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# Sedimentary talc in Neoproterozoic carbonate successions

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## Abstract

Mineralogical, petrographic and sedimentological observations document early diagenetic talc in carbonate-dominated successions deposited on two early Neoproterozoic (~800-700 million years old) platform margins. In the Akademikerbreen Group, Svalbard, talc occurs as nodules that pre-date microspar cements that fill molar tooth structures and primary porosity in stromatolitic carbonates. In the upper Fifteenmile Group of the Ogilvie Mountains, NW Canada, the talc is present as nodules, coated grains, rip-up clasts and massive beds that are several meters thick. To gain insight into the chemistry required to form early diagenetic talc, we conducted precipitation experiments at 25°C with low-SO<sub>4</sub> synthetic seawater solutions at varying pH, Mg<sup>2+</sup> and SiO<sub>2</sub>(aq). Our experiments reveal a sharp and reproducible pH boundary (at ~8.7) only above which does poorly crystalline Mg-silicate precipitate; increasing Mg<sup>2+</sup> and/or SiO<sub>2</sub>(aq) alone is insufficient to produce the material. The strong pH control can be explained by Mg-silica complexing activated by the deprotonation of silicic acid above ~8.6-8.7. FT-IR, TEM and XRD of the synthetic precipitates reveal a talc-like 2:1 trioctahedral structure with short-range stacking order. Hydrothermal experiments simulating burial diagenesis show that dehydration of the precipitate drives a transition to kerolite (hydrated talc) and eventually to talc. This formation pathway imparts extensive layer stacking disorder to the synthetic talc end-product that is identical to Neoproterozoic occurrences. Early diagenetic talc in Neoproterozoic

30 carbonate platform successions appears to reflect a unique combination of low Al concentrations  
31 (and, by inference, low siliciclastic input), near modern marine salinity and  $Mg^{2+}$ , elevated  
32  $SiO_2(aq)$ , and  $pH > \sim 8.7$ . Because the talc occurs in close association with microbially  
33 influenced sediments, we suggest that soluble species requirements were most easily met through  
34 microbial influences on pore water chemistry, specifically pH and alkalinity increases driven by  
35 anaerobic Fe respiration.

36

37 Keywords: Proterozoic; geobiology; mineralogy; geochemistry; carbonate; silica

38

## 39 **1. Introduction**

40 Talc,  $Mg_3Si_4O_{10}(OH)_2$ , is typically interpreted as a high-temperature mineral that forms  
41 from hydrothermal alteration or metamorphism of Mg-rich and ultrabasic rocks (Evans and  
42 Guggenheim, 1988; Marumo and Hattori, 1999). Lower temperature reactions can also produce  
43 talc-bearing assemblages, for example through the weathering of serpentinite deposits (Velde  
44 and Meunier, 2008); however, this class of reactions is far less common than its high temperature  
45 counterpart. As such, outside of the scattered reports of talc in evaporite or carbonate rich  
46 deposits (Bodine, 1983; Braitsch, 1971; Calvo et al., 1999; Friedman, 1965; Millot and Palausi,  
47 1959; Noack et al., 1989), talc is rarely reported as a sedimentary mineral. Here we document the  
48 unusual occurrence of early diagenetic talc associated with Neoproterozoic ( $\sim 800$ -700 Ma)  
49 carbonates deposited on two separate platform margins: the Akademikerbreen Group in Svalbard  
50 and the Fifteenmile Group in the Ogilvie Mountains of northwestern Canada. The formation of  
51 sedimentary talc and its mineralogical precursors requires a specific set of chemical conditions;

52 its presence places tight quantitative constraints on Neoproterozoic ocean chemistry and provides  
53 additional insight into the biogeochemistry of marine sediments at that time.

54 At low temperatures (i.e., less than  $\sim 30^{\circ}\text{C}$ ), the Mg-silicate system is controlled mainly  
55 by kinetic phenomena (Evans and Guggenheim, 1988; Jones, 1986; Wollast et al., 1968), and so  
56 constraints on early diagenetic chemistry are difficult to derive based on thermodynamics alone.  
57 To address this problem, we designed a series of experiments to evaluate the effects of changing  
58 pH,  $\text{Mg}^{2+}$  and  $\text{SiO}_2(\text{aq})$  on the formation of Mg-silicates from low- $\text{SO}_4$  ( $\sim 2.8$  mmol/kg),  
59 Neoproterozoic-like seawater solutions. When these experiments and companion modeling  
60 results are coupled with stratigraphically constrained geochemical data, we are able to posit that  
61 the early diagenetic talc in Neoproterozoic carbonate successions reflects a unique combination  
62 of low siliciclastic input, near marine salinity and  $\text{Mg}^{2+}$ , elevated  $\text{SiO}_2(\text{aq})$ , and pH greater than  
63  $\sim 8.6$ - $8.7$ . In what follows, we discuss: (1) the sedimentology, geochemistry and mineralogy of  
64 the Akademikerbreen and Fifteenmile talc occurrences, (2) experimental constraints on Mg-  
65 silicate formation from modified Neoproterozoic-like seawater solutions, and (3) reports of  
66 similar mineral assemblages from other Neoproterozoic successions. Finally, we consider both  
67 the specific constraints these data place on the chemistry of waters bathing Neoproterozoic  
68 carbonate platforms and why this interval in Earth history may have favored sedimentary talc  
69 formation.

70

## 71 **2. Geologic Setting**

72 Sedimentary talc occurs in Neoproterozoic strata that crop out discontinuously over a  
73 distance of more than 140 km in the Coal Creek and Hart River inliers of the Ogilvie Mountains,  
74 Yukon (for exact locations see Macdonald and Roots, 2009). The talc is stratigraphically



75 confined to the lower Callison Lake Dolostone (unit PF2 of the Fifteenmile Group), which  
76 consists predominantly of dolomite with interbedded shale (Fig. 1 & 2) (Macdonald and Roots,  
77 2009; Macdonald et al., 2010). A tuff within the lowermost map unit of the Fifteenmile Group  
78 provides a maximum age constraint on the talc of  $811.51 \pm 0.25$  Ma; a minimum constraint  
79 comes from a  $717.43 \pm 0.14$  Ma quartz-phyric rhyolite flow in the overlying Mount Harper  
80 volcanic complex (Macdonald et al., 2010).

81 On a ridge ~10 km to the northwest of Mt. Harper, the lower Callison Lake Dolostone is  
82 well exposed and measures 77 m thick (Macdonald and Roots, 2009). Here, these strata rest  
83 unconformably on a brecciated surface of PF1 platformal carbonate and consist of a basal 2 m of  
84 channelized, sub-rounded quartz gravel conglomerate. These beds are overlain by 17 m of green  
85 and red shale and siltstone with dolomite lenses containing microbialite textures. The  
86 microbialite is draped with a ~10 cm thick bed of hematite iron formation. Above the varicolored  
87 shale and siltstone are an additional 60 m of black shale with laterally discontinuous dolomitic  
88 bioherms and abundant microbialite. However, the black shale has a peculiar waxy luster,  
89 reminiscent of phosphorite, and XRD analyses indicate that this shale consists almost exclusively  
90 of talc. The black talc-bearing shale also contains lenses of redeposited talc rip-up clasts  
91 suspended in fine-grained dolomite matrix and abundant black chert nodules. These strata are  
92 succeeded gradationally by over 300 m of silicified dolostone (Unit PF3), dominated by  
93 stromatolites, microbialaminite, and edgewise conglomerate with cm-sized coated grains,  
94 occasional exposure surfaces, and patchy silicification. These facies all suggest deposition in a  
95 shallow-water, episodically exposed, marginal marine environment.

96 The talc is stratigraphically confined and laterally persistent along the outcrop belt for  
97 over 30 km to the east to Mt. Gibben, and occurs again an additional ~110 km to the east in the

98 Hart River inlier (Abbott, 1997). This lateral extent suggests that talc deposition was at least a  
99 basin-wide phenomenon. The Fifteenmile Group has been correlated with the Little Dal Group in  
100 the Mackenzie Mountains (Macdonald et al., 2010), which has been interpreted as a marginal  
101 marine carbonate bank deposited on a rifted passive margin (Turner and Long, 2008). However,  
102 the significant unconformity recently identified at the base of the Callison Lake Dolostone  
103 suggests that it may have formed in an additional distinct basin-forming episode (Macdonald and  
104 Roots, 2009), perhaps coeval with the Coates Lake Group, which lies stratigraphically above the  
105 Little Dal Group. The Coates Lake Group was deposited in narrow, restricted grabens (Jefferson  
106 and Parrish, 1989). Although neither evaporitic minerals or pseudomorphs have been identified  
107 in the Fifteenmile Group, evaporites are present in both the Little Dal and Coates Lake groups  
108 (Jefferson and Parrish, 1989), and we cannot rule out restriction on the platform.

109         In Svalbard, mm to cm scale talc nodules occur within shallow marine carbonates of the  
110 Hunnberg Formation, Nordaustlandet, and its lateral equivalents in Spitsbergen, the upper  
111 Grusdievbreen and Svanbergfjellet formations (Fig. 2 & 3; Knoll and Swett, 1990). As in  
112 Canada, the talc deposits occur in settings ranging from coastal to subtidal environments below  
113 storm wave base and can be traced along strike for several hundred kilometers, suggesting a  
114 basin-scale phenomenon. Also as observed in Canada, cm-scale hematite layers drape microbial  
115 dolomites in the talc-bearing interval. In the Svanbergfjellet Formation, talc forms cm-scale  
116 nodules within relatively deep carbonaceous shales and carbonates. More extensive and striking,  
117 however, are rounded nodules that formed within molar tooth structures and primary voids in  
118 microbialites, in both cases before penecontemporaneous void-filling microspar cements were  
119 deposited (Fig. 3; Knoll, 1984, who mistakenly identified the talc nodules as phosphorite).

120 No radiometric dates closely constrain the age of talc-bearing Svalbard carbonates, but C  
121 and Sr isotopic chemostratigraphy and biostratigraphy suggest an age broadly comparable to that  
122 of the Ogilvie succession (Halverson et al., 2007; Knoll et al., 1986; Macdonald et al., 2010).

123

### 124 **3. Analytical and experimental methods**

125 Our sample suite was selected from the lower Callison Lake Dolostone of the Fifteenmile  
126 Group and from throughout the Akademikerbreen Group (Fig. 2; Table 1). The Fifteenmile  
127 Group samples, all from outcrop, include dolostone hosting nodular talc, bedded talc deposits,  
128 and a small horizon of iron formation. With the exception of some visible surface staining, late  
129 stage alteration/oxidation of the samples generally appears minor. Samples from the  
130 Akademikerbreen Group are predominantly from the Svanbergfjellet Formation and correlative  
131 horizons in the Hunnberg Formation, where nodular talc was identified in the field, but they also  
132 include carbonates and shales from units above and below this interval. All Svalbard samples  
133 were collected from outcrop and were chosen to capture the range of carbonate lithofacies  
134 reported in Knoll and Swett (1990). Again, late stage alteration/oxidation is minor in Svalbard  
135 samples, as documented by geochemical screens (e.g., Sr concentration, Mn/Sr, Sr/Ca and  $\delta^{18}\text{O}$ ;  
136 Derry et al., 1989).

137 Mineralogical analyses included X-ray diffraction (XRD) of  $<2\mu\text{m}$  (and in some cases,  
138  $<0.2\mu\text{m}$ ) oriented aggregates from decarbonated samples, and bulk XRD of unfractionated  
139 samples. Petrographic analysis and electron microprobe analysis of selected samples were  
140 performed using polished, carbon-coated thin sections. Further details of sample preparation and  
141 analysis are given in the Supplementary file.

142           Precipitation experiments were performed by addition of SiO<sub>2</sub>(aq) to 1 kg batches of  
143 synthetic low-SO<sub>4</sub> seawater at various Mg<sup>2+</sup>(aq) concentrations and pH. Experiments were run in  
144 water baths at 25 ±0.1°C for a minimum of 4-5 weeks to a maximum of 7 months, depending on  
145 conditions. Filtered aqueous samples were collected periodically and analyzed by ICP-AES, and  
146 residual solid precipitates were collected at experiment termination, washed and analyzed by  
147 XRD, FT-IR and TEM. Selected solid precipitates were extracted and reacted with deionized  
148 water at 180°C and 400°C to evaluate mineralogical changes in response to heating/dehydration.  
149 Further details of the experimental and analytical procedures are given in the Supplementary file.

150

#### 151 **4. Mineralogy and petrography of Neoproterozoic talc**

##### 152 *4.1 Fifteenmile Group*

153           Nodular talc samples from the Callison Lake Dolostone have three components in  
154 varying proportions: dolomite, chert, and talc. Detrital siliciclastic input is apparent only in the  
155 lower 40 m of varicolored shale and siltstone with interbedded microbial dolomite (Fig. 2). The  
156 thin horizon (~10 cm) of iron formation that drapes the microbialite is mineralogically simple,  
157 consisting of euhedral hematite grains dispersed in a dolomite matrix, with minor silicification  
158 and rare detrital quartz grains. <2µm size fractions reveal a single 7Å kaolin-serpentine group  
159 phase with trioctahedral occupancy, consistent with greenalite. The dolomite is present both as  
160 primary microbial laminations, coated grains, and as interstitial microspar cement. Talc both  
161 drapes and fills laminae within the microbialites and, along with the black chert, forms early  
162 diagenetic nodules. Bedded chert is also common. In silicified dolostones of the Callison Lake  
163 Dolostone that host nodular talc, carbonate mineralogy consists exclusively of dolomite, with no  
164 calcite indicated from powder XRD. Aside from talc, the clay mineralogy of decarbonated

165 samples indicates lesser amounts of either discrete highly crystalline illite and/or mixed layer  
166 illite/smectite. The composition of the mixed layer phases is highly consistent from sample to  
167 sample, and analyses after ethylene glycol treatment are consistent with R0 (disordered)  
168 illite(0.7)/smectite.

169         The bedded talc horizons consist predominantly of black, talc-rich shale. Thin lenses of  
170 sub-angular to sub-rounded rip-up clasts of talc supported by very fine-grained dolomite matrix  
171 are interbedded with the talc horizons. The interstitial dolomite cements between the reworked  
172 talc clasts suggest that at least some of the talc formation predates the formation of these  
173 particular cements. The mineralogy of bedded talc samples is also simple; talc overwhelms bulk  
174 analyses and clay fractions in abundance. However, two samples of bedded talc revealed  
175 subordinate amounts of discrete highly crystalline illite and mixed layer R0 illite(0.7)/smectite  
176 (Table 1). In contrast to bulk samples, oriented <2 $\mu$ m size fractions of bedded talc indicate that  
177 no mixed layering is apparent. In other words, the talc is present as a discrete mineral phase. No  
178 other Mg-silicates were identified in any bulk or <2 $\mu$ m fractions from Fifteenmile Group  
179 samples (Fig. 4). Randomly oriented specimens of the <2 $\mu$ m clay fraction further indicate that  
180 the talc exhibits a high degree of stacking disorder; it is essentially turbostratic. A number of *hkl*  
181 peaks are significantly modulated, particularly in the 20-25 degree and 30-45 degree range. This  
182 type and extent of disordering is present in all of the Fifteenmile talc occurrences.

183         The carbonate overlying the talc horizons consists of silicified dolomite with microbial  
184 lamination, coated grains, and abundant stromatolites. Void-filling cements consist  
185 predominantly of dolomite and silica. Decarbonated samples from these strata also yielded talc  
186 with lesser amounts of discrete illite and mixed layered illite/smectite. The talc in these samples

187 is distributed throughout the carbonate matrix and not as nodules or other conspicuous  
188 sedimentary features otherwise resolvable by petrographic analysis.

189

#### 190 *4.2 Akademikerbreen Group*

191 Akademikerbreen talc occurs as mm- to cm-scale nodules and disseminated particles in  
192 the <2 $\mu$ m fraction of the carbonate matrix. Talc nodules fill molar tooth structures, primary void  
193 space in microbialites and intergranular space, predating precipitation of penecontemporaneous  
194 microspar cement. In general, nodules are petrologically homogeneous; there are no discernable  
195 nuclei nor is chemical zoning evident (Fig. 3).

196 Powder XRD of isolated and cleaned nodules hand picked from Akademikerbreen  
197 carbonates shows the same type and extent of layer stacking disorder as in the Fifteenmile talc  
198 samples (Fig. 5). That is, the Akademikerbreen talc is also highly turbostratic. XRD patterns  
199 again display modulated and/or extinguished *hkl* reflections in the 20-25 and 30-45 degree 2 $\Theta$   
200 ranges. Aside from talc, the carbonate mineralogy frequently includes ankerite in addition to  
201 dolomite and lesser amounts of calcite.

202 The clay mineralogy of decarbonated Akademikerbreen samples shows more variation  
203 among the Mg-silicates. Analyses of decarbonated residues reveal talc in the carbonate matrix in  
204 some samples where nodules are not apparent. The talc again shows no evidence of mixed  
205 layering or occurrences with other low temperature Mg-silicates such as sepiolite or palygorskite.  
206 However, saponite (a Mg-rich trioctahedral smectite) and its burial diagenetic equivalents, mixed  
207 layered chlorite/smectite and corrensite, have all been identified (Fig. 4; Table 1; Supplementary  
208 file).

209 In addition to Mg-silicates, Akademikerbreen clay fractions contain varying amounts of  
210 discrete highly crystalline illite, illite/smectite (most of which corresponds to R1  
211 illite(0.7)/smectite), kaolinite, and, in one sample only, chlorite. In general, the results  
212 summarized in Table 1 show that samples containing talc and other associated Mg-silicates  
213 consistently lack illite, I/S, and kaolinite. The reverse is also true: aluminous clay mineral  
214 assemblages are rarely accompanied by talc.

215 The Svanbergfjellet, Draken and Backlundtoppen Formations also contain discrete  
216 siliciclastic horizons that represent detrital pulses into the carbonate platform (Butterfield et al.,  
217 1994; Knoll and Swett, 1990). The clay mineralogy of these horizons is dominated by illite and  
218 kaolinite in the <2 $\mu$ m fraction; the <0.2 $\mu$ m fraction is composed almost entirely of discrete illite,  
219 with significant defect broadening.

220

#### 221 *4.3 Fifteenmile and Akademikerbreen Group Mg-silicate occurrences: Summary*

222 Sedimentology and petrology indicate that talc formed during early diagenesis, perhaps  
223 penecontemporaneously, in both the Akademikerbreen and the Fifteenmile Groups. In both  
224 environments the clay mineralogy also indicates that talc generally occurs in environments that  
225 received low background siliciclastic flux, and where alumino-silicates are present, talc has not  
226 been identified.

227 Saponite, chlorite/smectite and corrensite in Akademikerbreen carbonates, all indicate  
228 that saponite formed during early diagenesis and was transformed to chlorite-rich mineral species  
229 upon burial and late-stage alteration. Because there is little evidence for mafic input to the  
230 Akademikerbreen platform, saponite formation suggests that the initial deposition of smectite  
231 (originally as a dioctahedral smectite such as montmorillonite), or some other detrital precursor,

232 initiated a recrystallization/transformation to trioctahedral saponite, likely in response to  
233 favorable aqueous chemistry associated with the platformal carbonates (discussed below).

234 Samples from the Fifteenmile Group, on the other hand, yield very little decarbonated  
235 residue and show little variation in background siliciclastic component; they are dominated by  
236 highly crystalline illite (muscovite) and illite/smectite. Together this implies very low  
237 background detrital fluxes and negligible input of terrigenous clay beyond detrital muscovite.

238 The sedimentology, petrography and mineralogy of these deposits are indicative of  
239 unusual aqueous chemistry associated with platformal carbonates that facilitated the early  
240 diagenetic precipitation of Mg-silicates, whether talc or a precursor phase, from solution. What  
241 drove these reactions during Akademikerbreen and Fifteenmile Group deposition?

242

## 243 **5. Constraints from Mg-silicate precipitation experiments**

244 To better understand what chemical environment is required to initiate the precipitation  
245 of Mg-silicates, we performed a systematic series of experiments interrogating the role of  
246  $\text{SiO}_2(\text{aq})$  and pH on talc formation. We incubated one liter batches of standard, “modern”  
247 synthetic seawater at various  $\text{SiO}_2(\text{aq})$  concentrations and pH, monitoring the bottles for both  
248 precipitation of solid phases and changes in aqueous chemistry. In certain experiments, a visible  
249 precipitate formed within the first 48 hours. The precipitate often clouded the solution before  
250 flocculating and, eventually, settled to the bottom of the reaction vessel. In other experiments, no  
251 precipitate was formed over > 7 months.

252 When the experimental conditions favored precipitation, XRD analyses on randomly  
253 oriented powders showed broad and poorly resolvable *hkl* bands and no 001 reflections (Fig. 5).  
254 All XRD analyses showed weak bands at  $d = 1.55$  to  $1.52\text{\AA}$ , indicating the presence of



255 trioctahedral layers, and all *hkl* bands were reproducible from experiment to experiment,  
256 displaying little variation in their relative intensity and *d*-spacing. In only one case, the  
257 experiment conducted at the highest pH, a precipitate gave broad low-angle reflections  
258 corresponding to *d*-spacings of 28.7, 13.9 and 10.4 Å. With the exception of the highest pH  
259 experiment, the structure of the precipitate is both insoluble and reproducible from experiment to  
260 experiment. Perhaps most striking, however, is the observation that the precipitate only formed at  
261 a pH of 8.66 and above, implicating pH as a major control on Mg-silicate precipitation.

262         Although XRD data show poorly crystalline products, FT-IR spectra indicate that the  
263 experimental precipitates are almost identical to talc. The close correspondence between Mg-O  
264 vibrations from the precipitates and lattice vibrations from talc (including the diagnostic 535 cm<sup>-1</sup>  
265 <sup>1</sup> (Mg-O)-OH feature (Farmer, 1974; Zhang et al., 2006)) reflect a similar bonding environment  
266 for Mg (Fig. 6). Absorptions at ~1020 cm<sup>-1</sup> show the same bonding arrangement for SiO<sub>4</sub>  
267 tetrahedra: a 2:1 layered configuration of tetrahedral silicate layers and octahedral MgO<sub>6</sub> layers  
268 (Fig. 6). A trioctahedral occupancy (consistent with XRD peaks at 1.55-1.52 Å), manifested by  
269 the OH-stretching vibration at ~3676 cm<sup>-1</sup>, is also evident for both the precipitates and for talc  
270 standards. However, the lack of an observable basal 001 reflection in oriented XRD patterns  
271 suggests that there is little to no stacking order between TOT sheets, perhaps due to variable  
272 interlayer/surface hydration (consistent with absorptions at ~1630 and ~3400 cm<sup>-1</sup> indicating  
273 appreciable bound molecular H<sub>2</sub>O). Taken together, XRD, FT-IR and TEM data (shown in the  
274 Supplemental File) indicate the experimental precipitates are simply a hydrated, disordered form  
275 of talc; they are composed of 2-dimensional talc TOT sheets not neatly stacked as in true talc,  
276 but organized similar to a pile of bricks loosely cemented with water of hydration.

277 To ascertain the effects of mild heating on poorly crystalline Mg-silicate precipitated  
278 from modified seawater solutions, we also performed experiments involving the hydrothermal  
279 treatment of poorly crystalline Mg-silicate (the products of precipitation experiments) in the  
280 presence of deionized water. After 4 weeks of reaction at 180°C, the poorly crystalline Mg-  
281 silicate transformed to kerolite ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ), a distinct mineral phase and hydrated  
282 structural analog of talc (Fig. 5). The final product exhibited an apparent  $d(001)$  of 9.9 Å and  $hkl$   
283 peaks that correspond to the kerolite structure discussed in Brindley et al. (1977). Combined  
284 XRD, FT-IR and TEM data indicate that simple dehydration -- in this case, in response to  
285 temperature increase -- drives the transformation from poorly crystalline Mg-silicate to the  
286 mineral kerolite. Further heating at elevated temperature or over long timescales in turn causes  
287 additional dehydration and experiments conducted at 400°C and 1kbar show that this dehydration  
288 drives the transition from kerolite to talc (and minor cristobalite) (Fig. 5). The talc produced  
289 from this process exhibits significant turbostratic ordering and powder diffraction data show  
290 similar peak modulation to Neoproterozoic talc samples discussed above.

291

## 292 **6. Discussion**

### 293 *6.1 Mg-silicate system at low temperature*

294 Present-day seawater is supersaturated with respect to crystalline talc, yet modern and  
295 even ancient environments lack authigenic talc (Fig. 7). Like in the case of carbonate  
296 precipitation, there must exist a kinetic barrier to talc precipitation; a barrier that we can address  
297 through experimental interrogation. Our data and ensuing discussion allow talc precipitation to  
298 be reconstructed in an environmentally tuned, step-wise fashion.

299 Previous experimental work has targeted talc precipitation from modern-like seawater,  
300 and presents contrasting results to those described herein. Wollast et al. (1968) spiked filtered  
301 modern seawater with sodium metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) at 25°C and precipitated a Mg-  
302 silicate phase at  $\text{pH} > 8.3$ . The Mg-silicate was described as “poorly crystalline sepiolite” on the  
303 basis of FT-IR and XRD -- a phase not identified in any of our experiments. In addition, the  
304 apparent solubility calculated from their experiments is lower than the experiments described  
305 here (Fig. 7), implying a lower degree of supersaturation needed for precipitation. Upon closer  
306 inspection, however, the Mg-silicate precipitated by Wollast et al. (1968) is not inconsistent with  
307 our results. In fact, their FT-IR and XRD analyses also lack the most diagnostic features of  
308 sepiolite, including the 12 Å and 7.5 Å diffraction peaks and a Si-O feature in FT-IR attributed to  
309  $\text{Q}_3$  bonding of silica tetrahedra in chain silicates (Russell and Fraser, 1994). However, their  
310 material also appears to exhibit FT-IR features that ours does not.

311 Aside from the identity of the initial precipitate, there also remains a clear discrepancy in  
312 the literature in the aqueous conditions needed to initiate precipitation. To address this, we  
313 duplicated some of the experiments conducted by Wollast et al. (1968) using a synthetic  
314 “modern” seawater solution at elevated  $\text{SiO}_2(\text{aq})$ . The only difference is the nature of the silica  
315 source: TEOS solutions in experiments described here versus sodium metasilicate solutions in  
316 Wollast et al. (1968). The results show that Mg-silicate formation does not occur until higher  
317 levels of supersaturation than those reported by Wollast et al. (1968) and that the initial  
318 precipitate is a known kerolite precursor. We argue that the difference in silica source may well  
319 be critical. We have taken precautions to ensure that  $\text{SiO}_2(\text{aq})$  added to seawater solutions was  
320 equilibrated in the monomeric form prior to the addition of  $\text{MgCl}_2$  (Dietzel, 2000; Iler, 1979). In  
321 contrast, sodium metasilicate solutions are known to polymerize rapidly and form colloidal

322 material upon dilution (Iler, 1979), perhaps in response to decreasing silica levels and/or rapid  
323 changes in pH associated with their preparation. Thus, it is possible that the addition of  
324 metasilicate solutions to seawater solutions co-precipitated silica with  $Mg^{2+}$  in a way that may  
325 not be truly representative of natural surface environments. This is a complication avoided in  
326 our experiments through the use of TEOS as a  $SiO_2(aq)$  source.

327

## 328 *6.2 Mg-silicate formation: pH as a master variable*

329 To assess what special combination of  $Mg^{2+}$ ,  $SiO_2(aq)$  and pH results in Mg-silicate  
330 precipitation, we ran experiments varying  $Mg^{2+}$  concentrations (by 10 times over modern  
331 seawater) and at variable pH (Fig. 7). As discussed above, raising  $SiO_2(aq)$  alone was  
332 insufficient to drive precipitation. In fact, our experiments identify pH as the primary control on  
333 Mg-silicate formation. At a  $pH_f$  of 8.0, we observed no precipitation over the course of the  
334 experiment. Within error,  $SiO_2(aq)$  levels remained unchanged for > 5 months with no sign of  
335 precipitation. In contrast, the same  $Mg^{2+}$  and  $SiO_2(aq)$  at elevated pH resulted in the rapid  
336 precipitation of Mg-silicate on the timescale of days, suggesting that despite exceedingly high  
337  $Mg^{2+}$  levels, pH appears to be the primary control on Mg-silicate formation from seawater-  
338 derived solutions.

339 Solution chemistry at experiment termination tells a similar story. Relationships between  
340  $SiO_2(aq)$  loss and  $pH_f$  reveal a sharp speciation boundary for  $SiO_2(aq)$  at ~8.6-8.7 (Fig. 8).  
341 Below this threshold,  $SiO_2(aq)$  is unchanged within analytical error (compared to “blank”  
342 experiments conducted in the absence of  $MgCl_2$ ). At  $SiO_2(aq)$  concentrations between  
343 amorphous silica and quartz saturation, the dominant silica species in seawater is monomeric  
344 silica;  $H_4SiO_4^0$ . As pH is increased above ~8.5,  $H_4SiO_4^0$  deprotonates, favoring  $H_3SiO_4^-$  (Fig. 9).

345 As a result, at these higher pH values, the concentration of a Mg-silica complex ( $\text{MgH}_3\text{SiO}_4^+$ )  
346 increases sharply. The  $\text{MgH}_3\text{SiO}_4^+$  species alone is probably not representative of all possible  
347 aqueous Mg-silica complexes in solution, especially given the complexity of silica speciation  
348 revealed by NMR (Felmy et al., 2001). Nevertheless, the stability constant for this species  
349 (derived from actual potentiometric measurements of  $\text{SiO}_2(\text{aq})$  and Mg-bearing solutions at  
350 various pH and high salinity) shows that regardless of actual species distribution, the pH  
351 dependence of Mg-silica complexing is well represented by  $\text{MgH}_3\text{SiO}_4^+$  (Santschi and Schindler,  
352 1974).

353 It is possible that at low pH, the rate of crystallization is too slow to be observed.  
354 However, the idea of a minimum pH for Mg-silicate formation is well supported by previous  
355 synthesis experiments. For example, Siffert and Wey (1962), using dilute  $\text{MgCl}_2$  solutions and  
356 monomeric  $\text{SiO}_2(\text{aq})$ , precipitated “true” sepiolite at pH >8.5. At pH >9, talc and stevensite  
357 formed. Abtahi (1985) and La Iglesia (1978) obtained similar results. The same trends have been  
358 observed by workers synthesizing “Mg-silicate hydrate” for industrial applications, with some  
359 citing a canonical pH for “Mg-silicate scale” formation of ~8.5 (Brew and Glasser, 2005a; Brew  
360 and Glasser, 2005b; Delacailierie et al., 1995; Mizutani et al., 1990; Packter, 1986; Strese and  
361 Hofmann, 1941; Takahashi et al., 1994; Wei and Chen, 2006).

362  $\text{MgH}_3\text{SiO}_4^+$  and similar species are, in turn, the solution precursors to Mg-silicate  
363 precipitates (Packter, 1986). Theoretical treatments of layer silicate nucleation from solution  
364 require that an excess surface energy barrier be overcome by a critical supersaturation of a pre-  
365 existing solution complex (Carrado et al., 2006). The critical supersaturation barrier to initiate  
366 Mg-silicate formation, then, must occur close to pH 8.6-8.7. Below this point, speciation  
367 calculations show that aqueous Mg-silicate complexes, while present, are unlikely to be

368 concentrated enough to initiate the nucleation of a silicate phase; deprotonated silica species  
369 would be kept to scant amounts in solution, preventing appreciable interaction with  $Mg^{2+}$ . This  
370 strong kinetic control on Mg-silicate precipitation from seawater is reminiscent of the more  
371 familiar problem of  $CaCO_3$  precipitation from modern surface seawater. For both systems,  
372 despite a clear thermodynamic driving force, a critical level of supersaturation is required. For  
373 Mg-silicates, deprotonation of  $H_4SiO_4^0$  at elevated pH appears to be the “switch” that enables  
374 Mg-silica complexing, in turn driving Mg-silicate nucleation and precipitation.

375

### 376 *6.3 Burial diagenesis and turbostratic stacking disorder in talc*

377 The sedimentary record of authigenic Mg-silicates can be related to solution chemistry  
378 only with knowledge of thermal transformations possible during burial diagenesis. Our  
379 hydrothermal experiments run with poorly crystalline Mg-silicates precipitated from seawater  
380 show that upon dehydration, the material readily transforms to kerolite. Previous work has  
381 shown that with continued dehydration, either with time or at increased temperature, kerolite, in  
382 turn, transforms to crystalline disordered talc (Mitsuda and Taguchi, 1977). Our heating  
383 experiments with kerolite confirm these observations and show that the talc formed by  
384 dehydrating kerolite exhibits severe layer stacking disorder identical to the disorder observed in  
385 Akademikerbreen and Fifteenmile samples (Fig. 5).

386 Stacking disorder in talc is not uncommon. In fact, it results from an inherently weak  
387 electrostatic charge between 2:1 layers (Giese, 1975). The disorder observed in our samples is  
388 best matched by ordered stacking of 2:1 layers by  $a/3$  along one of the pseudo-hexagonal axes,  
389 with random displacements of  $\pm b/3$  along another (Gualtieri, 1999). It is not clear why this type  
390 of disordering results, but as others have noted, it may well be controlled by the pathway of

391 crystallization (in this case, dehydration) rather than solid state transformation (Baronnet, 1992;  
392 Kogure and Kameda, 2008). Specifically, the 2:1 layer dehydration mechanism of the low  
393 temperature precipitate, which initiates stacking to form kerolite and, in turn, talc, may well exert  
394 the most control on the type of disorder that results from this pathway. Nevertheless, this poorly  
395 understood feature is present in all Neoproterozoic samples, consistent with low temperature  
396 precipitation and subsequent dehydration during burial.

397         Although there are no direct temperature constraints on the samples described herein,  
398 Neoproterozoic strata in the Yukon are relatively low-grade for rocks of their age. Regionally,  
399 conodont alteration indices and vitrinite reflectance from the overlying Paleozoic strata suggest  
400 these rocks have not seen more than 140 °C (Van Kooten et al., 1997). A similar thermal history  
401 of the Svalbard samples is suggested by paleomagnetic studies in which demagnetization  
402 experiments removed a Caledonian thermochemical remnant magnetization at 150 °C (Maloof et  
403 al., 2004). Moreover, the orange-brown color of preserved organic matter in the  
404 Akademikerbreen Group indicates that the degree of graphitization and maximum burial  
405 temperatures were modest. In reconciling these constraints with experimental data discussed  
406 above, it is important to note that we have used elevated temperature (up to 400°C) purely to  
407 observe the dehydration of poorly crystalline Mg-silicate to kerolite and eventually to talc on  
408 convenient laboratory timescales. However, this transition is known to occur in response to  
409 lower temperature and longer reaction time (Mitsuda and Taguchi, 1977). Indeed, if the kinetics  
410 of the Mg-silicate dehydration reaction were to behave in a similar fashion to other burial  
411 diagenetic reactions involving clay minerals, the dehydration of poorly crystalline Mg-silicate to  
412 talc could, for example, take as little as 10<sup>5</sup> years at ~80°C (Velde, 1985).

413

414 *6.4 Mg-silicate formation on Neoproterozoic carbonate platforms*

415 Taken together, experimental data indicate that low temperature talc formation in  
416 association with carbonates requires: (1) elevated  $\text{SiO}_2(\text{aq})$ , between quartz and amorphous silica  
417 saturation; (2) sufficient (at least “modern”)  $\text{Mg}^{2+}$ ; (3) near marine salinity; (4) low Al (i.e., a  
418 low background detrital flux, see below) and (5) elevated pH of at least  $\sim 8.7$ .

419 One key requirement for talc precipitation that we have yet to discuss is low Al, requiring  
420 that detrital fluxes were low during deposition of the talc-bearing intervals in the  
421 Akademikerbreen and Fifteenmile groups. As  $\text{Al}^{3+}$  increases in concentration, talc, a nominally  
422 Al-free mineral, is no longer stable, being replaced instead by Al-bearing smectites, chlorites,  
423 palygorskite or other minerals depending on local pore water chemistry and sediment supply  
424 (Jones, 1986; Jones and Galan, 1988; Weaver and Beck, 1977). Low detrital fluxes have been  
425 episodic features of carbonate platform environments throughout recorded Earth history, and  
426 don't place a unique chemical constraint beyond that discussed. Thus, our mineralogical  
427 observations of low siliciclastic flux in talc-bearing facies of the Akademikerbreen and  
428 Fifteenmile successions helps to explain the distribution of early diagenetic talc in space but not  
429 in time.

430 The requirement of elevated  $\text{SiO}_2(\text{aq})$  concentration was also readily met in  
431 Neoproterozoic seawater. Indeed, prior to the evolution of silica skeletons in sponges,  
432 radiolarians and diatoms, Precambrian seawater should have carried higher silica concentrations  
433 relative to modern levels (Maliva et al., 2005). Consistent with this expectation, early diagenetic  
434 chert in Neoproterozoic carbonate successions, largely from peritidal or possibly mildly  
435 evaporitic environments, provides evidence for local pore water enrichment in  $\text{SiO}_2(\text{aq})$  on  
436 shallow water platforms (Maliva et al., 2005). The Akademikerbreen Group abounds with



437 evidence for early diagenetic silicification (e.g., Fairchild et al. 1991; Knoll, 1984; Knoll and  
438 Swett, 1990). Fifteenmile Group samples are also heavily silicified, but record a more complex  
439 history of silicification (Mustard and Donaldson, 1990).

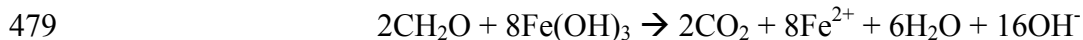
440         The Akademikerbreen and Fifteenmile Groups were likely deposited on marginal to  
441 isolated marine platforms (Knoll and Swett, 1990; Macdonald et al., 2010). Near marine salinity  
442 (~35‰) and  $Mg^{2+}$  concentrations are consistent with these settings, yet the salinity and  $Mg^{2+}$   
443 content of Proterozoic seawater is poorly constrained. Oolites in the Akademikerbreen Group  
444 provide petrographic and geochemical (high Sr) evidence for an aragonite sea at the time of their  
445 deposition, suggesting that contemporaneous seawater may have had  $Mg^{2+}$  concentrations  
446 broadly similar to those observed today (Swett and Knoll, 1989). Although no evaporite minerals  
447 or their associated pseudomorphs have been identified in either succession, episodic restriction in  
448 the Akademikerbreen and Fifteenmile Groups cannot be ruled out. On the other hand, seawater  
449 evaporation should *decrease* pH (e.g., McCaffrey et al., 1987), which is inconsistent with the  
450 stability of talc.

451         Talc formation by meteoric mixing faces a similar constraint, as freshwater influx would  
452 tend to drive pH below marine values. Additionally, salinity would further decrease in response  
453 to post-depositional meteoric influx. Higher water activity (or lower salinity) favors the  
454 precipitation of Mg-silicates of higher hydration, namely sepiolite. Lower water activity (or near  
455 normal marine salinity), on the other hand, favors kerolite and/or other 2:1 silicates, and  
456 synthesis work reinforces these constraints (Jones and Galan, 1988; Siffert and Wey, 1962;  
457 Stoessell and Hay, 1978). Mg-silicate occurrences in peri-marine and lacustrine environments  
458 also conform to this trend, so well, in fact, that Mg-silicate assemblages have been used to track  
459 salinity fluctuations and the influence of meteoric water in a number of modern and ancient

460 settings (Calvo et al., 1999; Jones, 1986; Stoessell and Hay, 1978; Weaver and Beck, 1977;  
461 Webster and Jones, 1994).

462 Of all the requirements for early diagenetic talc formation, elevated pH ( $\geq \sim 8.7$ ) is the  
463 most problematic, given the difficulty of increasing seawater pH, which is largely buffered by  
464 the carbon cycle, to the required level. The more realistic alternative is to increase pH in pore  
465 waters via microbial processes. Elevated pH can be achieved through certain microbial reactions  
466 that remineralize organic matter, a set of processes that need not have decreased salinity,  $Mg^{2+}$   
467 and/or  $SiO_2(aq)$  levels. Both the Akademikerbreen and Fifteenmile talc deposits are intimately  
468 associated with microbial facies: bedded talc drapes occur with microbialaminites and  
469 stromatolites in Fifteenmile samples, and both localities host talc nodules within microbialites.

470 Anaerobic respiration is a particularly attractive mechanism for increasing pH. In a  
471 Neoproterozoic world with low  $pO_2$  and no macrometazoan bioturbation, anoxia would have  
472 been a common feature of early diagenetic carbonate sediments. Given the additional likelihood  
473 that nitrate levels were also low (Fennel et al., 2005), ferric iron and sulfate would have been the  
474 most energetically favorable oxidants available for organic carbon remineralization, with  $Fe^{3+}$   
475 favored over  $SO_4^{2-}$  (Canfield et al., 2005). Under conditions where the reactive Fe flux was high,  
476 (perhaps ultimately sourced from hydrothermal Fe fluxes rather than detrital input in these  
477 sediment-starved environments) dissimilatory Fe reduction would have been particularly  
478 effective at increasing pH through the following reaction:



480 When the reactive Fe pool was kept low, either by exhaustion of reactive  $Fe^{3+}$  or by pyrite  
481 precipitation (Johnston et al., 2010; Lyons and Severmann, 2006), sulfate reduction would have  
482 contributed to a pH increase in solution:



484 Fe-speciation and isotopic analyses of other early Neoproterozoic successions indicate that these  
485 two metabolic pathways strongly influenced marine chemistry in both basinal and platform  
486 settings, with organic carbon fluxes and variations in basinal Fe and S cycles controlling the  
487 balance between them (Canfield et al., 2008; Johnston et al., 2010; Johnston et al., 2009). But  
488 regardless of the interplay between different types of anaerobic respiration, both pathways would  
489 have resulted in a pH increase without changes in other conditions needed for talc precipitation.  
490 Pore waters in microbially-dominated sediments would have been especially susceptible to pH  
491 increase driven by anaerobic respiration, where higher sediment to pore-water ratios favored  
492 more effective changes in chemistry

493 In addition to the Svalbard and Canadian occurrences described here, sedimentary (oolitic)  
494 talc has been reported in association with stromatolitic dolomites in an Infracambrian  
495 (Neoproterozoic) succession of the Volta Basin of West Africa (Millot and Palausi, 1959). The  
496 authors argue from petrographic analyses that talc formation preceded dolomitization and  
497 silicification. Noack et al. (1989) also reported oolitic talc in the Schisto-Calcaire Group of the  
498 West Congo Basin. Overlying the Upper Diamictite Formation, Schisto-Calcaire carbonates have  
499 strontium isotope values of 0.7073 (Frimmel et al., 2006; Poidevin, 2007), consistent with a  
500 Cryogenian age (716-635 Ma). The sedimentology of the Schisto-Calcaire Group has been  
501 interpreted to reflect alternately shallow marine and lagoonal conditions, separated from outer  
502 subtidal regions of the platform by stromatolitic reefs (Trompette and Boudzoumou, 1988).  
503 Noack et al. (1989) interpret the talc to have formed by transformation from stevensite or  
504 sepiolite on the basis of thermodynamic considerations. This interpretation is not incompatible  
505 with ours; stevensite precipitation is generally only observed from synthesis studies at high pH

506 and near marine salinity (La Iglesia, 1978; Siffert and Wey, 1962). We have not conclusively  
507 identified stevensite in our experiments, but have identified a corrensite-like phase forming with  
508 talc at high pH. Corrensite formation at low temperature requires the initial formation of a  
509 stevensite-like smectite into which brucite-like layers are precipitated (Reynolds, 1988).

510         The apparent concentration of low temperature talc deposits in mid-Neoproterozoic  
511 carbonate platforms may find explanation in the superposition of Neoproterozoic-specific  
512 environmental conditions on the broader set of requirements (low detrital influx, high silica, low  
513 oxygen, sufficient Mg, efficient sulfide scavenging (Ben-Yaakov, 1973)) likely to have  
514 characterized Precambrian carbonate platforms in general. Fe speciation chemistry indicates that  
515 iron played a more important role in organic remineralization after 800 million years ago than it  
516 did earlier in the Proterozoic Eon (Canfield et al., 2008; Johnston et al., 2010). Also, the  
517 hypothesized shift from a Mesoproterozoic biosphere with warm, high pCO<sub>2</sub> atmosphere with  
518 high seawater DIC to a more glacial-prone later Neoproterozoic world with lower pCO<sub>2</sub> and DIC  
519 would further have eased chemical resistance to increases in pore-water pH in Neoproterozoic  
520 carbonate platforms (Kah and Bartley, 2004). During deposition of the Akademikerbreen and  
521 Fifteenmile Groups, anaerobic respiration in microbial sediment receiving little terrigenous input  
522 provided a fortuitous combination of chemistry and depositional conditions to increase pH and  
523 precipitate authigenic Mg-silicate at near marine salinity. The subsequent burial of this material  
524 would have driven a thermal transformation to kerolite and eventually to turbostratically-  
525 disordered talc.

526         Talc is not the only product to result from unusual pore water chemistry on  
527 Neoproterozoic platforms. As discussed above, the identification of saponite, an Al-bearing  
528 trioctahedral smectite, suggests additional diagenetic reactions. In the absence of kinetic

529 constraints, but instead using thermodynamic considerations based on field data, Weaver and  
530 Beck (1977) suggest modern seawater need only increased  $\text{SiO}_2(\text{aq})$  and/or pH to drive a  
531 diagenetic conversion from detrital montmorillonite to saponite. Thus, the same chemical  
532 conditions that led to talc precipitation were also capable of driving smectite recrystallization.  
533 Bristow et al. (2009) identified saponite (and corrensite) in Member 2 of the Ediacaran  
534 Doushantuo Formation and suggested a lacustrine depositional environment. Our data, however,  
535 show that early diagenetic modification of Neoproterozoic seawater is also capable of producing  
536 saponite. Thus, in the absence of independent sedimentological evidence of non-marine  
537 deposition, saponite cannot be taken as evidence for lacustrine deposition in Neoproterozoic  
538 successions. Indeed, the common occurrence of saponite in modern lacustrine settings rather than  
539 marine may simply reflect decreased seawater silica levels after the radiation of siliceous  
540 plankton in addition to lower modern marine pH. This evolutionary innovation alone would have  
541 been sufficient to leave modern saline lakes among the few environments able to concentrate and  
542 drive saponite formation from a dioctahedral precursor.

543

## 544 **7. Conclusions**

545 Sedimentology, petrography and mineralogy all indicate that sedimentary talc reflects  
546 distinct aqueous chemistry recorded on two separate Neoproterozoic carbonate platform margins.  
547 Precipitation experiments with modified “Neoproterozoic-like” seawater show that elevated  
548  $\text{SiO}_2(\text{aq})$ , normal marine salinity and  $\text{Mg}^{2+}$  levels, and low  $\text{Al}^{3+}$  all favor talc formation. However,  
549 the switch that enables talc nucleation is elevated pH. Above pH 8.6-8.7, the deprotonation of  
550  $\text{H}_4\text{SiO}_4^0$  initiates Mg-silica complexation and nucleation, which leads to the subsequent  
551 formation of a kerolite precursor composed of hydrated 2:1 layers with little to no stacking order.

552 The progressive dehydration of this material, driven by low water activity in solution or by burial  
553 diagenesis, leads to the formation of kerolite and eventually turbostratic talc.

554 Our analyses, together with other reports of sedimentary talc through this interval,  
555 suggest that the later Neoproterozoic Era seawater unusually favorable for early diagenetic talc  
556 precipitation. Although we argue that talc precipitation was occurring within the sediment,  
557 contemporaneous seawater must have been specially poised, only requiring reasonable changes  
558 to chemistry within the pore-waters. Following from this, we suggest that anaerobic respiration  
559 may have provided the alkalinity pump that tipped the scales toward talc formation in soft  
560 sediments. The degree to which sedimentary processes altered overlying seawater, neither of  
561 which are known uniquely, hinders direct interpretation of paleo-seawater compositions and pH.  
562 Further, whether the Neoproterozoic was the first and last time talc formed with marine  
563 carbonates at low temperature is unclear, but its identification of multiple continents speaks to  
564 the state of the Cryogenian oceans. This study does elucidate that insight into seawater and pore-  
565 water chemistry is clearly recorded by early diagenetic Mg-silicates. An improved understanding  
566 of the kinetic and thermodynamic controls behind their formation will continue to exploit these  
567 minerals as recorders of early diagenetic chemistry in modern and ancient marine and lacustrine  
568 settings.

569

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577

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768

769 **Figure captions**

770 **Figure 1.** Bedded and nodular talc interbedded with microbialite in the Callison Lake Dolostone,  
771 Ogilvie Mountains, Yukon.

772

773 **Figure 2.** Stratigraphic sections of the Fifteenmile and Akademikerbreen talc-bearing deposits.

774

775 **Figure 3.** Void-filling talc nodules (in outcrop (A) and thin section (B) under cross-polarized  
776 light) formed in dolomitic stromatolite of the Hunnberg Fm, Nordaustlandet, Svalbard. The talc  
777 in (B) (orange-brown) appears penecontemporaneous with void-filling microspar cement.

778  
779 **Figure 4.** XRD patterns of oriented aggregates of the  $<2\mu\text{m}$  fraction extracted from talc-bearing  
780 rocks. Black lines indicate scans acquired in the air-dried (Ca-saturated) state and red lines  
781 indicate scans acquired in the EG-solvated state. (A) Talc from unit PF2 (U. Fifteenmile Group;  
782 F927-58m) (B) Talc, saponite, and chlorite/smectite from the Hunnberg Fm (K2016). (C)  
783 Saponite and illite/smectite from the Hunnberg Fm (HU1246). (D) Trioctahedral low-charge  
784 corrensite from the Svanbergfjellet Fm (86-G-3).

785  
786 **Figure 5.** Representative powder XRD patterns of randomly-oriented experimental precipitates  
787 formed by (A) low temperature precipitation from modified seawater, (B) heating a low  
788 temperature precipitate at  $180^{\circ}\text{C}$  for 4 weeks, (C) heating the precipitate from (B) at  $400^{\circ}\text{C}$  for 4  
789 days. For comparison, a cleaned talc nodule from the Svanbergfjellet Fm is shown (D),  
790 indicating extensive layer stacking disorder. “C” = cristobalite; “D” = dolomite.

791  
792 **Figure 6.** FT-IR spectra of experimental Mg-silicate precipitates (black) in comparison to talc  
793 collected from the Svanbergfjellet Fm (red). (A) Lattice vibration region, (B) Si-O stretching  
794 region, (C)  $\text{H}_2\text{O}$  and  $\text{CO}_3$  region, (D) OH stretching region.

795  
796 **Figure 7.** Solubility diagram showing the equilibrium solubilities of crystalline talc (Jones,  
797 1986), kerolite and sepiolite (Jones and Galan, 1988), “amorphous sepiolite” from Wollast et al.



798 (1968) and the equilibrium boundary between montmorillonite and saponite from Weaver and  
799 Beck (1978). Data points represent *apparent solubilities* calculated from solutions collected upon  
800 experiment termination. Experiments that have resulted in Mg-silicate precipitate form an  
801 apparent boundary approximately parallel to kerolite and/or sepiolite, but these data do not  
802 represent true equilibrium conditions with respect to either of these crystalline phases. Green  
803 point represents experiment at elevated Mg and  $\text{pH}_f = 8.0$  where no precipitate formed.

804

805 **Figure 8.**  $\text{SiO}_2(\text{aq})$  loss as a function of final pH showing the sharp pH control on Mg-silicate  
806 precipitation. Process blank experiments conducted with no  $\text{MgCl}_2(\text{aq})$  indicate that one  
807 experiment ( $\text{pH}_f \sim 9.2$ ) has resulted in  $\text{SiO}_2(\text{aq})$  loss that cannot be explained by experimental  
808 artifacts alone and suggests the formation of a precipitate that was unable to be extracted for  
809 analysis.

810

811 **Figure 9.** Thermodynamic calculations of  $\text{SiO}_2(\text{aq})$  species distribution in “Neoproterozoic-like”  
812 seawater as a function of pH. The sharp pH control on the  $\text{MgH}_3\text{SiO}_4^+$  species represents the  
813 effect of pH on potential nucleation of Mg-silicate from seawater at elevated  $\text{SiO}_2(\text{aq})$ . Initial  
814  $\text{SiO}_2(\text{aq}) = 60 \text{ mg/kg}$  and initial  $\text{SO}_{4\text{T}} = 2.8 \text{ mmol/kg}$ . Charge balance was satisfied by  
815 readjustment of  $\text{CO}_2\text{-HCO}_3\text{-CO}_3$  equilibria in an open system with respect to  $\text{CO}_2(\text{g})$ . All mineral  
816 precipitation was suppressed.

**Figure 1.**



**Figure 2.**

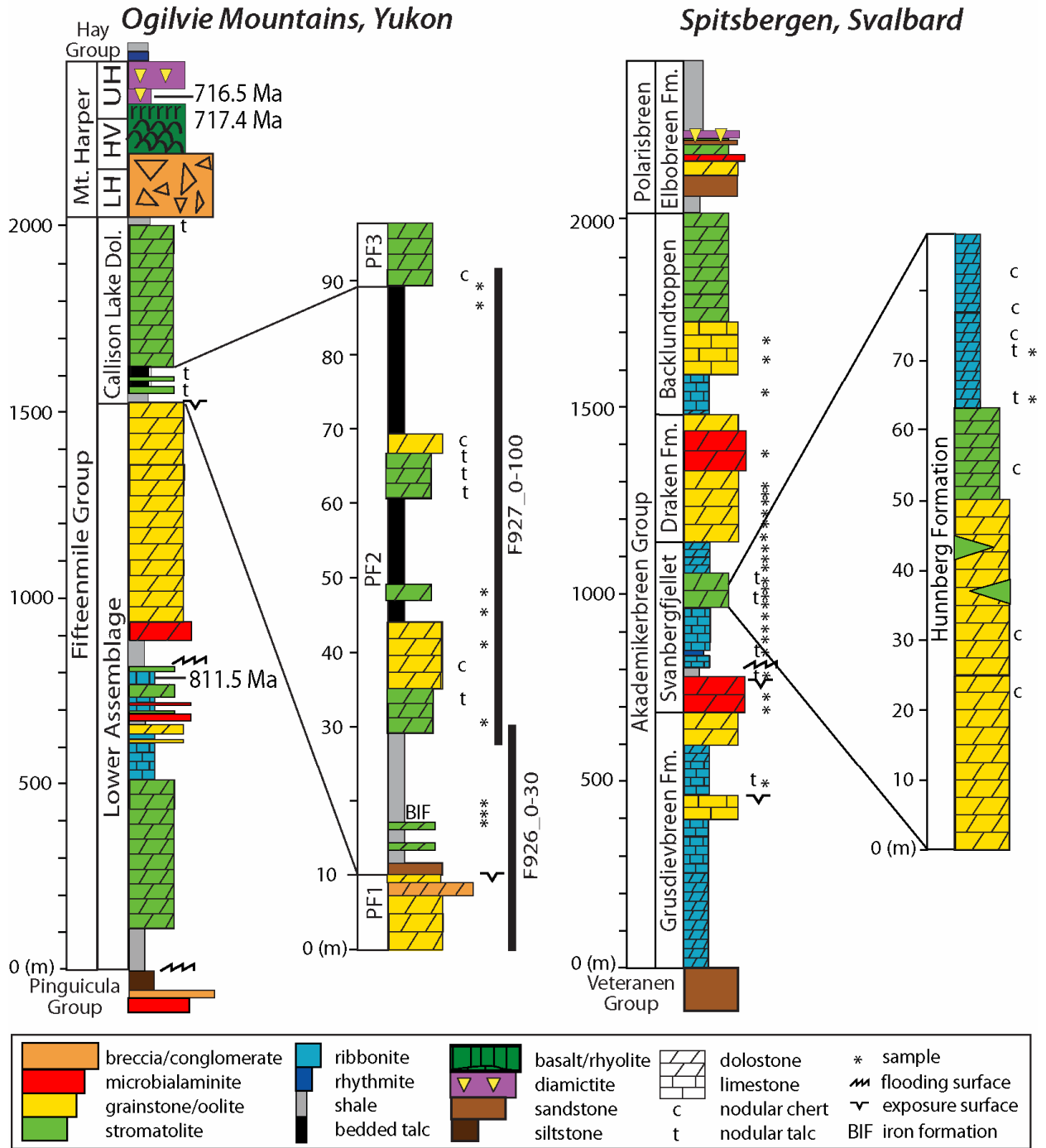


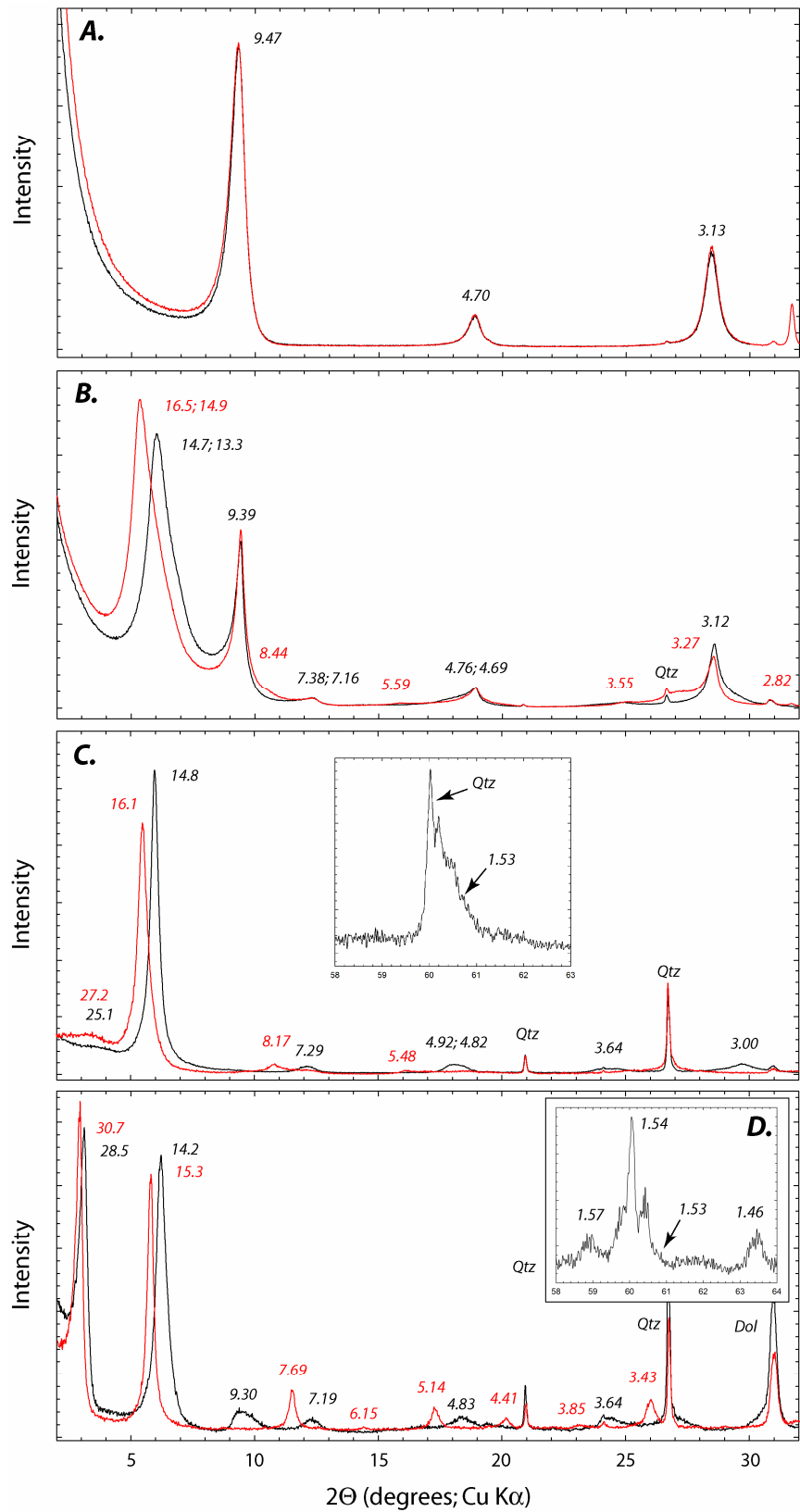


Figure 3.





Figure 4.



**Figure 5.**

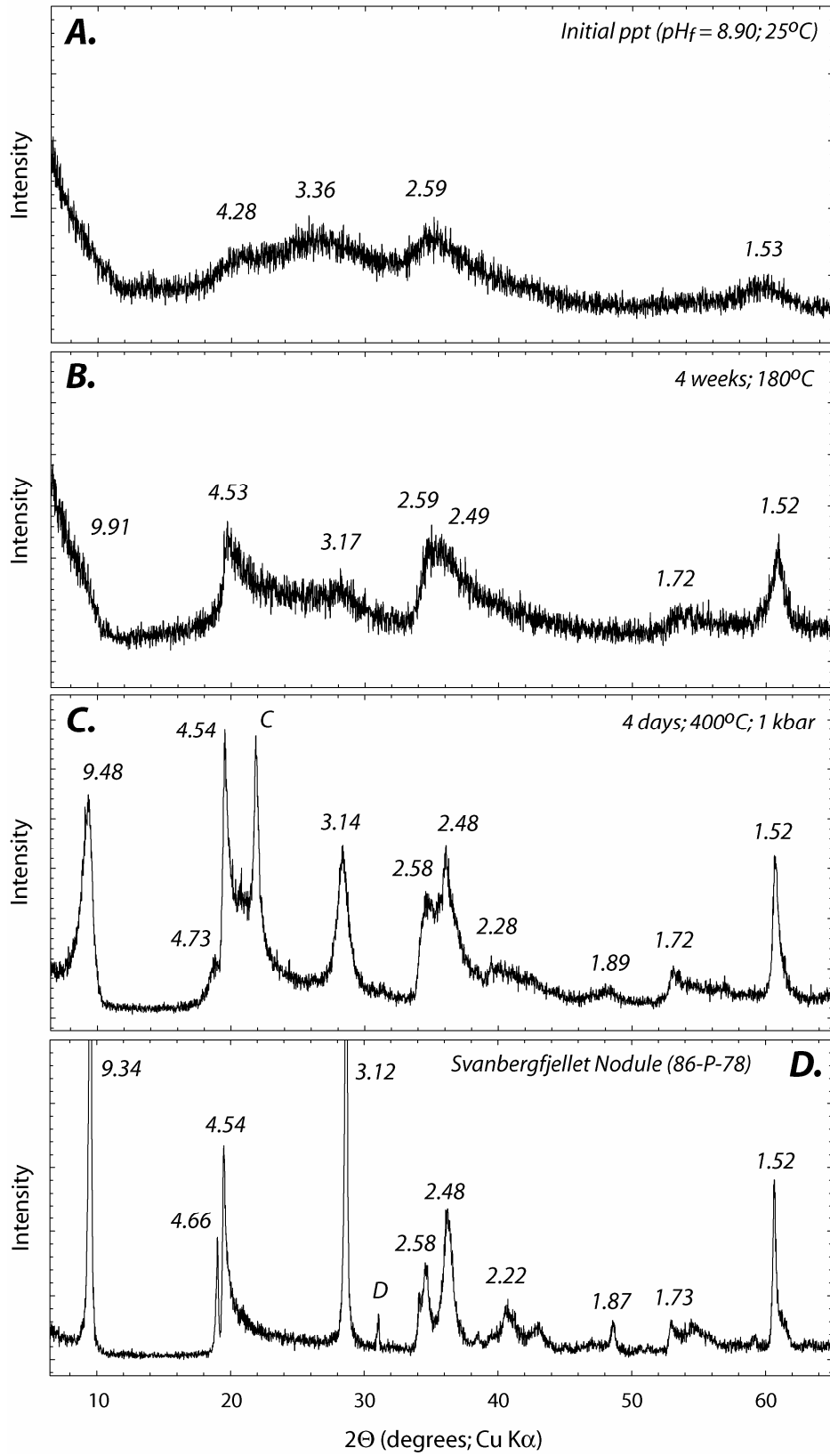
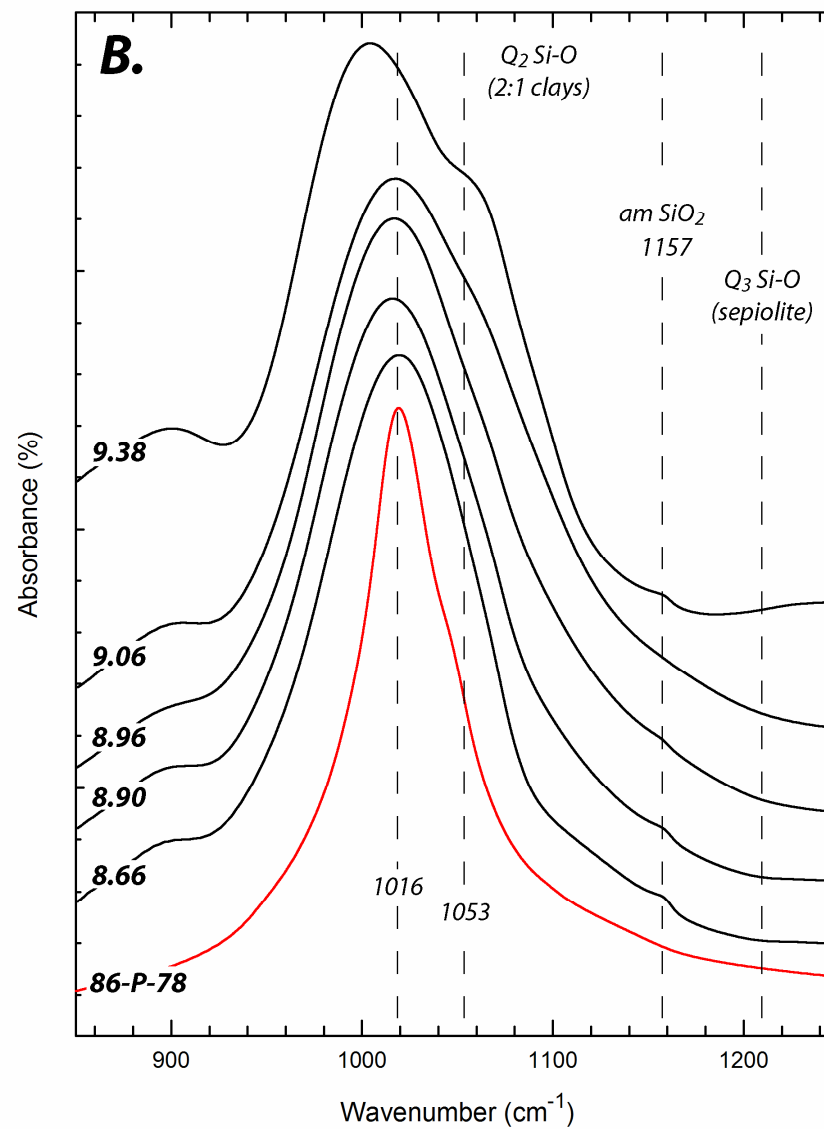
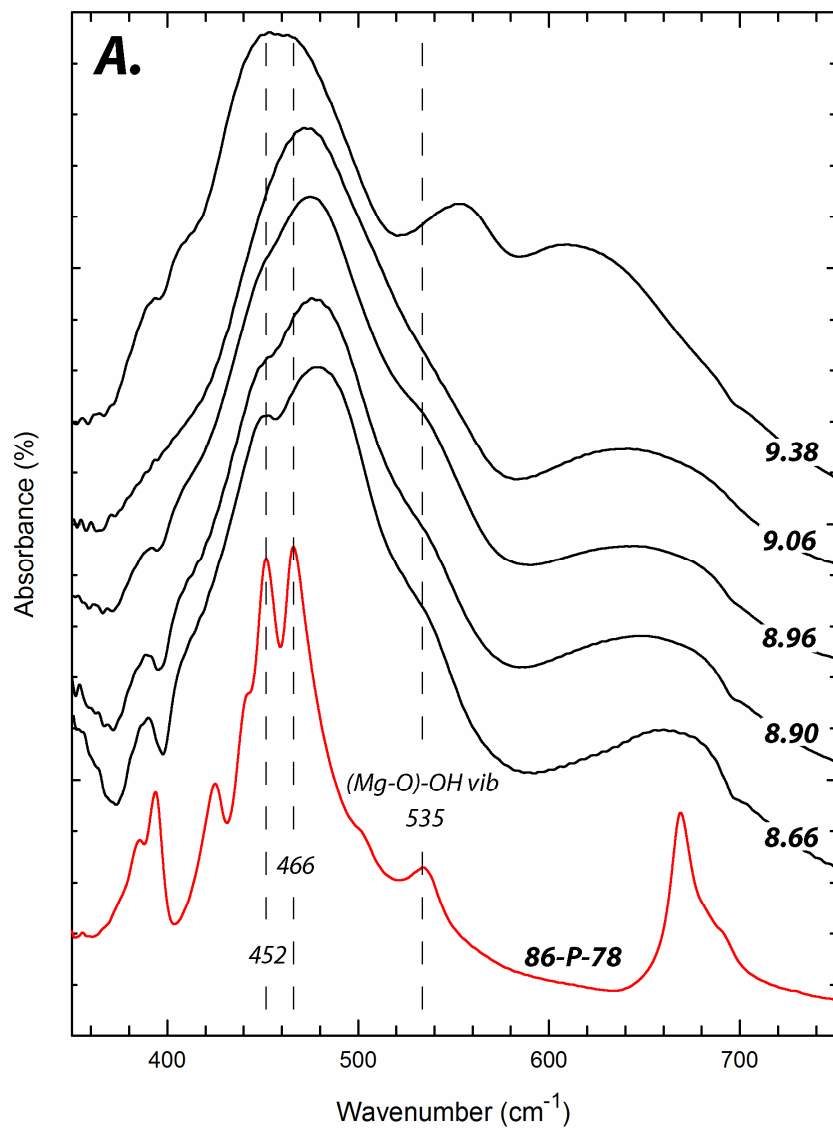


Figure 6.



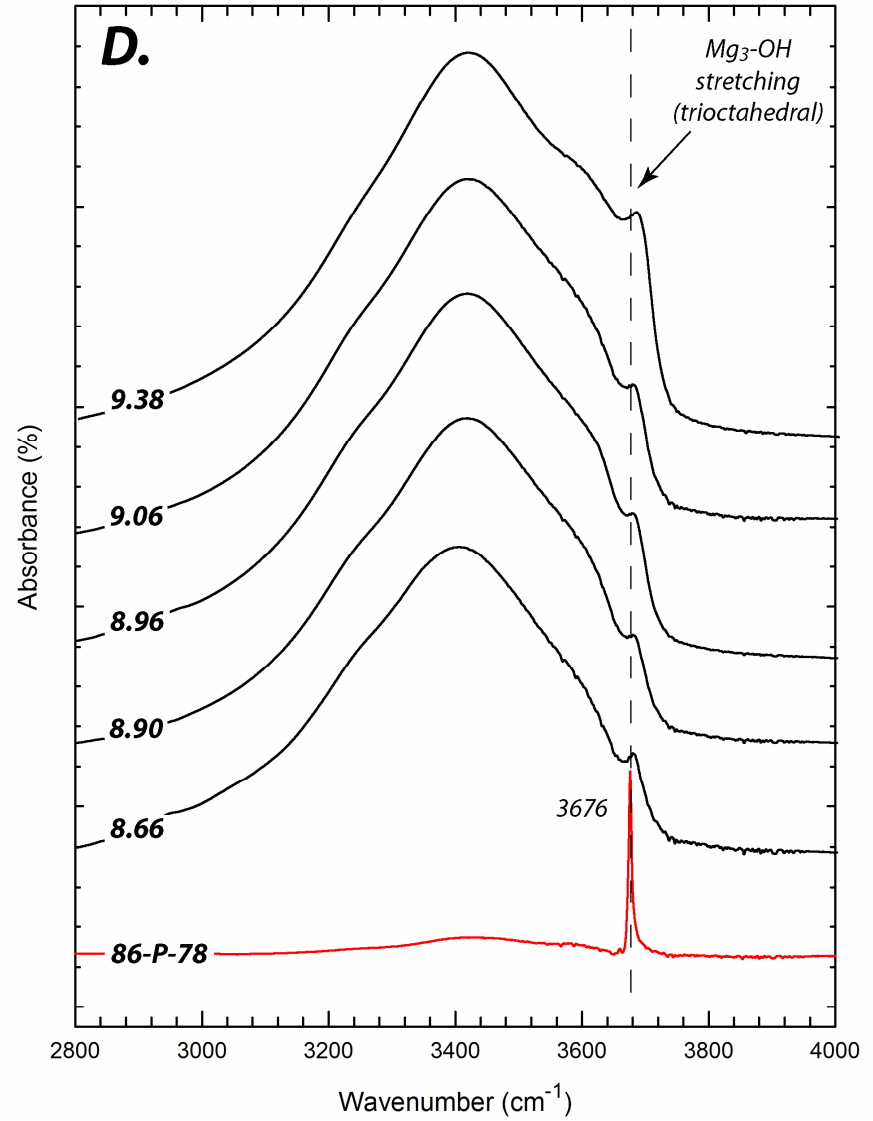
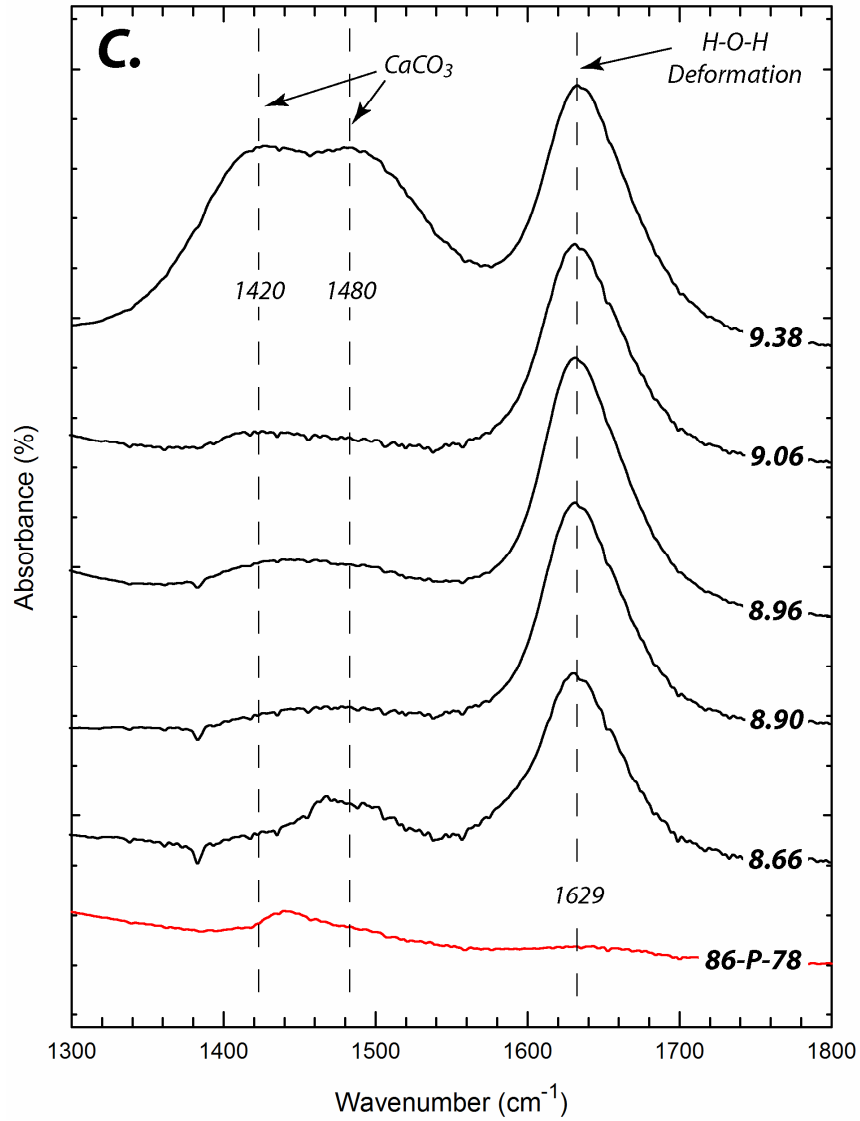




Figure 7.

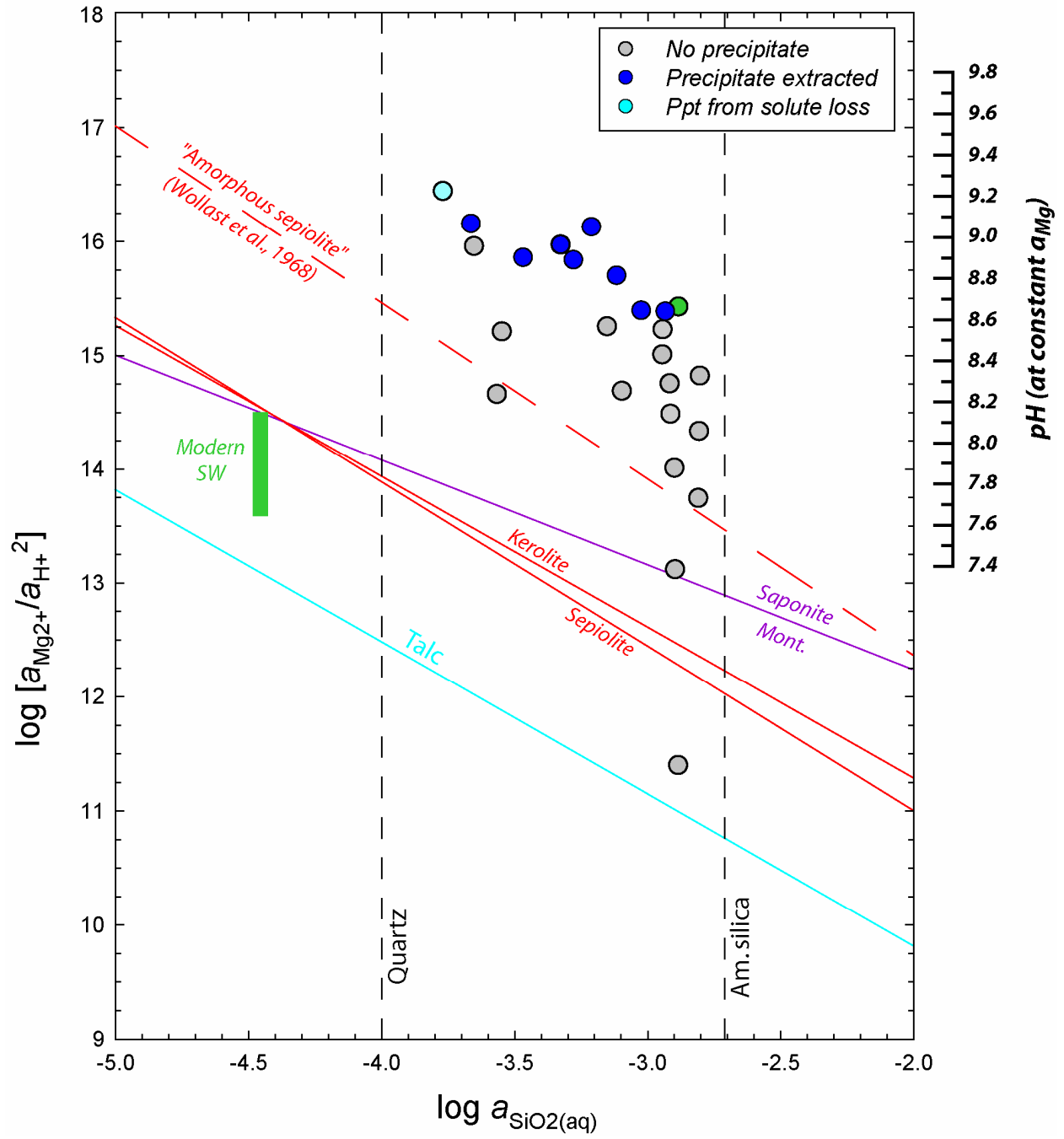
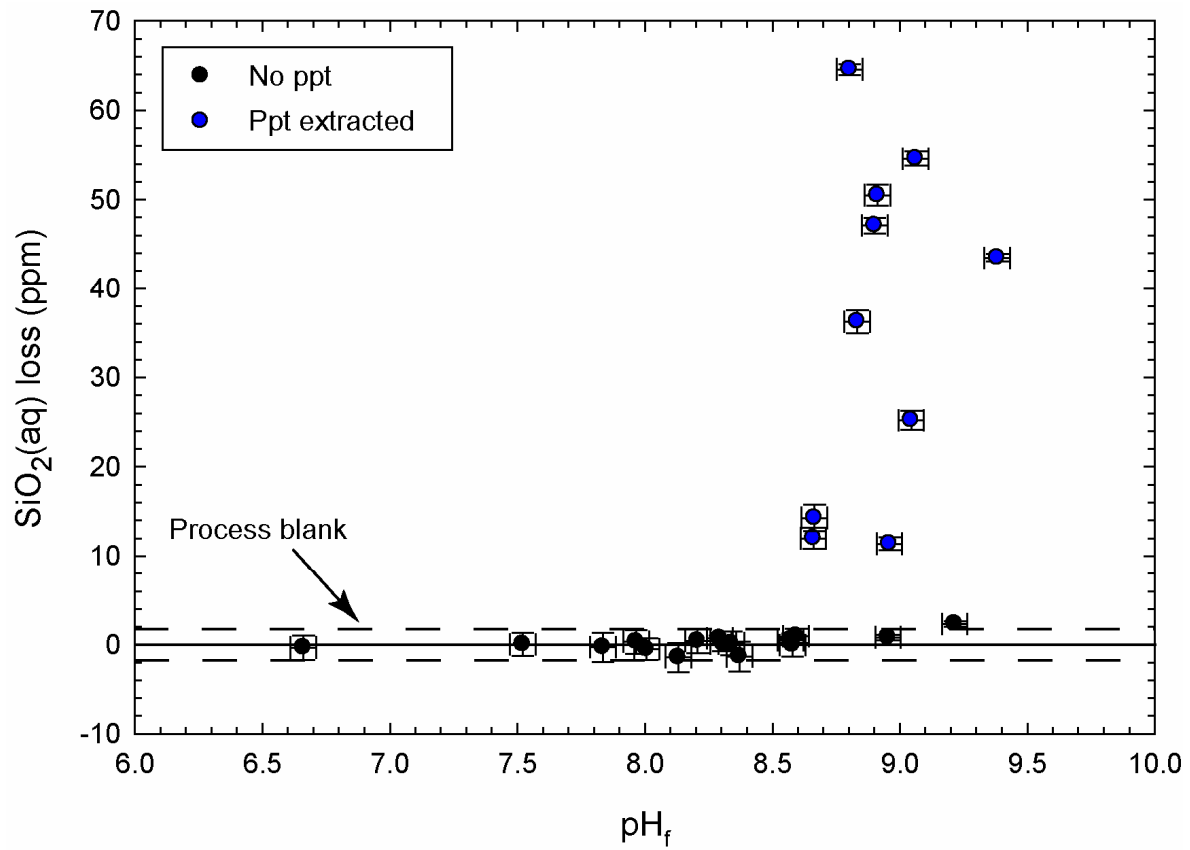
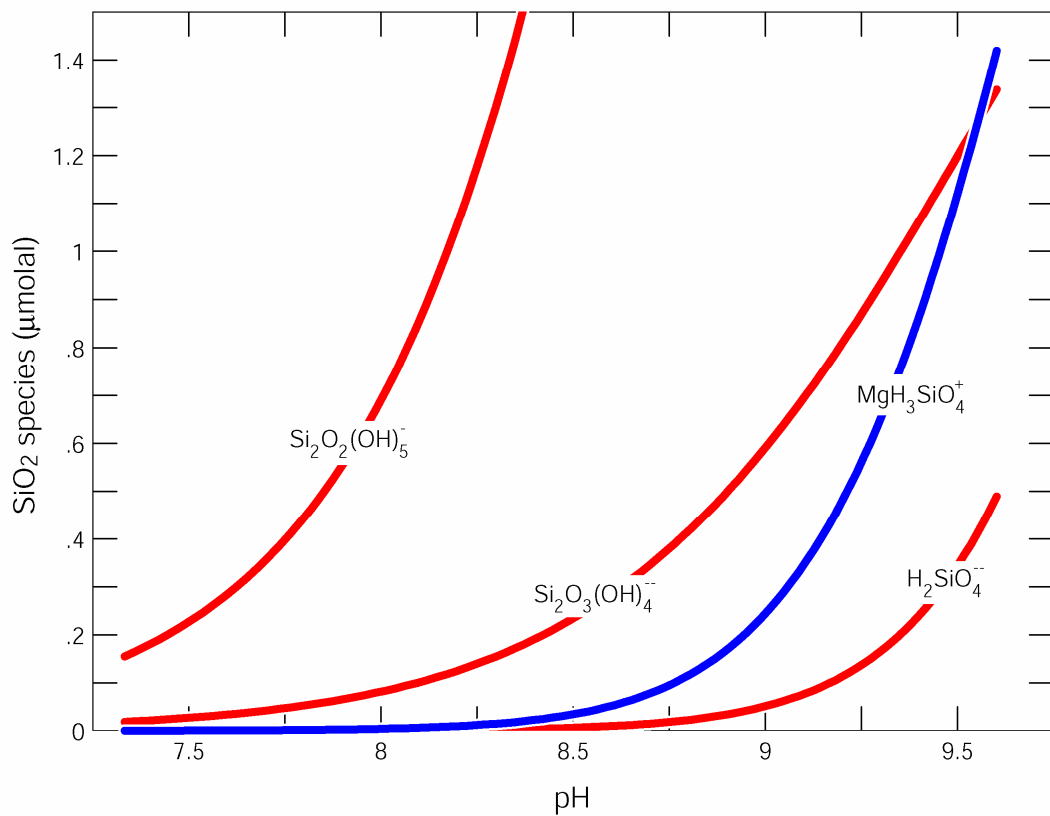
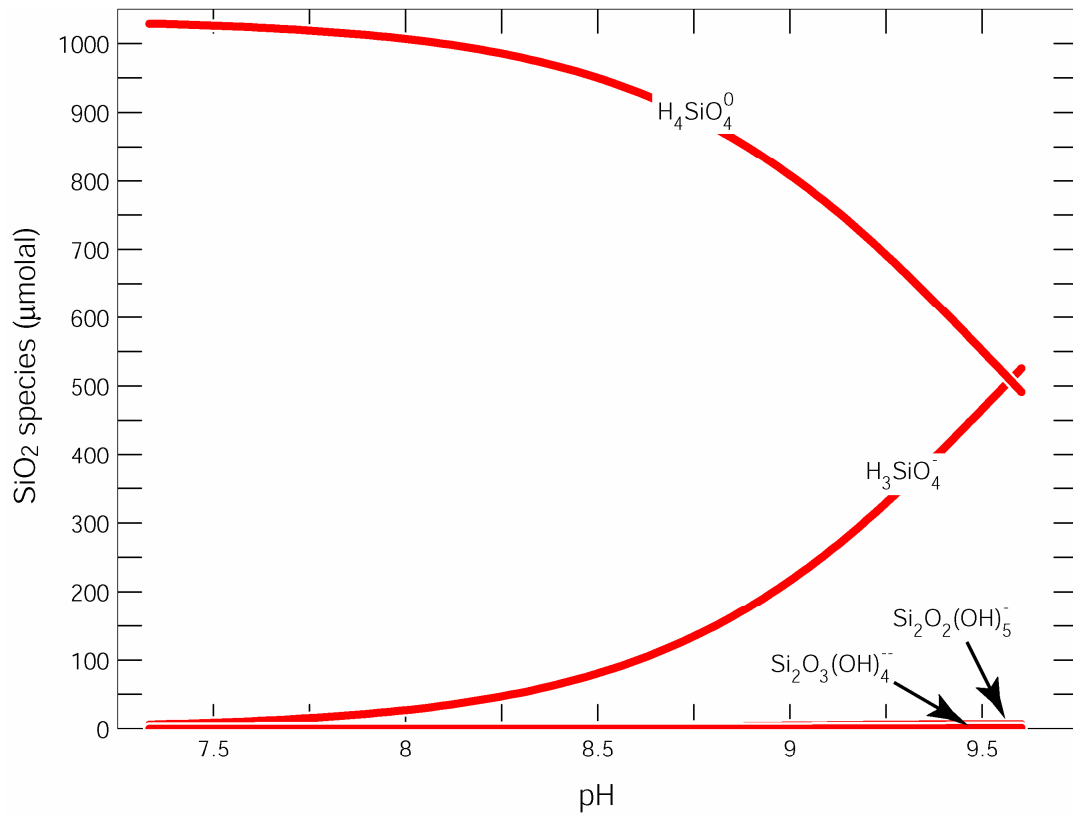


Figure 8.



**Figure 9.**



1 **Supplemental Data File (Tosca et al., Sedimentary talc in Neoproterozoic carbonate**  
2 **successions)**

3  
4 *Mineralogical and geochemical analyses*

5 Mineralogical analyses were performed on samples that were first cut on all sides to  
6 expose fresh surfaces. Samples were processed with a jaw crusher and then by hand in an agate  
7 mortar and pestle. To aid carbonate dissolution, some samples were pre-ground in an agate swing  
8 mill for <1-2 minutes at 200 rpm. Powders were again hand ground in an agate mortar and pestle,  
9 and dissolution was performed by step-wise addition of 0.3 mol/kg acetic acid. Solutions were  
10 monitored for effervescence to ensure that pH values did not drop below 4, minimizing Mg-  
11 silicate structural modification or dissolution (Moore and Reynolds Jr., 1997; Yebra-Rodriguez  
12 et al., 2003). Samples were repeatedly rinsed and re-suspended in de-ionized water with sodium  
13 phosphate as a dispersal agent and sonicated. The <2 $\mu$ m fraction was then separated by gravity  
14 settling and transferred to a clean glass slide in preparation for XRD using a filter-peel technique  
15 (Moore and Reynolds Jr., 1997). Samples were analyzed as air-dried oriented aggregates and  
16 again after ethylene glycol solvation by exposure to ethylene glycol vapor overnight at 60°C.

17 X-ray diffraction of clay separates and bulk samples was performed with a Bruker D-8  
18 Advance powder diffractometer with a Cu K $\alpha$  radiation at 40 kV and 30mA and also with a  
19 Siemens D5000 diffractometer at 30 kV and 20mA. Divergent slit sizes of 0.2 mm and receiving  
20 and anti-scatter slit sizes of 0.6 and 1.0 mm, respectively, were used. For oriented aggregates,  
21 samples were analyzed at intervals of 0.03 degrees with 4-8 seconds counting per step.  
22 Randomly oriented samples were analyzed from 3-65 degrees at 4 seconds per 0.02° step, with  
23 <2 $\mu$ m size fractions randomly oriented and analyzed from 50-65 degrees at 30 seconds per step  
24 to resolve weak 060 peaks that constrain octahedral occupancy. Electron microprobe analysis  
25 was performed on polished and carbon-coated thin sections with a Cameca SX-100 electron  
26 microprobe equipped with 5 wavelength dispersive spectrometers, capable of analyzing elements  
27 from B to U.

28  
29 *Experimental procedure*

30 The source of aqueous silica used in the experiments was a 99.9% reagent-grade  
31 anhydrous tetraethoxysilane (or TEOS) solution, which, upon contact with water, rapidly

32 hydrolyzes, producing  $\text{SiO}_2(\text{aq})$  and a small amount of residual ethanol. Although the hydrolysis  
33 of organo-silica complexes is rapid, there is a well-documented lag period during which the  
34 initially introduced  $\text{SiO}_2(\text{aq})$  de-polymerizes and reaches equilibrium with the surrounding  
35 solution in mostly monomeric (i.e.,  $\text{H}_4\text{SiO}_4$ ) form (Dietzel, 2000; Iler, 1979). With this in mind,  
36 all  $\text{SiO}_2(\text{aq})$  introduced in the experiment was given enough time to de-polymerize and  
37 equilibrate in the solution before Mg was introduced as  $\text{MgCl}_2(\text{aq})$ .

38 Aqueous samples (1 mL) were periodically extracted from the experiments and  
39 immediately filtered with 0.2  $\mu\text{m}$  syringe-driven nylon filters, acidified and stored for analysis.  
40 Solution samples were analyzed for major element chemistry using a Varian Vista Pro  
41 simultaneous ICP-AES. Calibration was performed with eight standard solutions bracketing  
42 expected sample concentrations. In addition, two external quality control standards (matrix  
43 matched) were periodically analyzed with samples to determine external precision (0.44%  
44 relative standard deviation for Mg and Si, and 0.69% for Ca) and accuracy (0.57-1.03%).

45 At experiment termination, remaining solution was filtered through a 0.2  $\mu\text{m}$  nylon filter  
46 membrane to extract any solid precipitate that formed over the course of the incubation period.  
47 Solid precipitates were dried overnight at 50°C and prepared as oriented aggregates and  
48 randomly oriented samples for XRD analysis. Solid samples were also analyzed by FT-IR using  
49 a Bruker IFS 66v infrared spectrometer. IR measurements were collected on KBr pellets with a  
50 sample:KBr ratio of 1:300. Measurements were collected from 350-5000  $\text{cm}^{-1}$  at 1  $\text{cm}^{-1}$   
51 resolution using a DTGS detector with a KBr window and beamsplitter. Selected samples were  
52 prepared for TEM analysis by dispersion in ethanol and deposition on Cu grids.

53 In addition to experiments run at 25°C, selected solid precipitates were loaded in Teflon  
54 vessels with deionized water at a solid:water ratio of 1:75. These experiments were run in  
55 hydrothermal bombs at  $180 \pm 1^\circ\text{C}$  for 2-4 weeks to simulate the effects of burial and heating on  
56 seawater precipitates over the course of burial diagenesis. Higher temperature experiments were  
57 run with precipitate and deionized water (at a solid:water ratio of 1:75) sealed in Au tubes and  
58 loaded into a cold-seal hydrothermal apparatus. Experiments were run at 3-4 days at 400°C and 1  
59 kbar hydrostatic pressure.

60

61 *Thermodynamic speciation calculations*

62 Thermodynamic speciation calculations for SiO<sub>2</sub>(aq)-bearing seawater were performed  
63 with Geochemists Workbench using a Pitzer-based method for ion activity coefficient  
64 calculation based on models developed by Harvie et al. (1984) and Marion and Farren (1999) for  
65 major seawater components. For silica speciation in solution, we included H<sub>4</sub>SiO<sub>4</sub> dissociation  
66 constants from Hershey and Millero (1986) and Pitzer coefficients for SiO<sub>2</sub> species calculated by  
67 Felmy et al. (2001). We also included aqueous silica complexes from Felmy et al. (2001) and  
68 Santschi and Schindler (1974). Speciation calculations discussed in the text were conducted as  
69 follows: initial low-SO<sub>4</sub> (2.8 mmol/kg) Al- and Fe-free seawater compositions were equilibrated  
70 with 60 mg/kg SiO<sub>2</sub>(aq) and a CO<sub>2</sub>-containing atmosphere at a pCO<sub>2</sub> to yield an initial pH of  
71 7.25 (log fCO<sub>2</sub> = -1.0). CO<sub>2</sub> fugacity was then decreased while maintaining equilibrium with  
72 seawater by pH adjustment until the final seawater pH reached ~9.7 at a log fCO<sub>2</sub> = -4.0.

73

#### 74 *Details of clay mineral identification*

75 Saponite was identified by a strong basal 001 reflection in air dried oriented aggregates  
76 which shifted to 16.1 Å after ethylene glycol treatment. XRD analyses of randomly oriented  
77 <2µm powders revealed a 060 peak at 1.529Å, corresponding to trioctahedral occupancy. The  
78 saponite was found only in samples from the Hunnberg Formation. One sample dominated  
79 entirely by finely laminated dolomicrite and abundant molar tooth structures yielded almost pure  
80 saponite (with a small amount of R1 illite(0.5)/smectite) after decarbonation.

81 Corrensite, a mixed layered regularly ordered chlorite(0.5)/smectite was identified in one  
82 sample from the Svanbergfjellet Formation (86-G-3). An intense superstructure 001\* reflection  
83 in both the air dried and ethylene glycol-solvated states, along with a rational series of 00/  
84 reflections upon ethylene glycol-solvation, were sufficient to unambiguously identify corrensite  
85 in this sample. The corrensite is of the trioctahedral low-charge variety, indicating that the  
86 chlorite component is mixed with trioctahedral saponite.

87 Figure 4B in the manuscript shows an XRD pattern of the <2µm decarbonated residue  
88 from sample K2016 (Hunnberg Fm). Talc can be clearly identified from the reflection at 9.37Å.  
89 However, the broad peak centered at ~6 degrees 2θ contains two reflections: 14.7 Å and 13.3 Å  
90 in the air-dried state, and at 16.5 Å and 14.9 Å in the EG-solvated state. From high angle XRD  
91 scans of random powders, an 060 peak is present at 1.528 Å, which, combined with reflections at  
92 14.7 and 16.5 Å in air-dried and EG-solvated, respectively, can be identified as saponite. The 00/

93 reflections of the additional phase are all well-matched by R1 chlorite(0.75)/smectite. Calculated  
94 X-ray diffraction patterns of this phase (using the program NEWMOD; (Reynolds Jr. and  
95 Reynolds, 1996)) correspond precisely with observed reflections throughout the 00 $l$  series. Such  
96 a mixed-layer phase is relatively uncommon in natural samples; corrensite is by far the most  
97 common chlorite/smectite species, but other forms of chlorite/smectite mixed layering have been  
98 reported in association with carbonate and/or evaporite deposits (e.g., (Hillier, 1993)).

99

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131 **Figure 1.** Comparison of oriented <2mm fraction (EG-solvated) of sample K2016 from the  
132 Hunnberg Formation, Nordaustlandet, Svalbard (A) with (B) a simulated one dimensional X-ray  
133 diffraction pattern (calculated by NEWMOD) for a physical mixture of: 67% talc, 27% tri-  
134 octahedral smectite (saponite), and 7% R0 tri-tri chlorite 0.7/tri-smectite.

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136 **Figure 2.** Transmission electron micrograph of poorly crystalline Mg-silicate precipitated at a  
137 pH of 8.901 (with selected area electron diffraction pattern shown in inset). Photomicrographs of  
138 experimental precipitates show a crinkly morphology at the nanometer scale, and in some  
139 regions, the development of hexagonally-shaped particles. Some regions of the precipitate  
140 exhibit observable patterns in selected area electron diffraction implying crystalline order at the  
141 nanometer scale. The smearing of diffracted spots into weak circular patterns is consistent with  
142 low stacking order in the *z* direction.

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154 **Table 1.** Experimental conditions

<i>Expt ID</i>	<i>pH<sub>f</sub></i>	<i>[SiO<sub>2</sub>]<sub>i</sub> (ppm)</i>	<i>[Mg]<sub>i</sub> (ppm)</i>	<i>Composition</i>	<i>Precipitate</i>
<i>MgSi_1</i>	6.661	69.70	1182	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_2</i>	7.521	68.80	1181	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_3</i>	7.966	69.88	1178	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_4</i>	8.339	69.17	1178	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_5</i>	8.661	69.39	1180	SW (2.8 mmol/kg SO <sub>4</sub> )	PCMS
<i>MgSi_6</i>	8.901	69.39	1180	SW (2.8 mmol/kg SO <sub>4</sub> )	PCMS
<i>MgSi_7</i>	8.307	45.53	1165	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_8</i>	8.593	42.87	1159	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_9</i>	8.959	43.04	1167	SW (2.8 mmol/kg SO <sub>4</sub> )	PCMS
<i>MgSi_10</i>	9.382	43.81	1157	SW (2.8 mmol/kg SO <sub>4</sub> )	Corr; pc-Talc
<i>MgSi_11</i>	8.294	16.07	1165	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_12</i>	8.570	17.25	1165	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_13</i>	8.953	15.70	1165	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_14</i>	9.215	15.50	1165	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_15</i>	9.062	69.90	1165	SW (2.8 mmol/kg SO <sub>4</sub> )	PCMS
<i>MgSi_16</i>	7.835	84.70	1174	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_17</i>	8.131	85.06	1171	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_18</i>	8.371	85.65	1168	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_19</i>	8.665	85.14	1195	SW (2.8 mmol/kg SO <sub>4</sub> )	PCMS
<i>MgSi_20</i>	8.833	85.14	1200	SW (2.8 mmol/kg SO <sub>4</sub> )	PCMS
<i>MgSi_21</i>	8.912	85.14	1175	SW (2.8 mmol/kg SO <sub>4</sub> )	PCMS
<i>MgSi_22</i>	8.207	68.92	1164	SW (28 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_23</i>	8.579	67.75	1165	SW (28 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_24</i>	9.044	68.34	1164	SW (28 mmol/kg SO <sub>4</sub> )	PCMS
<i>MgSi_25</i>	8.007	62.94	12900	SW (2.8 mmol/kg SO <sub>4</sub> )	--
<i>MgSi_26</i>	8.803	64.88	12900	SW (2.8 mmol/kg SO <sub>4</sub> )	PCMS

**PCMS:** Poorly crystalline Mg-silicate

**pc-Talc:** Poorly crystalline talc

**Corr:** Corrensite (trioctahedral)

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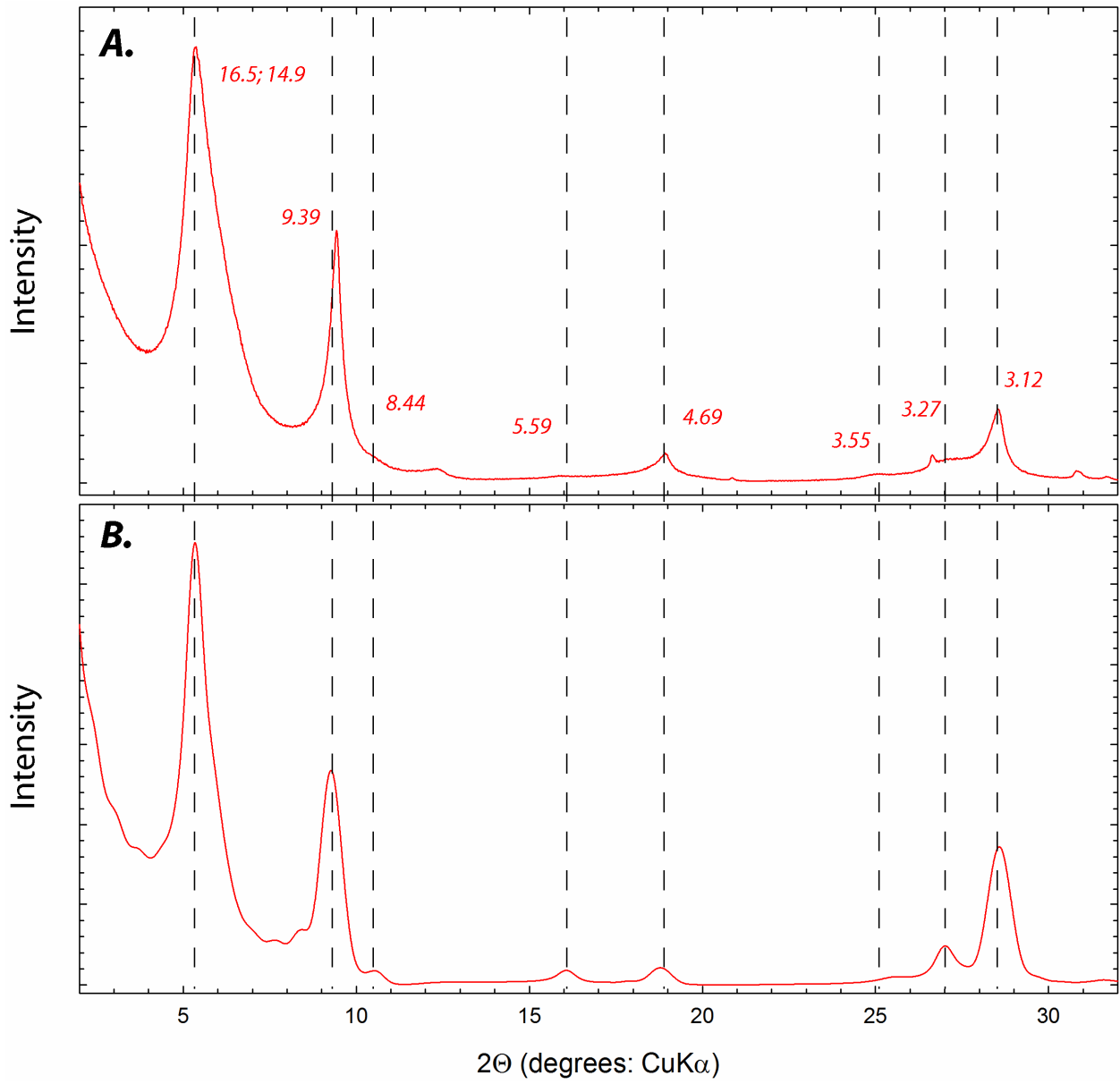
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162 **Figure 1.**



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172 **Figure 2.**

