.g., the lowest pH of 7.02 was recorded in 19 days on Expt. D). All solutions turned dark ~1 day after O₂ (g) was introduced into the headspace due to the oxidation of the catechol (e.g., Maier et al., 2018) (Fig. 2).

3.1.2 Carbonate silicification experiments (Type I and Type II)

The solution chemistry of experiments varied during the time-series measurements. The concentration of Si in solution remarkably increased in both *Type I* (calcite supersaturation) and *Type II* (calcite saturation) carbonate silicification experiments, due to the dissolution of the initially added silica gel. The experiments were first run in anaerobic conditions, and achieved steady-state silica concentrations within only 1 day. *Type II* experiments (H and I) record generally higher Si concentrations (6.6 mmol/kg) compared to *Type I* (F and G) (4.8 mmol/kg), at slightly lower W/R ratios (Fig. 3a, Table 1, 3). Experiment F' showed the lowest concentration of silica (4.1 mmol/kg) compared to experiment G' (4.8 mmol/kg), but also contained the highest concentration of Na (~12 mmol/kg) compared to F, G and G'. When O₂ (g) was introduced in the bottles, the concentration of silica in solution decreased in *Type I* and *Type II* experiments only in those (G, G' and H) that were not filtered (i.e. permitted to retain the silica gel; Fig. 3a).

Calcium concentrations remained almost constant for all the experiments in both anaerobic and aerobic conditions (Fig. 3b). Only experiment F' showed a slight decrease of calcium in solution in the first day of reaction, a change that is probably related to the precipitation of secondary calcite. The pH of the solutions decreased in just one day, from 8.1-8.5 to 7.2-7.5, and remained almost constant until the end of the experiments (Table 3, Fig. 3d). In all experiments, the colour of the

solution changes from “light pink” to “dark black” after ~1 day of exposure to aerobic conditions, again due to the oxidation of the catechol (Fig.2).

The saturation index of the initial solutions suggest supersaturation with respect to calcite in both *Type I* and *Type II* experiments, consistent with chemical conditions favourable for calcite precipitation (Table 1, 2 and 3). However, only the samples collected through the course of the *Type I* experiments were calculated to be supersaturated ($SI \gg 0$) with respect to calcite, suggesting possible precipitation of secondary calcite in those experiments.

3.2 Characterization of the reacted samples

Scanning electron microscopy images show the presence of a dark organic material enriched in silica on the surfaces of reacted minerals (Fig. 4a). Interestingly, the organic material preferentially appeared on the reacted surfaces of calcite rather than amorphous silica. However, samples that were rinsed with deionized water after the experiments show minor presence of organic material on the primary mineral seeds (Fig. 4b-c), possibly because water removes them from the surfaces or perhaps because this material is the result of evaporation of the experimental solution onto the mineral surfaces. The experimental products that were rinsed prior to SEM observation reveal the development of a silica coating on primary calcite and amorphous silica surfaces. The silica coating formed preferentially in confined zones such as mineral surface defects where the fluid could be trapped and remains longer (Fig 4b). The silica coating precipitated as small spheres attached to the surface of primary minerals (Fig. 4d-e). Moreover, secondary calcite appears to have precipitated on the surface of primary silica seeds on *Type I* experiments run with strongly calcite-supersaturated fluids (Expt. F, F', G and G') (Fig. 4f). In addition, secondary spheres of silica also precipitated on the surface of this secondary calcite.

4. DISCUSSION

The experiments presented here reveal the capacity of different physical/chemical parameters to enhance or diminish the stability of the organo-silica complexes in incipient stages of carbonate diagenesis as well as the development of a silica coating on calcite and silica surfaces as the organo-

silica complexes become unstable. Hereafter, we discuss the nature of these processes and their consequences on the effective reactions during carbonate sediment diagenesis.

4.1 The stability of aqueous organo-silica complexes

We have observed that variations of redox state strongly affect the solubility of silica in the presence of dissolved catechol (Fig. 1-3). We infer that these variations could be related more generally to the oxidation capacity of some organic compounds. The organic compound used in this study, catechol, is a diphenol which contains two hydroxyl -OH groups/radicals that play an important role in oxidation reactions (e.g., Maier et al., 2018; Roginsky and Alegria, 2005, Monchizuki et al., 2002). The following abbreviation will be used in this paper to represent the catechol and biproduct (ortho-quinone) (Fig. 5):

The effects of pH on the oxidation kinetics of catechol (H_2L) investigated by Maier et al. (2018) revealed faster rates of oxidation by O_2 at pH greater than 7. The oxidation reaction of catechol in the presence of dioxygen produces a red/dark solid compound called ortho-quinone (L° - also called 1,2-benzoquinone) and two molecules of water, according to Eq. 1 (Mason et al. 1956, Gerdemann et al. 2002, Magdziak et al., 2002). During the oxidation reaction, the hydrogen from the hydroxyl group of the catechol is lost along and the remaining oxygen then forms double bonds with the carbon.

As previously suggested by other authors (e.g., Ohman et al., 1991; Bennet and Siegel, 1987; Pokrovski and Schott, 1998) the presence of catechol is effective in dissolving silica (in the form of an amorphous gel and/or crystalline quartz) (e.g., Ohman et al., 1991, Coleman, 1981). During SiO_2 dissolution, an anionic catechol-Si complex (SiL_3^{2-}) is formed (Eq. 2). In this hexacoordinated complex, the silicon atom occupies the central atom and is bounded to three ligands (L°), with each ligand binding at two sites (bidentate).

In our study, we propose a simplified reaction that involves the hydrolysis and oxidation of SiL_3^{2-} complex. This reaction yields reactive $\text{SiO}_2(\text{s})$ and ortho-quinone (L°) according to Eq.3 (which is derived from Eqns. 1 and 2). This reaction consumes H^+ , and, as a result, increases the pH of the solution. This could help to explain the slight increase of the pH in experiments during the oxidative stage (Fig. 1-3 and Table 2-3).

The anaerobic conditions inhibit the degradation of the catechol that would impact the dissolution of silica. Such preservation of catechol results in elevated concentration of Si (as the SiL_3^{2-} complex) in solution in such anaerobic conditions (Eq. 2, Fig.1a). However, the presence of oxygen triggers degradation of the previously formed Si-catechol complex (Eq. 3) resulting in a decrease of Si concentration in solution and consequently the formation of solid biproducts (e.g, $\text{SiO}_2(\text{s})$ and ortho-quinone). However, we cannot exclude the possible formation of intermediary complexes with silanol functionalities during the reaction. In addition, the aerobic conditions trigger the oxidation of the catechol, which, in turn, directly impacts the silica dissolution process. Such processes explain the decrease of Si concentration in solution under aerobic conditions. In addition, a general estimate on catechol-silica complexation and degradation rates provided in Appendix A (Fig. A1), shows the rate of formation of SiL_3^{2-} complex is overall ~1 order of magnitude faster compared to the rate of degradation of the SiL_3^{2-} complex. This could be directly related to the individual precipitation rate of silica and ortho-quinone. Our observations are in good agreement with those related to the silicification of wood (Hesse et al., 1989), and establish that, in order to facilitate silicification, the aqueous environment ought to be anoxic to prevent rapid oxidation, and should contain a moderate concentration of silica (up to 2.3 mmol/kg) over an extended period of time (Hesse et al., 1989).

We have modelled the solubility of silica in presence of dissolved catechol at different concentrations using the stability constants ($\log K_{25^\circ\text{C}}$) of the catechol-silica complex in seawater and freshwater solutions from Ohman et al. (1991) and Pokrovski and Schott (1998). Geochemical modelling reveals that the concentration of catechol in solution contributes to enhance or diminish the stability of the catechol-silica complexes (Fig. 6). An increase of catechol concentrations in solution

effectively increases the solubility of silica. This geochemical modelling exercise reveals that the maximum Si concentrations in amorphous silica-equilibrated solutions occur over the pH range 6.6 - 7.2 for solutions containing NaCl at concentrations similar to seawater (Fig. 6), but that lower salinity conditions yield maximum solubilities in the pH range 7.4 – 8.0. Our experiments with higher ionic strength ($I \approx 0.5$, similar to seawater), show overall lower silica concentrations in solution compared to solutions run with very low values ($I \approx 0.01$), regardless of the redox state of the system. Hence, we suggest that lower concentrations of silica in experiments run with saline solutions (Expt. C and E) result from the more alkaline starting pH (~ 8.3). This observation could elucidate for instance observations of silicification in hypersaline environments (e.g., Chowns and Elkins, 1974; Milliken, 1979; Maliva, 1987). In addition, high salinities and/or reducing pore water conditions retard organic matter decomposition (e.g., Golubic and Barghoorn, 1977; Horodyski and Dibaldson, 1983; Knoll, 1985), so the preferential preservation of organic matter in sediments may itself facilitate early diagenetic chert formation by providing nucleation sites for silica precipitation (Knoll, 1985).

As discussed above, geochemical modelling have revealed that silica solubility in organic-rich waters is strongly pH dependent; the pH peak occurs between pH 6.6-8.0, depending on the concentration of catechol and the ionic strength in the pore fluids (Fig. 6). This result lends support for the proposed organo-silica complexation mechanism for carbonate silicification, since a progressive instability of organics in solution (e.g., organic matter oxidation) would lead to the production of CO_2 (Eq. 4), which in turn, would lower the pH and decrease silica solubility.

Moreover, we have observed that the saturation index of calcite in the diagenetic fluid also may affect dissolution of amorphous silica in the presence of catechol. *Type I – Calcite supersaturation* experiments started with initially higher saturation index ($\text{SI} \approx 2$) and demonstrate considerably lower concentration of silica in solution compared to *Type II – Calcite saturation* experiments initialized with lower saturation index ($\text{SI} \approx 0.7$) (Table 3). The formation of secondary carbonate should be dependent on the solution supersaturation; *Type I* being more favourable than *Type II*. Additionally, the pH of the solutions decreases from the initial pH (~ 8.5) to a lower value ($\text{pH} \approx 7$) in *Type I*

experiments compared to ($\text{pH} \approx 7.5$) in *Type II* experiments (Table 3) and this could be explained by the precipitation of secondary calcite in *Type II* experiments. This reaction would lower the pH according to :

SEM images of the reacted seeds extracted from *Type I* experiments shows the precipitation of calcite on the surface of primary amorphous silica seeds (Fig.4f). The possible precipitation and/or absorption of secondary calcite on the surface of the amorphous silica seeds could limit their dissolution and in turn reduce the amount of amorphous silica that dissolved during the experiments. However, further investigation should be interesting to perform on this topic to clarify these observations.

4.2 Silica precipitation during breakdown of organo-silica complexes

Our experiments have demonstrated that a change of the solution redox conditions destabilizes organo-silica complexes. Silica concentration in solution decreases due to the precipitation of a secondary silica coating on calcite and primary silica mineral surfaces (Fig. 4). As discussed above, the oxidation of catechol decreases the solubility of silica. Hence, the solutions become supersaturated in silica minerals, thus promoting silica mineral precipitation.

However, silica coatings exclusively develop in experiments that contain silica seeds during the period of catechol oxidation. Because our experiments were performed at similar pH and degrees of silica supersaturation, the results can be interpreted using the kinetic theory of mineral nucleation. The rates of heterogeneous nucleation of quartz and amorphous silica at 25°C in Fig. 7 were calculated using equations and methods presented by Steefel and Van Cappellen (1990), using interfacial energies of 350 and 46 mJ/m² for quartz and amorphous silica, respectively. For comparison, we represent the Si depletion rate of the solutions sampled during the oxidative period on Fig. 7 in order to determine the energetics of nucleation conditions in our experiments (Fig. 7). These samples plot preferentially in the so-called *crystal growth controlled* region, which suggests that the concentration of silica in solution is not enough to overcome the energetic barriers for homogeneous

nucleation of silica nuclei. This is consistent with our observations of maximum silica depletion rates in experiments which were permitted to retain the initially-added silica seeds during the oxidative period (Fig. 7). This suggests that favourable silica growth surfaces may be a prerequisite for the precipitation of silica coatings. Importantly, our results also demonstrate that silica will only preferentially grow in the presence of favourable nuclei (i.e., silica minerals or gel), because experiments run with exclusively calcite seeds (e.g., Expt. F, F' and I) show only minor silica depletion during the oxidative period (Fig. 7). In addition, the high reactive surface of amorphous silica seeds compared to calcite seeds (Roerdink et al., 2015) could potentially favour the growth on amorphous silica gel seeds. The adsorption of hydroxyl groups on the surface of amorphous silica during reaction with aqueous solutions (Zhuravlev et al., 1987) may favour the bonding with the hydroxyl groups in the silanol molecule (i.e., $\text{Si}(\text{OH})_4$) during the catechol-silica complex oxidation. In addition, the rapid increase in measured Si depletion rates combined with the observation that the experiments containing silica seeds behaved different to those without silica seeds (Fig. 7) suggest that silica seeds lower the threshold of energy required for growth and in turn contribute to increase the silica precipitation kinetics, consistent with the curves plotted in Fig. 7. These data suggest that the thermodynamics and kinetics of silica precipitation during organic matter oxidation would only promote silica precipitation in instances where silica reaction surfaces were already present in the sedimentary reservoir. In addition, the role of silica reactive surface areas on the silicification reaction rate must be considered, because high reactive surface area must be created during the dissolution of primary amorphous silica seeds and could create favourable environments for secondary silica material to grow. In modern oceans, this is commonly accommodated through the deposition of biogenic silica such as sponge spicules or radiolarian tests. Prior to the evolution of these organisms, this could be similarly accommodated by the deposition of silica granules from Si-saturated Precambrian seawater.

Assuming a linear relationship between Si depletion in the fluid and Si uptake in silica coatings, we obtained a silicification rate in all the experiments during the oxidation period (Fig. 8). The silicification rate represents the mass (wt. %) of silica trapped in silica coatings related to the

mass of aqueous silica before oxygen was introduced in the bottles. Our results indicate that the fastest silicification rates were achieved in the presence of silica seeds, no matter the nature of the aqueous solutions (i.e., cation concentration and ionic strength) (e.g., ~56% of aqueous silica was precipitated in silica coatings after 33 days in experiment A'). However, we observed the fastest rates during the first 10 days of reaction and then a slowdown probably due to a decrease in the reactive surface of the seeds by the development of silica coatings (e.g., Daval et al., 2011), and/or the decrease in the thermodynamic drive for silica precipitation. Importantly, when only calcite seeds are present in solution, the silicification rate is lower than 2% after 5 days of reaction compared to 18 % in presence of calcite + silica seeds and 14 % with only silica seeds. This suggests calcite seeds may have a minor impact on silicification, but that silica minerals or gel are required to promote rapid silicification rates (Fig. 8). We confirm previous experiments examining silica-carbonate interactions that demonstrate that carbonate mineral surfaces have no unique properties to promote silica nucleation and growth (e.g., Lakshtanov and Stipp, 2010; Klein and Walter, 1995; Tutolo and Tosca, 2018). Thus, silica seeds kinetically facilitate the silicification process.

4.3 New insights for carbonate silicification during early carbonate diagenesis

The experimental results and analysis presented here help to provide additional support to consider the role of silica reactive moieties (here simulated by catechol) during early diagenetic silicification of carbonate rocks. Importantly, our results have confirmed that our hypothesis implicating the formation and subsequent destabilization of organo-silica complexes in the silicification of carbonate rocks is plausible.

Specifically, the novel model for carbonate silicification via the reaction of dissolved organic components with silica (e.g., here we use catechol stated as DOC(Si)) can be conceptualized as follows (Fig. 9). The presence of DOC(Si) promotes the formation of catechol-silica complexes in the pore fluids, thereby increasing the solubility of silica (Eq. 6, Fig. 9b).

The presence of biogenic silica (e.g., sponge spicules, diatoms, and/or radiolarian tests) and/or authigenic silica granules prior to the evolution of silica-secreting organisms (Stefurak et al. 2014) in carbonate pore space could serve as a silica source, such that dissolved silica concentrations may have been controlled by both the dissolution of these sources as well as the dissolution of accompanying organic matter.

However, changes in oxidative conditions in the reservoir (e.g., bacterial metabolism, nutrients consumption or water mixing) oxidize the organic matter, leading to the reversal of equation 6 and a destabilization of the organo-silica complexes. Thus, we propose that the organic matter oxidation in the pore fluids and the precipitation of secondary calcite (if pore fluids are supersaturated in calcite (i.e., $SI > 0$)) leads to the production of CO_2 , which in turn, will lower pore water pH, and thus decrease the silica solubility and supersaturate the pore fluids in silica polymorphs (Fig. 9c).

Consistent with this observation, Hesse (1989) postulate that the Flint formation in the Cretaceous chalk shows that the change from anoxic to oxic conditions thus appears to coincide with the cemented chalk/flint boundary. Once the solutions overcome silica saturation, silica polymorphs are thermodynamically poised to precipitate. However, our experiments and calculations suggest that a silica nucleus (such as those same materials that provided a silica source to begin with, i.e. biogenic silica and/or silica granules) is required to initiate the replacement during when organo-silica complexes break down. This is in good agreement with field observations which established that siliceous sponge spicules are a common constituent of many Mesozoic to middle Paleozoic platform, shelf, and foreslope chert nodules, including those from limestones in which moulds of spicules are absent or rare (e.g., Jurassic Portland Limestone in England and Cow Head Group western Newfoundland) (e.g., Maliva and Siever, 1989; Coniglio, 1987). However, there is no petrographic evidence for skeletal silica sources in Proterozoic cherty carbonates (e.g., Knoll, 1985; Horodyski and Donaldson, 1980, 1983), which suggests that the higher concentrations of silica in ancient oceans (Siever, 1992) and the authigenic precipitation of silica granules (Stefurak et al. 2014) likely played a role in assisting the initial nucleation and subsequent growth of diagenetic silica. These observations suggest that differences in chert distribution between Proterozoic and Silurian to Cretaceous

carbonates may well relate to the absence of a significant biological sink for silica in Proterozoic oceans.

The type of the precipitated silica polymorph is a question of debate. Maliva and Siever (1988) proposed that most of the silica likely precipitated directly as quartz, although the possibility of an opal-CT precursor for chalcedony and microcrystalline quartz cannot be definitively excluded. In our experiments, the nature of silica coating on the surface of calcite and silica seeds seems to have non-crystalline nature (e.g., amorphous silica). The slow kinetics of quartz precipitation compared to opaline phases at shallow burial temperatures (Rimstidt and Barnes, 1980) lends further support to this suggestion. Moreover, more recent publications (e.g., Liesegang et al., 2017) observe the replacement of Cretaceous calcite bivalve shells by amorphous silica nanoparticles; their estimated rates of nucleation and crystal growth suggest the precipitation of an opal-A or opal-CT polymorph precursor during incipient stages of reaction. The time constant for the production of opal-CT diatomites, porcellanites, and cherts is about 10 Ma under the thermal conditions of the average seafloor (Maliva et al., 1989). With continued diagenesis, opal-CT gradually transforms to quartz with a time scale of about 40 Ma (Maliva et al., 1989). Some experimental studies suggest that the direct precipitation of quartz from dissolved opal-A without an opal-CT precursor is favoured by a lack of Mg (Hinman, 1987) but others (Brown et al., 1969; Meyers, 1977) see no evidence that a lack of Mg in fluids causes replacement of calcitic fossils by quartz minerals.

5. SUMMARY AND CONCLUSIONS

Our study strongly suggests that organo-silica complexes can play a significant role in the diagenetic silicification of carbonate rocks. We have confirmed previous studies (Bennett et al., 1991; Pokrovski and Schott, 1998; Baumann, 1965; Swanson, 1988) which proposed that the presence of organics in solution can effectively increase the solubility of silica via an organo-silica complexation mechanism. In this study, we have used catechol ($C_6H_6O_2$) as organic matter analogue which is a di-phenol with two $-OH$ radicals (e.g., Maier et al., 2018). We have observed that anaerobic conditions inhibit the degradation of the catechol that would impact the dissolution of silica and results in

elevated concentration of Si (as SiL_3^{2-} complex) in solution. However, aerobic conditions trigger the oxidation of the catechol that directly impacts the silica dissolution process. This produces a decrease of Si concentration in solution when the Si-catechol complex is degraded and consequently the formation of solid biproducts (e.g, silica and ortho-quinone). However, we cannot exclude the possible formation of intermediary complexes species during the reaction (with silanol functionalities). Complementary molecular analysis (such as NMR or FT-ICR-MS) on the reacted products could yield important insights into secondary-intermediary phases and molecular bonding.

In addition, the oxidation of the organic matter (e.g., by microbial processes) and precipitation of secondary calcite produces CO_2 and lowers the pH of the pore fluids. This process further destabilizes the organo-silica complexes and thus lowers silica solubility, and produces Si-rich fluids capable of overcoming the thermodynamic barriers of nucleation and growth of silica polymorphs. However, our experiments have focused on the influence of $\text{O}_2(\text{g})$ on the oxidation of organic matter (i.e., catechol) and their effect on carbonate silicification. The presence and/or absence of light in carbonate basins during early stages of diagenesis may have also an influence on oxidation of organic matter (i.e., by photo-oxidation) and in turn, on silicification processes. Thus, we propose that further investigation should evaluate the influence of light on oxidation process during carbonate silicification.

We have additionally demonstrated that the increased concentration of silica in solution before the oxidation period alone is not enough to nucleate silica minerals, and that a silica nucleation surface must be present to assist the growth of new silica polymorphs. These nucleation surfaces could be either biogenic or abiogenic.

Our study brings new insights for the exploration and exploitation of carbonate reservoirs for both hydrocarbon reserves as well as geologic storage of anthropogenic CO_2 . The presence of silica in carbonate rocks provides a negative impact for hydrocarbon exploitation because silica fills porosity and reduces permeability, and thereby hinders the migration of hydrocarbons into and reservoir development within them. Moreover, efforts to inject anthropogenic CO_2 into carbonate reservoirs to reduce greenhouse gas emissions may be stymied by silica in the pore space. A better understanding

of the feedback effects between geochemical and hydrologic processes in carbonates reservoirs due to carbonate silicification will elucidate economic exploitation methods for these reservoirs.

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694 **Table caption**

695 **Table 1.** Experimental parameters

696 **Table 2.** Fluid chemistry of organo-silica complexation experiments

697 **Table 3.** Fluid chemistry of carbonate silicification experiments (*Type I* and *Type II*)

698 **Figure caption**

699 **Fig. 1.** Fluid chemistry of the reacted fluids described as a function of time throughout *Organo-*
 700 *silica complexation experiments* (A to E). (a) Si concentration and (b) pH. Filled-red symbols
 701 represent the experiments with a deionized solution matrix and filled – yellow symbols represent the
 702 experiments containing a matrix of 0.5 NaCl (C and E). White-filled symbols represent the absence of
 703 silica seeds in the bottles during the oxidative period.

Fig. 2. Colour change occurred on the reacted solutions during the oxidative period. *Exp.t* refers to the experimental time.

Fig. 3. Fluid chemistry of the reacted fluids described as a function of time of *carbonate silicification experiment*. Dark green symbols represent *Type I - Calcite supersaturation* and light green symbols represent *Type II - Calcite saturation* (a) Si concentration. (b) Ca concentration. (c) Na concentration and (d) pH. White-filled symbols represent the absence of silica seeds in the bottles during the oxidative period.

Fig. 4. Scanning electron microscopy images of the reacted solids. (a) Calcite seed covered with an organic “glue” enriched in silica of experiment F. The reacted solid was not rinsed with DI water. (b-c) Silica coating precipitating in a confined space on a calcite seed of experiment G’. The silica coating contains minor organic “glue” as was rinsed after experiments with DI water. (d) Silica coating developing on the surface of calcite seed of experiment G’. (e) Silica coating developing on the surface of primary amorphous silica seed of experiment A. (f) Secondary calcite precipitated attached to a primary amorphous silica seed of experiment G. Small silica coating develops on the surface of the secondary calcite.

Fig. 5. Graphical representation of the catechol and ortho-quinone molecules.

Fig. 6. A plot of the change in dissolved Si as a function of the change in pH for a variety of different catechol concentration (0.05, 0.1 and 0.2 M) and ionic strength (DI, $I=0.01 \text{ mol.kg}^{-1}$ and SW, $I=0.6 \text{ mol.kg}^{-1}$) calculated with GWB (Bethke and Yeakel, 2015). The plot represents also the dissolved Ca as a function of the change in pH in the absence of organic compound and in a solution with a $I=0.01 \text{ mol.kg}^{-1}$.

Fig. 7. Rate of heterogeneous nucleation of amorphous silica and quartz as a function of $\text{aSiO}_2(\text{aq})$ at 25°C (Steefel and Van Capellen (1990)). For comparison, the Si depletion rates measured in our experiments were also plotted as a function of $\text{aSiO}_2(\text{aq})$. All of our data plot in the *crystal growth controlled* region, which means that precipitation of silica requires a surface to overcome the energetic barriers of nucleation and growth. Experiments with silica seeds shows a

faster Si depletion rate compared to those experiments with the absence of silica seeds, which directly reflects the effect of a “nucleus” on the nucleation conditions.

Fig. 8. Silicification rates of the present results during the oxidative period. Experiments with silica seeds present show a faster silicification rate than those performed without silica seeds.

Fig. 9. Proposed mechanism for carbonate silicification during early diagenetic stages. (a) Activity-Activity diagram representing the solubility of silica at 25°C. Modern seawater is undersaturated to amorphous silica. (b) The presence of organic compounds in the pore space produces the increase of silica solubility due to the formation of organo-silica complexes. Here we use catechol at 0.1 M as an analogy for organic compounds. (c) However, changes on the oxidative environmental conditions produce the breakdown of the organo-silica complexes and as consequence silica solubility decreases leading pore fluids supersaturated in silica minerals capable to precipitate.

Appendix A

Fig. A1. Representation of the catechol-silica complexation and decomplexation reaction rates in anaerobic/aerobic conditions as a function of the initial pH. The rates of each experiment were calculated from the data plotted in Figs. 1 and 3. The total concentration of silica in solution as a function of time was fit by a linear regression and the rate of complexation and/or decomplexation was taken as the slope of the linear regression.

The contribution of aqueous catechol-silica complexes to silicification during carbonate diagenesis

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Abstract

Pore-filling and carbonate-replacing silica is exceedingly common in carbonates, but the fundamental geochemical mechanisms that drive these silicification reactions during diagenesis remain poorly understood. An existing model has proposed that carbonate silicification proceeds through an interface-coupled dissolution-precipitation reaction, but it lacks a mechanism that enables pore fluids to reach the requisite level of supersaturation with respect to silica to allow nucleation and growth. Here, we present a sequence of batch experiments ranging in duration from 7 to 49 days designed to test the hypothesis that these reactions are facilitated by the formation and destruction of organo-silica complexes during diagenesis. Our results illustrate that the stability of organo-silica complexes is dependent upon the concentration of organic molecules in solution, as well as pH, salinity, and solution redox state. Together, these results allow us to present the following scheme for organo-silica complex mediation of silicification reactions: Firstly, the breakdown of organic matter in the presence of siliceous material creates organo-silica complexes, leading to silica-enriched pore fluids, a process which is enhanced by the anoxic conditions accompanying sediment burial. Then, as environmental conditions evolve (fO_2 , salinity, light, fCO_2 , pH...), the stability of the organo-silica complexes diminishes, and the organo-silica complexes break down. Simultaneously, the pore fluids become intensely silica-supersaturated, in direct proportion to the amount of organic material remaining in solution. The resulting supersaturation drives carbonate silicification via the precipitation of silica minerals, a process which is aided by the presence of silica “nuclei” (such as

sponge spicules). This study contributes new data and a conceptual model that will aid in the ongoing quest to understand carbonate silicification reactions and their potential applications in hydrocarbon exploitation and geologic CO₂ storage. Moreover, it helps to explain the common association between silica precipitates and organic mineral in the sedimentary rock record.

1. INTRODUCTION

Pore-filling and carbonate-replacing silica is exceedingly common in carbonate rocks (e.g., Maliva et al., 1989). This silica (e.g., quartz, chalcedony, Opal-A and/or Opal-CT) is interpreted to have been deposited by silica-rich solutions during a diagenetic process known as silicification. Because the silica fills porosity and reduces permeability, this process has significant implications for both hydrocarbon exploitation and efforts to inject anthropogenic CO₂ into carbonate reservoirs.

Over more than 30 years, scientists have attempted to understand this process (e.g., Butts and Briggs, 2010; Butts, 2014; Calvert, 1974; Maliva and Siever, 1988; Ehrlich et al., 2010; Hesse, 1989; Bustillo, 2010). An early model put forward by Schmitt and Boyd (1981) suggested that one possible replacement mechanism is bulk dissolution of carbonate and later precipitation of pore-filling silica in the resulting void. This void-filling process is commonly observed during the silicification of wood, for instance (Hesse, 1989; Götze et al., 2019). In contrast to this earlier model, Maliva and Siever (1988) presented numerous observations of silica minerals replacing primary carbonate minerals, rather than filling in pre-existing voids. Based on their petrographic evidence and thermodynamic calculations, Maliva and Siever (1988) postulated that carbonate replacement occurs via an interface-coupled dissolution-precipitation reaction (Putnis, 2002). According to this model, the force of crystallization of growing silica crystals results in increased pressure at silica-carbonate contacts, locally increasing the solubility of carbonate (e.g., calcite) through pressure-solution.

In the Maliva and Siever (1988) model, the solution film between the growing silica mineral and the primary carbonates must be supersaturated with respect to the precipitating silica phase and undersaturated with respect to the carbonate in order for the replacement reaction to proceed. Importantly, seawater itself has likely never had SiO₂ concentrations in excess of silica saturation,

52 even in deep time prior to the evolution of silica-secreting organisms (Siever, 1992; Fisher and Knoll,
53 2009, Stefurak et al., 2014). In the modern oceans, the dissolution of biogenic silica of SiO₂-secreting
54 organisms (e.g., diatoms, radiolaria, and sponges) during diagenesis could be a source of
55 supersaturation of silica in pore fluids, but even these materials can only dissolve to the point of
56 equilibrium with respect to amorphous silica, and are therefore likely never more than a factor of 10
57 or so supersaturated with respect to the quartz, the least soluble low-temperature diagenetic silica
58 phase (Rimstidt, 1997). However, in the absence of SiO₂-secreting organisms, Precambrian silica
59 must have largely been removed by chemical processes (Maliva et al., 1989), such as the direct
60 precipitation of silica gel on the seafloor (Stefurak et al. 2014) or interaction with basaltic weathering
61 products during low-temperature hydrothermal circulation (Siever 1992).

62 Because its silica concentration has likely never exceed equilibrium with respect to amorphous
63 (1.9 mmolal at 25°C, Gunnarsson and Arnórsson, 2000), seawater itself cannot ever have been the
64 strongly silica-supersaturated solution required to drive the silicification scheme proposed by Maliva
65 and Siever (1988). Some studies have hypothesized that in Late Proterozoic oceans with higher than
66 present day concentrations of dissolved silica, downward diffusion of silica from seawater into
67 sediments might fuel the growth of chert nodules nucleated on organic matter or some other attractant
68 (Siever, 1992), but, even in this case, the significant supersaturation required for silica growth and
69 carbonate pressure solution/replacement could not be achieved without additional silica being added
70 to solution.

71 Field and experimental observations have demonstrated that dissolved organic carbon (DOC) can
72 significantly enhance silica solubility through the formation of organo-silica complexes, such that
73 quartz rapidly dissolves into DOC-rich solutions far above even the thermodynamic solubility of
74 amorphous silica (e.g., Bennett and Siegel, 1987, Bennett, 1991, Pokrovski and Schott, 1998, Ohman
75 et al., 1991, Klein and Walter, 1995; Swanson, 1988). Biological growth of diatoms and plant
76 phytoliths also present enticing evidence for the ability of organic carbon molecules to selectively
77 control the solubility of silica (e.g., Ehrlich et al., 2010; Sangster et al., 2001; Hildebrand et al., 2018).

78 Nevertheless, the nature and stability of these organo-silica complexes, and their role in the diagenesis
79 of carbonate rocks, remains poorly constrained.

80 Based on the evidence that organic matter (e.g., catechol) can strongly enhance the solubility of
81 silica at relative high concentrations (~ 0.1 mol/kg) and pH ~ 8 (e.g., Pokrovski and Schott, 1998 and
82 Ohman et al., 1991), that dissolved organic matter exists in the oceans at 34 to ~ 80 $\mu\text{mol/kg}^{-1}$ (Hansell
83 et al., 2009), and that diagenetic silica are commonly found together in the rock record (Knoll, 1985),
84 we hypothesize a mechanism for producing the significant pore fluid silica supersaturation required
85 for carbonate silicification as follows: 1) organo-silica complexes create strongly silica-enriched pore
86 fluids during the earliest stages of organic matter decay and accumulation; 2) reservoir conditions
87 evolve, causing the organo-silica complexes become unstable; and 3) silica becomes strongly
88 supersaturated in pore fluids, with the degree of supersaturation being directly proportional to the
89 amount of relevant dissolved organic molecules remaining in solution. To test this hypothesis – in
90 particular the mechanisms by which organo-silica complexes form and destabilize – we performed a
91 series of batch experiments at ambient temperatures characteristic of the earliest stages of diagenesis
92 when silicification reactions are interpreted to occur (Bustillo, 2010; Berner, 1980; Hesse, 1989).
93 Using the results of these experiments, we are able to delineate the conditions which promote as well
94 as hinder the stability of organo-silica complexes. We then put these results into a geological context
95 and present a conceptual model for the conditions under which this organo-silica complexing
96 mechanism can lead to significant carbonate silicification.

97 2. METHODS

98 In order to constrain the interactions between organic compounds and silica minerals during
99 silicification of carbonates in diagenetic conditions, we have performed 12 batch experiments at 25°C .
100 These experiments were specifically designed to evaluate:

- 101 1) The stability of aqueous organo-silica complexes in variable physical and chemical
102 conditions. This group of experiments will be referred to as *organo-silica complexation*

experiments. Experiments were performed by reacting an organic-rich solution with amorphous silica gel in anaerobic and/or aerobic conditions.

2) The evolution of the carbonate silicification process during changes in the stability of the organo-silica complexes. This group of experiments will henceforth be referred to as *silicification experiments*. Experiments were performed by reacting an organic-rich solution calcite saturated and/or supersaturated with amorphous silica gel and/or calcite bearing minerals in anaerobic and/or aerobic conditions.

The experimental parameters for both groups of experiments are reported in Table 1.

2.1 Experimental design

2.1.1) Organo-silica complexation experiments

The organo-silica complexation experiments (labeled A to E) involved the reaction of 125 g of an organic-rich solution with amorphous silica gel (Baker Analyzed Reagent) over 1 to 49 days at room temperature (22°C). Experiments A and A' were duplicates. The solutions were prepared with nanopure (18 M $\cdot\Omega$) deionized water and with a concentration of 0.01 M of NaOH (Anachemia) and 0.1 M of catechol (C₆H₆O₂) (Acros organics). Catechol is representative of a class of organic compounds present in early diagenetic pore waters; they are found in numerous higher plants, lignin, humic acids, as well as arthropod cuticles (Swanson, 1988; Moussian, 2013), and was used here because it is easily obtained in quantity from chemical suppliers, has been previously shown to form complexes with aqueous silica (e.g., Bennett, 1991, Pokrovski and Schott, 1998, Ohman et al., 1991), and has reliable thermodynamic data for aqueous geochemical calculations. It is likely that numerous other aqueous organic compounds form strong complexes with silica in diagenetic pore waters (Kubicki and Heaney, 2003), although these species are not well described and therefore less amenable to study. To ensure silica gel would be in excess, amorphous silica gel (0.75 g) was added to the solutions, rendering a concentration of 10 mmol/kg. The solutions were continuously shaken throughout the duration of the experiments with a rotary or orbital shaker at 100-150 RPM (VWR). Solutions were prepared in polycarbonate (PC) bottles with lined septum closures. The bottles were

covered with aluminium foil throughout the experiments in order to prevent catechol photo-oxidation (Sato et al., 2017). The addition of catechol in solution triggers a decrease on the initial pH (Swanson, 1988). In order to obtain a basic pH near 8.5 (seawater pH) the solutions were adjusted by adding 1 M NaOH drop-wise into the solution. Additionally, to evaluate the effect of the ionic strength on the organo-silica complexation, Experiments C and D were prepared with a concentration of 0.5 M NaCl (Fisher chemical), which is approximately consistent with the salinity of seawater (~35 ‰, Millero et al. 2008).

Catechol is strongly sensitive to oxidation when in contact with the atmosphere (Baumann, 1965). To quantify the effects of oxidation on organo-silica complex stability, Experiments A - C were first conducted in a Coy anaerobic chamber under an anoxic atmosphere (<1 ppm O₂) composed dominantly of N₂ (~97.5%) and H₂ (~2.5%). After 5 or 15 days, the bottles were removed from the anaerobic chamber and the N₂ gas headspace in the bottles was removed with a syringe and replaced with pure compressed oxygen (Alphagaz) in order to simulate organic matter oxidation during early diagenesis at depths close to the sediment-water interface (e.g., Martin and Sayles, 2003; Hammond et al., 1996). In Experiment B, the solution was filtered after 5 days (before oxygen was introduced into the bottles) using 0.22 µm Nylon membrane syringe filter to remove silica seed particles > 0.22 µm before introducing O₂ into the bottles. Experiments D and E were exclusively run under pure oxygen atmosphere and not filtered.

2.1.2 Carbonate silicification experiments

Type I - Carbonate supersaturation

Type I experiments were designed to simulate pore waters enriched in organics and supersaturated with respect to primary calcite. Experiments F - G involved reacting 105 g of organic-rich solution with amorphous silica gel and pure ground Iceland spar calcite over a period of 9 days at room temperature (22°C), first in anaerobic conditions in the Coy anaerobic chamber (described above) and subsequently in aerobic conditions. The Iceland spar calcite used in our experiments was prepared by grinding a large, transparent crystal of Iceland spar and sieving it to obtain a size fraction

of 106 – 212 μm . This size fraction was then repeatedly sonicated in order to remove fine particles clinging to the mineral surfaces. In this experimental sequence, two duplicates (F' and G') were performed. The experimental solutions were prepared using nanopure deionized water matrix and concentrations of 0.01 M NaOH and 0.1 M catechol ($\text{C}_6\text{H}_6\text{O}_2$). The solutions contain Ca concentrations ~ 5 times higher than the calcite for a pH 7.5 solution equilibrated with atmospheric $\text{pCO}_2=10^{-3.5}$, rendering an initial saturation index (SI) of the solutions with respect to calcite of 2.1 – 1.7 and initial $\text{Ca}^{2+}:\text{CO}_3^{2-}$ ratio of 611-220 (Table 1). The saturation index of the fluid with respect to a mineral was calculated using Geochemist's Workbench (GWB, Bethke and Yeakel, 2015) (see section 2.3). In order to avoid complications associated with the sluggish rates of atmosphere-solution equilibration (Johnson, 1982), this pCO_2 was achieved through the addition of an appropriate amount of NaHCO_3 reagent to achieve a concentration calculated to be in equilibrium to atmospheric $\text{pCO}_2=10^{-3.5}$ at pH 7.5. The equilibrated solutions were prepared using CaCl_2 at 2.75% w/v (VWR chemical) and NaHCO_3 (Fisher chemical) reagents.

Amorphous silica gel (0.75 g) was introduced in the bottles immediately after the solution was made. Similar to the *organo-silica complexation experiments*, solutions were prepared in polycarbonate (PC) bottles with lined septum closures and covered with aluminium film to prevent catechol photo-oxidation. Once the silica was added to solution, the bottles were systematically shaken with a rotary (under anaerobic conditions) or orbital (under aerobic conditions) shaker. The experiments were first run in anaerobic atmosphere and then, after 3 days (i.e., once steady-state concentrations were expected to have been reached), the gas atmosphere was removed following the same protocol described above. Before oxygen was introduced in the bottles, solutions of experiments F and F' were filtered using 0.22 μm Nylon membrane syringe filters to remove silica seed particles $>0.22 \mu\text{m}$. Then, 0.5 g of calcite spar were introduced in the bottles of experiments F-F' and G-G'. The supersaturation of solutions with calcite prevents dissolution of the Iceland spar, but may result in secondary precipitation on the surface of the Iceland spar.

Type II – Carbonate saturation

Type II experiments simulate pore water enriched in organics (i.e., catechol) and *at equilibrium with respect to calcite*. Experiments H and I involved reacting 125 g of organic-rich solution with silica gel and Iceland spar calcite over a period of 18 days at room temperature (22°C) under anaerobic and aerobic conditions. The experimental solutions were prepared using nanopure deionized water and concentrations of 0.01 M NaOH and 0.1 M catechol (C₆H₆O₂). The solutions contain an amount of Ca calculated to be in equilibrium with calcite for a pH 7.5 and equilibrated with atmospheric pCO₂ = 10^{-3.5} following the same protocol described for *Type I* experiments. They were prepared using CaCl₂·2H₂O (VWR analytical) and NaHCO₃ (Fisher chemical) reagents. The initial saturation index (SI) of the solutions with respect to calcite was 0.7 and initial Ca²⁺:CO₃⁻² ratio was 398-354 (Table 1).

Silica gel (0.75 g) was introduced into the bottles following solution preparation. Solutions were prepared using the same method as *Type I*. The experiments were first run in anaerobic atmosphere and then, after 8 days to ensure steady-state concentrations had been reached in the carbonate saturation solutions, the N₂ gas atmosphere was removed following the same protocol described above. Before oxygen was introduced in the bottles, solution of Experiment I was filtered using 0.22 µm Nylon membrane syringe filters to remove substantial amount of amorphous silica seed. Then, 0.5 g of Iceland calcite spar was introduced in the bottles. The saturation of solutions with calcite limits dissolution of the calcite seed and may maintain unreacted surfaces.

2.2 Analytical procedures

Fluid samples (2 mL) were taken periodically throughout the experiments with a 5 mL syringe and filtered through 0.22 µm Whatman® PVDF syringe filters. Aliquots of 0.5 mL were acidified and diluted 20 times with 2% analytical reagent grade nitric acid (Anachemia) in order to prevent mineral precipitation during storage before fluid analysis. In addition, pH was measured on 1.5 mL non-acidified samples using a Thermo Scientific™ Orion Dual Star™ pH/SE meter outfitted with a Thermo Scientific™ Orion™ 8103BN ROSS™ Combination Semi-micro pH Electrode, which was calibrated before each measurement using NIST-traceable pH 4, 7, and 10 buffers. The

reproducibility and accuracy of the pH measurements was assessed using the NIST-traceable pH 4, 7 and 10 buffers, and was better than ± 0.02 pH units. Concentrations of Si, Ca and Na were measured using a Varian 725-ES Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) at the University of Calgary. Individual samples were analysed in triplicate. The reproducibility and accuracy of the chemical analysis was assessed using certified standard SANGAMON-03 (NRC) and was better than 4 % and 8 %, respectively.

After experiments were finished, solids phases were prepared following the method described by Tutolo and Tosca (2018). First, materials were vacuum-filtered onto 0.22 μm Durapore[®] membrane filters and rinsed with at least 500 mL of deionized water. Second, solids were dried in air in a natural convection oven at 60°C. Solid phases from experiments F and G were not rinsed with deionized water prior to drying, and the potential effects of this are discussed below. Following drying, solid phases were characterized using scanning electron microscopy (SEM) imaging coupled to energy dispersive X-ray spectroscopy (EDS) for chemical analysis. Samples were prepared for SEM-EDS analyses by adhering well mixed disaggregated solids to conductive carbon tape. SEM imaging and measurement were performed using a FEI Quanta 250 FEG instrument at high vacuum mode at the University of Calgary. For the Everhart-Thornley Detector, an electron beam with 2.50 kV accelerating voltage was used, and on the Back Scattered Electron Detector with 7.50-15 kV accelerating voltage was used.

2.3 Geochemical calculations

Geochemical calculations were performed using the Geochemist's Workbench (GWB, Bethke and Yeakel, 2015) with a database modified after that presented by Tutolo and Tosca (2018) to include the stability constant at 25°C of the catechol aqueous species (Sillen and Martell, 1971) and Si complexes with catechol in saline (0.6 M NaCl) and saline-free solutions, $\log K_{25^\circ\text{C}} = -10.44$ (Ohman et al., 1991) and $\log K_{25^\circ\text{C}} = -11.5$ (Pokrovski and Schott, 1998) respectively. The saturation index (SI) of the initial solutions and samples extracted through the course of the experiments were calculated using the GWB software. The saturation index (SI) is defined as:

$$SI = \log\left(\frac{IAP}{K}\right)$$

Where IAP is the ion activity product and K is the equilibrium constant. When SI is negative for a given mineral ($SI < 0$), the solution is under saturated and can potentially dissolve this mineral. When it is positive ($SI > 0$), the solution is supersaturated and this mineral has the potential to precipitate, provided nucleation occurs and kinetics are favourable. The saturation index of the solutions are reported in Table 1, and for the fluid samples extracted throughout the course of the experiment SI are reported on Tables 2 and 3.

3. RESULTS

3.1 Fluid chemistry

3.1.1 Organo-silica complexation experiments (Expts. A - E)

Time-series measurements demonstrate the impact of solution chemistry on the variations of species in solution (Table 2 and Fig.1). In all experiments, the concentrations of Si in solution increase due to the dissolution of the silica gel in the presence of catechol (Fig. 1a, Table 2). In anaerobic conditions, silica concentration in solution achieves a steady state of 4.9 – 6.0 mmol/kg in only 1 day (Expts. A - C), which is almost 2.6 to 3.2 times more than the solubility of amorphous silica in dilute solutions (1.9 mmol/kg) (Gunnarsson and Arnórsson, 2000). However, during experiments run exclusively in aerobic conditions (Expts. D and E) the concentration of silica was lower (~3 mmol/kg) and attained steady state in 5 days. This result highlights the possible kinetic effect of the oxygen fugacity on organo-silica complexation reactions. In addition, NaCl solutions obtained lower concentration of silica (4.9 mmol/kg) at steady state compared to those in nanopure deionized water (6.0 mmol/kg). Once steady state was reached in anaerobic conditions, silica concentrations in solution remained almost constant, but then drastically decreased when O₂ (g) was introduced in the headspace of the bottles (Fig. 1a). Importantly, this decrease only occurs in unfiltered experimental solutions (i.e., those which were permitted to retain the remaining silica gel - Expts. A, A' and C). Expt. A and A' showed a Si depletion of 3 mmol/kg in 33 and 36 days at aerobic

conditions, respectively, and, in Expt. C, silica concentration decreased by 0.8 mmol/kg after 6 days at aerobic conditions.

The initial pH (8.3 - 8.5) of the solutions decreased in ~1 day to lower values (7.2 -7.5), which remain almost constant until the end of the experiments. Measured pH increased slightly when O₂ was introduced into the headspace of Expts. A', B and C, but slightly decreased when the same was done to Expt. A. In addition, experiments run with NaCl in solutions (Expts. D and E) maintained generally lower pH when compared to solutions run with nanopure water (e.g., the lowest pH of 7.02 was recorded in 19 days on Expt. D). All solutions turned dark ~1 day after O₂ (g) was introduced into the headspace due to the oxidation of the catechol (e.g., Maier et al., 2018) (Fig. 2).

3.1.2 Carbonate silicification experiments (Type I and Type II)

The solution chemistry of experiments varied during the time-series measurements. The concentration of Si in solution remarkably increased in both *Type I* (calcite supersaturation) and *Type II* (calcite saturation) carbonate silicification experiments, due to the dissolution of the initially added silica gel. The experiments were first run in anaerobic conditions, and achieved steady-state silica concentrations within only 1 day. *Type II* experiments (H and I) record generally higher Si concentrations (6.6 mmol/kg) compared to *Type I* (F and G) (4.8 mmol/kg), at slightly lower W/R ratios (Fig. 3a, Table 1, 3). Experiment F' showed the lowest concentration of silica (4.1 mmol/kg) compared to experiment G' (4.8 mmol/kg), but also contained the highest concentration of Na (~12 mmol/kg) compared to F, G and G'. When O₂ (g) was introduced in the bottles, the concentration of silica in solution decreased in *Type I* and *Type II* experiments only in those (G, G' and H) that were not filtered (i.e. permitted to retain the silica gel; Fig. 3a).

Calcium concentrations remained almost constant for all the experiments in both anaerobic and aerobic conditions (Fig. 3b). Only experiment F' showed a slight decrease of calcium in solution in the first day of reaction, a change that is probably related to the precipitation of secondary calcite. The pH of the solutions decreased in just one day, from 8.1-8.5 to 7.2-7.5, and remained almost constant until the end of the experiments (Table 3, Fig. 3d). In all experiments, the colour of the

solution changes from “light pink” to “dark black” after ~1 day of exposure to aerobic conditions, again due to the oxidation of the catechol (Fig.2).

The saturation index of the initial solutions suggest supersaturation with respect to calcite in both *Type I* and *Type II* experiments, consistent with chemical conditions favourable for calcite precipitation (Table 1, 2 and 3). However, only the samples collected through the course of the *Type I* experiments were calculated to be supersaturated ($SI \gg 0$) with respect to calcite, suggesting possible precipitation of secondary calcite in those experiments.

3.2 Characterization of the reacted samples

Scanning electron microscopy images show the presence of a dark organic material enriched in silica on the surfaces of reacted minerals (Fig. 4a). Interestingly, the organic material preferentially appeared on the reacted surfaces of calcite rather than amorphous silica. However, samples that were rinsed with deionized water after the experiments show minor presence of organic material on the primary mineral seeds (Fig. 4b-c), possibly because water removes them from the surfaces or perhaps because this material is the result of evaporation of the experimental solution onto the mineral surfaces. The experimental products that were rinsed prior to SEM observation reveal the development of a silica coating on primary calcite and amorphous silica surfaces. The silica coating formed preferentially in confined zones such as mineral surface defects where the fluid could be trapped and remains longer (Fig 4b). The silica coating precipitated as small spheres attached to the surface of primary minerals (Fig. 4d-e). Moreover, secondary calcite appears to have precipitated on the surface of primary silica seeds on *Type I* experiments run with strongly calcite-supersaturated fluids (Expt. F, F', G and G') (Fig. 4f). In addition, secondary spheres of silica also precipitated on the surface of this secondary calcite.

4. DISCUSSION

The experiments presented here reveal the capacity of different physical/chemical parameters to enhance or diminish the stability of the organo-silica complexes in incipient stages of carbonate diagenesis as well as the development of a silica coating on calcite and silica surfaces as the organo-

silica complexes become unstable. Hereafter, we discuss the nature of these processes and their consequences on the effective reactions during carbonate sediment diagenesis.

4.1 The stability of aqueous organo-silica complexes

We have observed that variations of redox state strongly affect the solubility of silica in the presence of dissolved catechol (Fig. 1-3). We infer that these variations could be related more generally to the oxidation capacity of some organic compounds. The organic compound used in this study, catechol, is a diphenol which contains two hydroxyl -OH groups/radicals that play an important role in oxidation reactions (e.g., Maier et al., 2018; Roginsky and Alegria, 2005, Monchizuki et al., 2002). The following abbreviation will be used in this paper to represent the catechol and biproduct (ortho-quinone) (Fig. 5):

The effects of pH on the oxidation kinetics of catechol (H_2L) investigated by Maier et al. (2018) revealed faster rates of oxidation by O_2 at pH greater than 7. The oxidation reaction of catechol in the presence of dioxygen produces a red/dark solid compound called ortho-quinone (L° - also called 1,2-benzoquinone) and two molecules of water, according to Eq. 1 (Mason et al. 1956, Gerdemann et al. 2002, Magdziak et al., 2002). During the oxidation reaction, the hydrogen from the hydroxyl group of the catechol is lost along and the remaining oxygen then forms double bonds with the carbon.

As previously suggested by other authors (e.g., Ohman et al., 1991; Bennet and Siegel, 1987; Pokrovski and Schott, 1998) the presence of catechol is effective in dissolving silica (in the form of an amorphous gel and/or crystalline quartz) (e.g., Ohman et al., 1991, Coleman, 1981). During SiO_2 dissolution, an anionic catechol-Si complex (SiL_3^{2-}) is formed (Eq. 2). In this hexacoordinated complex, the silicon atom occupies the central atom and is bounded to three ligands (L°), with each ligand binding at two sites (bidentate).

In our study, we propose a simplified reaction that involves the hydrolysis and oxidation of SiL_3^{2-} complex. This reaction yields reactive $\text{SiO}_2(\text{s})$ and ortho-quinone (L°) according to Eq.3 (which is derived from Eqns. 1 and 2). This reaction consumes H^+ , and, as a result, increases the pH of the solution. This could help to explain the slight increase of the pH in experiments during the oxidative stage (Fig. 1-3 and Table 2-3).

The anaerobic conditions inhibit the degradation of the catechol that would impact the dissolution of silica. Such preservation of catechol results in elevated concentration of Si (as the SiL_3^{2-} complex) in solution in such anaerobic conditions (Eq. 2, Fig.1a). However, the presence of oxygen triggers degradation of the previously formed Si-catechol complex (Eq. 3) resulting in a decrease of Si concentration in solution and consequently the formation of solid biproducts (e.g, $\text{SiO}_2(\text{s})$ and ortho-quinone). However, we cannot exclude the possible formation of intermediary complexes with silanol functionalities during the reaction. In addition, the aerobic conditions trigger the oxidation of the catechol, which, in turn, directly impacts the silica dissolution process. Such processes explain the decrease of Si concentration in solution under aerobic conditions. In addition, a general estimate on catechol-silica complexation and degradation rates provided in Appendix A (Fig. A1), shows the rate of formation of SiL_3^{2-} complex is overall ~1 order of magnitude faster compared to the rate of degradation of the SiL_3^{2-} complex. This could be directly related to the individual precipitation rate of silica and ortho-quinone. Our observations are in good agreement with those related to the silicification of wood (Hesse et al., 1989), and establish that, in order to facilitate silicification, the aqueous environment ought to be anoxic to prevent rapid oxidation, and should contain a moderate concentration of silica (up to 2.3 mmol/kg) over an extended period of time (Hesse et al., 1989).

We have modelled the solubility of silica in presence of dissolved catechol at different concentrations using the stability constants ($\log K_{25^\circ\text{C}}$) of the catechol-silica complex in seawater and freshwater solutions from Ohman et al. (1991) and Pokrovski and Schott (1998). Geochemical modelling reveals that the concentration of catechol in solution contributes to enhance or diminish the stability of the catechol-silica complexes (Fig. 6). An increase of catechol concentrations in solution

effectively increases the solubility of silica. This geochemical modelling exercise reveals that the maximum Si concentrations in amorphous silica-equilibrated solutions occur over the pH range 6.6 - 7.2 for solutions containing NaCl at concentrations similar to seawater (Fig. 6), but that lower salinity conditions yield maximum solubilities in the pH range 7.4 – 8.0. Our experiments with higher ionic strength ($I \approx 0.5$, similar to seawater), show overall lower silica concentrations in solution compared to solutions run with very low values ($I \approx 0.01$), regardless of the redox state of the system. Hence, we suggest that lower concentrations of silica in experiments run with saline solutions (Expt. C and E) result from the more alkaline starting pH (~ 8.3). This observation could elucidate for instance observations of silicification in hypersaline environments (e.g., Chowns and Elkins, 1974; Milliken, 1979; Maliva, 1987). In addition, high salinities and/or reducing pore water conditions retard organic matter decomposition (e.g., Golubic and Barghoorn, 1977; Horodyski and Dibaldson, 1983; Knoll, 1985), so the preferential preservation of organic matter in sediments may itself facilitate early diagenetic chert formation by providing nucleation sites for silica precipitation (Knoll, 1985).

As discussed above, geochemical modelling have revealed that silica solubility in organic-rich waters is strongly pH dependent; the pH peak occurs between pH 6.6-8.0, depending on the concentration of catechol and the ionic strength in the pore fluids (Fig. 6). This result lends support for the proposed organo-silica complexation mechanism for carbonate silicification, since a progressive instability of organics in solution (e.g., organic matter oxidation) would lead to the production of CO_2 (Eq. 4), which in turn, would lower the pH and decrease silica solubility.

Moreover, we have observed that the saturation index of calcite in the diagenetic fluid also may affect dissolution of amorphous silica in the presence of catechol. *Type I – Calcite supersaturation* experiments started with initially higher saturation index ($\text{SI} \approx 2$) and demonstrate considerably lower concentration of silica in solution compared to *Type II – Calcite saturation* experiments initialized with lower saturation index ($\text{SI} \approx 0.7$) (Table 3). The formation of secondary carbonate should be dependent on the solution supersaturation; *Type I* being more favourable than *Type II*. Additionally, the pH of the solutions decreases from the initial pH (~ 8.5) to a lower value ($\text{pH} \approx 7$) in *Type I*

experiments compared to ($\text{pH} \approx 7.5$) in *Type II* experiments (Table 3) and this could be explained by the precipitation of secondary calcite in *Type II* experiments. This reaction would lower the pH according to :

SEM images of the reacted seeds extracted from *Type I* experiments shows the precipitation of calcite on the surface of primary amorphous silica seeds (Fig.4f). The possible precipitation and/or absorption of secondary calcite on the surface of the amorphous silica seeds could limit their dissolution and in turn reduce the amount of amorphous silica that dissolved during the experiments. However, further investigation should be interesting to perform on this topic to clarify these observations.

4.2 Silica precipitation during breakdown of organo-silica complexes

Our experiments have demonstrated that a change of the solution redox conditions destabilizes organo-silica complexes. Silica concentration in solution decreases due to the precipitation of a secondary silica coating on calcite and primary silica mineral surfaces (Fig. 4). As discussed above, the oxidation of catechol decreases the solubility of silica. Hence, the solutions become supersaturated in silica minerals, thus promoting silica mineral precipitation.

However, silica coatings exclusively develop in experiments that contain silica seeds during the period of catechol oxidation. Because our experiments were performed at similar pH and degrees of silica supersaturation, the results can be interpreted using the kinetic theory of mineral nucleation. The rates of heterogeneous nucleation of quartz and amorphous silica at 25°C in Fig. 7 were calculated using equations and methods presented by Steefel and Van Cappellen (1990), using interfacial energies of 350 and 46 mJ/m² for quartz and amorphous silica, respectively. For comparison, we represent the Si depletion rate of the solutions sampled during the oxidative period on Fig. 7 in order to determine the energetics of nucleation conditions in our experiments (Fig. 7). These samples plot preferentially in the so-called *crystal growth controlled* region, which suggests that the concentration of silica in solution is not enough to overcome the energetic barriers for homogeneous

nucleation of silica nuclei. This is consistent with our observations of maximum silica depletion rates in experiments which were permitted to retain the initially-added silica seeds during the oxidative period (Fig. 7). This suggests that favourable silica growth surfaces may be a prerequisite for the precipitation of silica coatings. Importantly, our results also demonstrate that silica will only preferentially grow in the presence of favourable nuclei (i.e., silica minerals or gel), because experiments run with exclusively calcite seeds (e.g., Expt. F, F' and I) show only minor silica depletion during the oxidative period (Fig. 7). In addition, the high reactive surface of amorphous silica seeds compared to calcite seeds (Roerdink et al., 2015) could potentially favour the growth on amorphous silica gel seeds. The adsorption of hydroxyl groups on the surface of amorphous silica during reaction with aqueous solutions (Zhuravlev et al., 1987) may favour the bonding with the hydroxyl groups in the silanol molecule (i.e., $\text{Si}(\text{OH})_4$) during the catechol-silica complex oxidation. In addition, the rapid increase in measured Si depletion rates combined with the observation that the experiments containing silica seeds behaved different to those without silica seeds (Fig. 7) suggest that silica seeds lower the threshold of energy required for growth and in turn contribute to increase the silica precipitation kinetics, consistent with the curves plotted in Fig. 7. These data suggest that the thermodynamics and kinetics of silica precipitation during organic matter oxidation would only promote silica precipitation in instances where silica reaction surfaces were already present in the sedimentary reservoir. In addition, the role of silica reactive surface areas on the silicification reaction rate must be considered, because high reactive surface area must be created during the dissolution of primary amorphous silica seeds and could create favourable environments for secondary silica material to grow. In modern oceans, this is commonly accommodated through the deposition of biogenic silica such as sponge spicules or radiolarian tests. Prior to the evolution of these organisms, this could be similarly accommodated by the deposition of silica granules from Si-saturated Precambrian seawater.

Assuming a linear relationship between Si depletion in the fluid and Si uptake in silica coatings, we obtained a silicification rate in all the experiments during the oxidation period (Fig. 8). The silicification rate represents the mass (wt. %) of silica trapped in silica coatings related to the

mass of aqueous silica before oxygen was introduced in the bottles. Our results indicate that the fastest silicification rates were achieved in the presence of silica seeds, no matter the nature of the aqueous solutions (i.e., cation concentration and ionic strength) (e.g., ~56% of aqueous silica was precipitated in silica coatings after 33 days in experiment A'). However, we observed the fastest rates during the first 10 days of reaction and then a slowdown probably due to a decrease in the reactive surface of the seeds by the development of silica coatings (e.g., Daval et al., 2011), and/or the decrease in the thermodynamic drive for silica precipitation. Importantly, when only calcite seeds are present in solution, the silicification rate is lower than 2% after 5 days of reaction compared to 18 % in presence of calcite + silica seeds and 14 % with only silica seeds. This suggests calcite seeds may have a minor impact on silicification, but that silica minerals or gel are required to promote rapid silicification rates (Fig. 8). We confirm previous experiments examining silica-carbonate interactions that demonstrate that carbonate mineral surfaces have no unique properties to promote silica nucleation and growth (e.g., Lakshtanov and Stipp, 2010; Klein and Walter, 1995; Tutolo and Tosca, 2018). Thus, silica seeds kinetically facilitate the silicification process.

4.3 New insights for carbonate silicification during early carbonate diagenesis

The experimental results and analysis presented here help to provide additional support to consider the role of **silica reactive moieties (here simulated by catechol)** during early diagenetic silicification of carbonate rocks. Importantly, our results have confirmed that our hypothesis **implicating** the formation and subsequent destabilization of organo-silica complexes in the silicification of carbonate rocks is plausible.

Specifically, the novel model for carbonate silicification via the reaction of dissolved organic components with silica (e.g., here we use catechol stated as DOC(Si)) can be conceptualized as follows (Fig. 9). The presence of DOC(Si) promotes the formation of **catechol-silica complexes** in the pore fluids, thereby increasing the solubility of silica (Eq. 6, Fig. 9b).

The presence of biogenic silica (e.g., sponge spicules, diatoms, and/or radiolarian tests) and/or authigenic silica granules prior to the evolution of silica-secreting organisms (Stefurak et al. 2014) in carbonate pore space could serve as a silica source, such that dissolved silica concentrations may have been controlled by both the dissolution of these sources as well as the dissolution of accompanying organic matter.

However, changes in oxidative conditions in the reservoir (e.g., bacterial metabolism, nutrients consumption or water mixing) oxidize the organic matter, leading to the reversal of equation 6 and a destabilization of the organo-silica complexes. Thus, we propose that the organic matter oxidation in the pore fluids [and the precipitation of secondary calcite \(if pore fluids are supersaturated in calcite \(i.e., \$SI > 0\$ \)\) leads to the production of \$CO_2\$](#) , which in turn, will lower pore water pH, and thus decrease the silica solubility and supersaturate the pore fluids in silica polymorphs (Fig. 9c).

Consistent with this observation, Hesse (1989) postulate that the Flint formation in the Cretaceous chalk shows that the change from anoxic to oxic conditions thus appears to coincide with the cemented chalk/flint boundary. Once the solutions overcome silica saturation, silica polymorphs are thermodynamically poised to precipitate. However, our experiments and calculations suggest that a silica nucleus (such as those same materials that provided a silica source to begin with, i.e. biogenic silica and/or silica granules) is required to initiate the replacement during when organo-silica complexes break down. This is in good agreement with field observations which established that siliceous sponge spicules are a common constituent of many Mesozoic to middle Paleozoic platform, shelf, and foreslope chert nodules, including those from limestones in which moulds of spicules are absent or rare (e.g., Jurassic Portland Limestone in England and Cow Head Group western Newfoundland) (e.g., Maliva and Siever, 1989; Coniglio, 1987). However, there is no petrographic evidence for skeletal silica sources in Proterozoic cherty carbonates (e.g., Knoll, 1985; Horodyski and Donaldson, 1980, 1983), which suggests that the higher concentrations of silica in ancient oceans (Siever, 1992) and the authigenic precipitation of silica granules (Stefurak et al. 2014) likely played a role in assisting the initial nucleation and subsequent growth of diagenetic silica. These observations suggest that differences in chert distribution between Proterozoic and Silurian to Cretaceous

carbonates may well relate to the absence of a significant biological sink for silica in Proterozoic oceans.

The type of the precipitated silica polymorph is a question of debate. Maliva and Siever (1988) proposed that most of the silica likely precipitated directly as quartz, although the possibility of an opal-CT precursor for chalcedony and microcrystalline quartz cannot be definitively excluded. In our experiments, the nature of silica coating on the surface of calcite and silica seeds seems to have non-crystalline nature (e.g., amorphous silica). The slow kinetics of quartz precipitation compared to opaline phases at shallow burial temperatures (Rimstidt and Barnes, 1980) lends further support to this suggestion. Moreover, more recent publications (e.g., Liesegang et al., 2017) observe the replacement of Cretaceous calcite bivalve shells by amorphous silica nanoparticles; their estimated rates of nucleation and crystal growth suggest the precipitation of an opal-A or opal-CT polymorph precursor during incipient stages of reaction. The time constant for the production of opal-CT diatomites, porcellanites, and cherts is about 10 Ma under the thermal conditions of the average seafloor (Maliva et al., 1989). With continued diagenesis, opal-CT gradually transforms to quartz with a time scale of about 40 Ma (Maliva et al., 1989). Some experimental studies suggest that the direct precipitation of quartz from dissolved opal-A without an opal-CT precursor is favoured by a lack of Mg (Hinman, 1987) but others (Brown et al., 1969; Meyers, 1977) see no evidence that a lack of Mg in fluids causes replacement of calcitic fossils by quartz minerals.

5. SUMMARY AND CONCLUSIONS

Our study strongly suggests that organo-silica complexes can play a significant role in the diagenetic silicification of carbonate rocks. We have confirmed previous studies (Bennett et al., 1991; Pokrovski and Schott, 1998; Baumann, 1965; Swanson, 1988) which proposed that the presence of organics in solution can effectively increase the solubility of silica via an organo-silica complexation mechanism. In this study, we have used catechol ($C_6H_6O_2$) as organic matter analogue which is a di-phenol with two $-OH$ radicals (e.g., Maier et al., 2018). We have observed that anaerobic conditions inhibit the degradation of the catechol that would impact the dissolution of silica and results in

elevated concentration of Si (as SiL_3^{2-} complex) in solution. However, aerobic conditions trigger the oxidation of the catechol that directly impacts the silica dissolution process. This produces a decrease of Si concentration in solution when the Si-catechol complex is degraded and consequently the formation of solid biproducts (e.g. silica and ortho-quinone). However, we cannot exclude the possible formation of intermediary complexes species during the reaction (with silanol functionalities). Complementary molecular analysis (such as NMR or FT-ICR-MS) on the reacted products could yield important insights into secondary-intermediary phases and molecular bonding.

In addition, the oxidation of the organic matter (e.g., by microbial processes) and precipitation of secondary calcite produces CO_2 and lowers the pH of the pore fluids. This process further destabilizes the organo-silica complexes and thus lowers silica solubility, and produces Si-rich fluids capable of overcoming the thermodynamic barriers of nucleation and growth of silica polymorphs. However, our experiments have focused on the influence of $\text{O}_2(\text{g})$ on the oxidation of organic matter (i.e., catechol) and their effect on carbonate silicification. The presence and/or absence of light in carbonate basins during early stages of diagenesis may have also an influence on oxidation of organic matter (i.e., by photo-oxidation) and in turn, on silicification processes. Thus, we propose that further investigation should evaluate the influence of light on oxidation process during carbonate silicification.

We have additionally demonstrated that the increased concentration of silica in solution before the oxidation period alone is not enough to nucleate silica minerals, and that a silica nucleation surface must be present to assist the growth of new silica polymorphs. These nucleation surfaces could be either biogenic or abiogenic.

Our study brings new insights for the exploration and exploitation of carbonate reservoirs for both hydrocarbon reserves as well as geologic storage of anthropogenic CO_2 . The presence of silica in carbonate rocks provides a negative impact for hydrocarbon exploitation because silica fills porosity and reduces permeability, and thereby hinders the migration of hydrocarbons into and reservoir development within them. Moreover, efforts to inject anthropogenic CO_2 into carbonate reservoirs to reduce greenhouse gas emissions may be stymied by silica in the pore space. A better understanding

of the feedback effects between geochemical and hydrologic processes in carbonates reservoirs due to carbonate silicification will elucidate economic exploitation methods for these reservoirs.

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694 **Table caption**

695 **Table 1.** Experimental parameters

696 **Table 2.** Fluid chemistry of organo-silica **complexation** experiments

697 **Table 3.** Fluid chemistry of carbonate silicification experiments (*Type I* and *Type II*)

698 **Figure caption**

699 **Fig. 1.** Fluid chemistry of the reacted fluids described as a function of time throughout *Organo-*
 700 *silica complexation experiments* (A to E). (a) Si concentration and (b) pH. Filled-red symbols
 701 represent the experiments with a deionized solution matrix and filled – yellow symbols represent the
 702 experiments containing a matrix of 0.5 NaCl (C and E). White-filled symbols represent the absence of
 703 silica seeds in the bottles during the oxidative period.

Fig. 2. Colour change occurred on the reacted solutions during the oxidative period. *Exp.t* refers to the experimental time.

Fig. 3. Fluid chemistry of the reacted fluids described as a function of time of *carbonate silicification experiment*. Dark green symbols represent *Type I - Calcite supersaturation* and light green symbols represent *Type II - Calcite saturation* (a) Si concentration. (b) Ca concentration. (c) Na concentration and (d) pH. White-filled symbols represent the absence of silica seeds in the bottles during the oxidative period.

Fig. 4. Scanning electron microscopy images of the reacted solids. (a) Calcite seed covered with an organic “glue” enriched in silica of experiment F. The reacted solid was not rinsed with DI water. (b-c) Silica coating precipitating in a confined space on a calcite seed of experiment G’. The silica coating contains minor organic “glue” as was rinsed after experiments with DI water. (d) Silica coating developing on the surface of calcite seed of experiment G’. (e) Silica coating developing on the surface of primary amorphous silica seed of experiment A. (f) Secondary calcite precipitated attached to a primary amorphous silica seed of experiment G. Small silica coating develops on the surface of the secondary calcite.

Fig. 5. Graphical representation of the catechol and ortho-quinone molecules.

Fig. 6. A plot of the change in dissolved Si as a function of the change in pH for a variety of different catechol concentration (0.05, 0.1 and 0.2 M) and ionic strength (DI, $I=0.01 \text{ mol.kg}^{-1}$ and SW, $I=0.6 \text{ mol.kg}^{-1}$) calculated with GWB (Bethke and Yeakel, 2015). The plot represents also the dissolved Ca as a function of the change in pH in the absence of organic compound and in a solution with a $I=0.01 \text{ mol.kg}^{-1}$.

Fig. 7. Rate of heterogeneous nucleation of amorphous silica and quartz as a function of $\text{aSiO}_2(\text{aq})$ at 25°C (Steefel and Van Capellen (1990)). For comparison, the Si depletion rates measured in our experiments were also plotted as a function of $\text{aSiO}_2(\text{aq})$. All of our data plot in the crystal growth controlled region, which means that precipitation of silica requires a surface to overcome the energetic barriers of nucleation and growth. Experiments with silica seeds shows a

faster Si depletion rate compared to those experiments with the absence of silica seeds, which directly reflects the effect of a “nucleus” on the nucleation conditions.

Fig. 8. Silicification rates of the present results during the oxidative period. Experiments with silica seeds present show a faster silicification rate than those performed without silica seeds.

Fig. 9. Proposed mechanism for carbonate silicification during early diagenetic stages. (a) Activity-Activity diagram representing the solubility of silica at 25°C. Modern seawater is undersaturated to amorphous silica. (b) The presence of organic compounds in the pore space produces the increase of silica solubility due to the formation of organo-silica complexes. Here we use catechol at 0.1 M as an analogy for organic compounds. (c) However, changes on the oxidative environmental conditions produce the breakdown of the organo-silica complexes and as consequence silica solubility decreases leading pore fluids supersaturated in silica minerals capable to precipitate.

Appendix A

Fig. A1. Representation of the catechol-silica complexation and decomplexation reaction rates in anaerobic/aerobic conditions as a function of the initial pH. The rates of each experiment were calculated from the data plotted in Figs. 1 and 3. The total concentration of silica in solution as a function of time was fit by a linear regression and the rate of complexation and/or decomplexation was taken as the slope of the linear regression.

Table 1

Table 1. Experimental parameters

Experiment		Duration (days)	Solution Matrix	Gas atmosphere	Initial pH	Amorphous silica (g)	Calcite (g)	Catechol (g)	Solution (g)	Am.silica seeds in aerobic conditions	W/R ratio	Ca ⁺² : CO ₃ ⁻² ratio	SI Calcite
A	Organo-silica complexion	48.1	DI	N ₂ /O ₂	8.56	0.76	(-)	1.36	124.99	yes	165		
A'	Organo-silica complexion	49.0	DI	N ₂ /O ₂	8.56	0.76	(-)	1.38	125.01	yes	164		
B	Organo-silica complexion	10.2	DI	N ₂ /O ₂	8.54	0.76	(-)	1.37	124.98	no (-)	165		
C	Organo-silica complexion	19.0	NaCl	N ₂ /O ₂	8.34	0.76	(-)	1.37	125.06	yes	165		
D	Organo-silica complexion	19.0	DI	O ₂	8.33	0.75	(-)	1.38	125.04	yes	166		
E	Organo-silica complexion	19.0	NaCl	O ₂	8.52	0.76	(-)	1.38	125.00	yes	165		
F	Carbonate silicification (Type I)	7.1	DI	N ₂ /O ₂	8.52	0.76	0.51	1.37	105.66	no (-)	83	327	1.95
F'	Carbonate silicification (Type I)	7.0	DI	N ₂ /O ₂	8.52	0.77	0.49	1.37	105.58	no (-)	84	220	2.11
G	Carbonate silicification (Type I)	7.1	DI	N ₂ /O ₂	8.52	0.76	0.49	1.37	105.66	yes	85	278	2.01
G'	Carbonate silicification (Type I)	9.0	DI	N ₂ /O ₂	8.14	0.76	0.51	1.38	105.60	yes	83	611	1.69
H	Carbonate silicification (Type II)	18.9	DI	N ₂ /O ₂	8.52	0.77	0.50	1.37	125.03	yes	99	398	0.72
I	Carbonate silicification (Type II)	18.9	DI	N ₂ /O ₂	8.51	0.76	0.37	1.38	125.02	no (-)	110	345	0.67

(-) Silica seeds were substantially removed from the solution by filtering

Table 2

Table 2. Fluid chemistry of organo-silica complexation experiments

a) Organo-silica complexon experiments																													
Experiment A										Experiment A'																			
Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/kg)	Na (mmol/kg)	Seeds in solution	Si SiO ₂ (am)	Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/kg)	Na (mmol/kg)	Seeds in solution	Si SiO ₂ (am)										
A.B	0.00	0.00	N ₂	DI	8.56	0.01	9.24	SiO ₂ (am)	-11.99	A'B	0.00	0.00	N ₂	DI	8.56	0.00	8.73	SiO ₂ (am)	-11.98										
A.1	25.92	1.08	N ₂	DI	7.49	5.92	9.15	SiO ₂ (am)	-0.12	A'.1	23.50	0.98	N ₂	DI	7.64	5.44	8.44	SiO ₂ (am)	-0.32										
A.2	48.68	2.03	N ₂	DI	7.58	5.96	8.98	SiO ₂ (am)	-0.26	A'.2	120.90	5.04	N ₂	DI	7.44	5.60	8.35	SiO ₂ (am)	-0.02										
A.3	73.05	3.04	N ₂	DI	7.52	6.04	9.24	SiO ₂ (am)	-0.11	A'.3	195.50	8.15	N ₂	DI	7.38	5.64	8.40	SiO ₂ (am)	-0.02										
A.4	167.80	6.99	N ₂	DI	7.45	5.90	8.88	SiO ₂ (am)	-0.12	A'.4	312.30	13.01	N ₂	DI	7.34	5.69	8.58	SiO ₂ (am)	0.11										
A.5	360.90	15.04	N ₂	DI	7.58	5.96	9.04	SiO ₂ (am)	-0.26	A'.5	340.75	14.20	O ₂	DI	7.56	5.56	8.52	SiO ₂ (am)	-0.30										
A.6	385.70	16.07	O ₂	DI	7.53	5.86	9.36	SiO ₂ (am)	-0.12	A'.6	387.88	16.16	O ₂	DI	7.57	5.20	8.49	SiO ₂ (am)	-0.34										
A.7	406.50	16.94	O ₂	DI	7.52	5.62	9.28	SiO ₂ (am)	-0.15	A'.7	455.20	18.97	O ₂	DI	7.50	4.87	8.71	SiO ₂ (am)	-0.22										
A.8	477.90	19.91	O ₂	DI	7.51	5.14	9.27	SiO ₂ (am)	-0.20	A'.8	1176.47	49.02	O ₂	DI	7.38	2.65	7.82	SiO ₂ (am)	-0.37										
A.9	674.47	28.10	O ₂	DI	7.35	4.24	9.42	SiO ₂ (am)	-0.16	* Oxygen was introduced at 312.6 h										* Oxygen was introduced at 136 h (c) Silica seeds were substantially removed from the solution by filtering									
A.10	1154.95	48.12	O ₂	DI	7.18	2.61	9.23	SiO ₂ (am)	-0.15																				
* Oxygen was introduced at 363.9 h										Experiment B										Experiment E									
Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/kg)	Na (mmol/kg)	Seeds in solution	Si SiO ₂ (am)	Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/kg)	Na (mmol/kg)	Seeds in solution	Si SiO ₂ (am)	Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/kg)	Na (mmol/kg)	Seeds in solution	Si SiO ₂ (am)
B.B	0.00	0.00	N ₂	DI	8.54	0.00	8.40	SiO ₂ (am)	-11.81	E.B	0.00	0.00	O ₂	DI	8.52	0.01	8.52	SiO ₂ (am)	-11.81										
B.1	28.22	1.18	N ₂	DI	7.53	5.18	8.27	SiO ₂ (am)	-0.19	E.1	23.00	0.96	O ₂	DI	8.16	1.12	8.13	SiO ₂ (am)	-2.19										
B.2	73.45	3.06	N ₂	DI	7.50	5.23	8.19	SiO ₂ (am)	-0.19	E.2	120.40	5.02	O ₂	DI	7.39	3.18	8.38	SiO ₂ (am)	-0.29										
B.3	96.57	4.02	N ₂	DI	7.48	5.29	8.23	SiO ₂ (am)	-0.18	E.3	195.00	8.11	O ₂	DI	7.39	3.31	8.41	SiO ₂ (am)	-0.27										
B.4	120.25	5.01	N ₂	DI	7.42	5.23	8.08	SiO ₂ (am)	-0.05	E.4	455.10	18.96	O ₂	DI	7.27	2.80	8.31	SiO ₂ (am)	-0.23										
B.5	144.38	6.02	O ₂	DI	7.64	5.31	8.24	(-)	-0.33	* Oxygen was introduced at 136 h (c) Silica seeds were substantially removed from the solution by filtering																			
B.6	172.75	7.20	O ₂	DI	7.65	5.20	8.21	(-)	-0.50																				
B.7	197.32	8.22	O ₂	DI	7.61	5.19	8.19	(-)	-0.34																				
B.8	220.23	9.18	O ₂	DI	7.49	5.16	8.13	(-)	-0.19																				
B.9	244.20	10.18	O ₂	DI	7.54	5.16	8.26	(-)	-0.19	Experiment C										Experiment D									
Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/kg)	Na (mmol/kg)	Seeds in solution	Si SiO ₂ (am)	Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/kg)	Na (mmol/kg)	Seeds in solution	Si SiO ₂ (am)	Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/kg)	Na (mmol/kg)	Seeds in solution	Si SiO ₂ (am)
C.B	0.00	0.00	N ₂	NaCl	8.34	0.00	453.83	SiO ₂ (am)	-11.94	D.B	0.00	0.00	O ₂	NaCl	8.33	0.00	430.79	SiO ₂ (am)	-11.93	E.B	0.00	0.00	O ₂	DI	8.52	0.01	8.52	SiO ₂ (am)	-11.81
C.1	24.20	1.01	N ₂	NaCl	7.22	4.98	452.32	SiO ₂ (am)	-0.13	D.1	24.00	1.00	O ₂	NaCl	7.81	1.15	425.04	SiO ₂ (am)	-1.89	E.1	23.00	0.96	O ₂	DI	8.16	1.12	8.13	SiO ₂ (am)	-2.19
C.2	121.80	5.08	N ₂	NaCl	7.16	4.93	450.99	SiO ₂ (am)	-0.14	D.2	121.20	5.05	O ₂	NaCl	7.11	2.92	445.60	SiO ₂ (am)	-0.28	E.2	120.40	5.02	O ₂	DI	7.39	3.18	8.38	SiO ₂ (am)	-0.29
C.3	196.50	8.19	N ₂	NaCl	7.11	4.92	446.10	SiO ₂ (am)	-0.02	D.3	195.80	8.16	O ₂	NaCl	7.12	2.97	453.55	SiO ₂ (am)	-0.26	E.3	195.00	8.11	O ₂	DI	7.39	3.31	8.41	SiO ₂ (am)	-0.27
C.4	313.10	13.05	N ₂	NaCl	7.09	4.92	444.04	SiO ₂ (am)	-0.02	D.4	456.10	19.00	O ₂	NaCl	7.02	2.41	455.64	SiO ₂ (am)	-0.25	E.4	455.10	18.96	O ₂	DI	7.27	2.80	8.31	SiO ₂ (am)	-0.23
C.5	341.50	14.23	O ₂	NaCl	7.34	4.76	435.97	SiO ₂ (am)	-0.29	* Oxygen was introduced at 312.6 h										Experiment D									
C.6	388.80	16.20	O ₂	NaCl	7.33	4.41	429.32	SiO ₂ (am)	-0.34											Experiment E									
C.7	455.90	19.00	O ₂	NaCl	7.23	4.08	423.83	SiO ₂ (am)	-0.23											Experiment F									
* Oxygen was introduced at 363.9 h										Experiment G										Experiment H									

Table 3

Table 3. Final chemistry of carbonate silicification experiments (Type I and Type II).

II. Carbonate silicification experiments

Type I: Calcite supersaturation

Experiment F

Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/L)	Ca (mmol/L)	Na (mmol/L)	Seeds in solution	Si SiO ₂ (mm)	SI
F.B	0.0	0.0	N ₂	DI	8.5	0.0	21.7	10.6	SiO ₂ (mm)	-12.0	2.0
F.1	21.5	0.9	N ₂	DI	7.2	4.6	22.1	11.5	SiO ₂ (mm)	0.0	0.7
F.2	45.5	1.9	N ₂	DI	7.3	4.6	21.9	11.4	SiO ₂ (mm)	-0.1	0.8
F.3	53.5	2.2	N ₂	DI	7.3	4.6	21.5	11.2	SiO ₂ (mm)	-0.1	0.8
F.4	69.2	2.9	N ₂	DI	7.2	4.6	21.7	11.4	SiO ₂ (mm)	0.0	0.7
F.5	77.0	3.2	O ₂	DI	7.4	4.5	21.6	11.3	Calcite spur	-0.6	0.3
F.6	97.7	4.1	O ₂	DI	7.5	4.5	21.4	11.1	Calcite spur	-0.4	1.0
F.7	122.4	5.1	O ₂	DI	7.5	4.5	21.6	11.2	Calcite spur	-0.4	1.0
F.8	145.3	6.1	O ₂	DI	7.4	4.5	21.5	11.5	Calcite spur	-0.3	0.9
F.9	169.3	7.1	O ₂	DI	7.4	4.5	21.5	11.5	Calcite spur	-0.3	0.9

* Oxygen was introduced at 69.6 h

Experiment G

Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/L)	Ca (mmol/L)	Na (mmol/L)	Seeds in solution	Si SiO ₂ (mm)	SI
G.B	0.0	0.0	N ₂	DI	8.5	0.0	21.7	10.6	SiO ₂ (mm)	+22.0	2.0
G.1	21.4	0.9	N ₂	DI	7.2	4.5	21.3	11.0	SiO ₂ (mm)	0.0	0.8
G.2	45.8	1.9	N ₂	DI	7.2	4.5	21.2	11.0	SiO ₂ (mm)	0.0	0.8
G.3	53.5	2.2	N ₂	DI	7.2	4.4	20.6	10.6	SiO ₂ (mm)	0.0	0.7
G.4	69.4	2.9	N ₂	DI	7.1	4.6	21.1	11.0	SiO ₂ (mm)	0.1	0.6
G.5	77.0	3.2	O ₂	DI	7.3	4.6	21.5	11.0	SiO ₂ (mm)/calcite spur	-0.4	1.1
G.6	97.7	4.1	O ₂	DI	7.5	4.5	21.5	11.1	SiO ₂ (mm)/calcite spur	-0.4	1.1
G.7	122.4	5.1	O ₂	DI	7.5	4.2	21.5	11.1	SiO ₂ (mm)/calcite spur	-0.4	1.1
G.8	145.4	6.1	O ₂	DI	7.4	4.0	21.4	11.1	SiO ₂ (mm)/calcite spur	-0.3	1.0
G.9	169.5	7.1	O ₂	DI	7.4	3.8	21.2	11.2	SiO ₂ (mm)/calcite spur	-0.3	1.0

* Oxygen was introduced at 69.6 h

Experiment F

Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/L)	Ca (mmol/L)	Na (mmol/L)	Seeds in solution	Si SiO ₂ (mm)	SI
F.B	0.0	0.0	N ₂	DI	8.5	0.0	21.7	10.6	SiO ₂ (mm)	-12.0	2.1
F.1	21.0	1.0	N ₂	DI	7.2	4.1	19.5	12.2	SiO ₂ (mm)	0.0	0.8
F.2	47.0	2.0	N ₂	DI	7.2	4.1	19.9	12.5	SiO ₂ (mm)	0.0	0.8
F.3	117.7	4.9	O ₂	DI	7.5	4.1	19.7	12.4	Calcite spur	-0.4	1.1
F.4	147.1	6.1	O ₂	DI	7.3	4.1	19.6	12.3	Calcite spur	-0.2	0.9
F.5	167.0	7.0	O ₂	DI	7.4	4.1	20.2	12.8	Calcite spur	-0.3	1.0

* Oxygen was introduced at 47.1 h

Experiment G

Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/L)	Ca (mmol/L)	Na (mmol/L)	Seeds in solution	Si SiO ₂ (mm)	SI
G.B	0.0	0.0	N ₂	DI	8.1	0.0	21.7	10.6	SiO ₂ (mm)	-11.3	1.7
G.1	28.6	1.2	N ₂	DI	7.2	4.8	21.1	10.7	SiO ₂ (mm)	0.0	0.8
G.2	50.3	2.1	N ₂	DI	7.2	4.8	21.0	10.9	SiO ₂ (mm)	0.0	0.8
G.3	72.7	3.0	N ₂	DI	7.2	4.8	20.5	10.8	SiO ₂ (mm)	0.0	0.8
G.4	96.8	4.0	O ₂	DI	7.5	4.7	21.0	10.8	SiO ₂ (mm)/calcite spur	-0.4	1.1
G.5	167.3	7.0	O ₂	DI	7.5	4.0	19.8	10.3	SiO ₂ (mm)/calcite spur	-0.5	1.1
G.6	196.7	8.2	O ₂	DI	7.4	4.0	21.0	10.9	SiO ₂ (mm)/calcite spur	-0.3	1.0
G.7	216.6	9.0	O ₂	DI	7.5	3.9	20.4	10.7	SiO ₂ (mm)/calcite spur	-0.5	1.1

* Oxygen was introduced at 73.4 h

Type II: Calcite saturation

Experiment I

Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/L)	Ca (mmol/L)	Na (mmol/L)	Seeds in solution	Si SiO ₂ (mm)	SI
I.B	0.0	0.0	N ₂	DI	8.5	0.0	3.9	9.9	SiO ₂ (mm)	-11.9	0.7
I.1	25.2	1.0	N ₂	DI	7.4	5.9	3.8	10.2	SiO ₂ (mm)	0.0	-0.5
I.2	49.7	2.1	N ₂	DI	7.4	5.8	3.8	9.9	SiO ₂ (mm)	0.0	-0.5
I.3	72.4	3.0	N ₂	DI	7.4	5.6	3.7	9.6	SiO ₂ (mm)	-0.1	-0.5
I.4	96.7	4.0	N ₂	DI	7.4	5.8	3.8	10.0	SiO ₂ (mm)	0.0	-0.5
I.5	165.7	6.9	N ₂	DI	7.4	6.4	4.1	10.7	SiO ₂ (mm)	0.0	-0.4
I.6	189.4	7.9	N ₂	DI	7.4	6.6	4.7	10.1	SiO ₂ (mm)	0.0	-0.4
I.7	212.8	8.9	O ₂	DI	7.2	5.9	4.8	10.3	calcite spur	0.2	-0.6
I.8	237.2	9.9	O ₂	DI	7.2	5.6	5.0	10.7	calcite spur	0.2	-0.6
I.9	262.4	10.9	O ₂	DI	7.2	5.3	4.9	10.2	calcite spur	0.1	-0.6
I.10	337.0	14.0	O ₂	DI	7.1	5.8	5.1	10.0	calcite spur	0.3	-0.7
I.11	428.7	17.9	O ₂	DI	7.0	5.7	5.2	9.7	calcite spur	0.3	-0.8

* Oxygen was introduced at 193.8 h

Experiment H

Sample	hour	day	Atm.	Matrix solution	pH	Si (mmol/L)	Ca (mmol/L)	Na (mmol/L)	Seeds in solution	Si SiO ₂ (mm)	SI
H.B	0.0	0.0	N ₂	DI	8.5	0.0	4.5	10.1	SiO ₂ (mm)	-11.9	0.7
H.1	25.3	1.1	N ₂	DI	7.5	5.9	4.2	9.8	SiO ₂ (mm)	-0.2	-0.3
H.2	49.6	2.1	N ₂	DI	7.4	6.1	4.3	10.2	SiO ₂ (mm)	0.0	-0.4
H.3	72.2	3.0	N ₂	DI	7.4	6.4	4.6	10.8	SiO ₂ (mm)	0.0	-0.4
H.4	96.6	4.0	N ₂	DI	7.4	6.0	4.3	10.1	SiO ₂ (mm)	0.0	-0.4
H.5	165.6	6.9	N ₂	DI	7.5	5.5	4.1	9.1	SiO ₂ (mm)	-0.2	-0.3
H.6	189.2	7.9	N ₂	DI	7.5	6.1	5.3	10.2	SiO ₂ (mm)	-0.2	-0.3
H.7	212.8	8.9	O ₂	DI	7.4	5.9	5.3	10.0	SiO ₂ (mm)/calcite spur	0.0	-0.3
H.8	237.1	9.9	O ₂	DI	7.4	5.6	4.7	9.7	SiO ₂ (mm)/calcite spur	-0.1	-0.4
H.9	262.4	10.9	O ₂	DI	7.4	5.6	4.8	9.6	SiO ₂ (mm)/calcite spur	-0.1	-0.4
H.10	337.0	14.0	O ₂	DI	7.3	4.9	4.7	10.1	SiO ₂ (mm)/calcite spur	0.0	-0.5
H.11	428.7	17.9	O ₂	DI	7.3	4.5	4.8	10.2	SiO ₂ (mm)/calcite spur	0.0	-0.5

* Oxygen was introduced at 193.8 h

Figure 1

Fig. 1 (Escario et al.)

Figure 2

Fig.2 (Escario et al.)

Figure 3

Fig. 3 (Escario et al.)

Fig. 4 (Escario et al.)

Figure 5

Fig. 5 (Escario et al.)

Catechol

*First
dissociation*

$$\rightleftharpoons$$

*Second
dissociation*

$$\rightleftharpoons$$

Ortho-quinone

Figure 6

Fig. 6 (Escario et al.)

Figure 7

Fig. 7 (Escario et al.)

Figure 8

Fig. 8 (Escario et al.)

Fig. 9 (Escario et al.)