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10 **Review of calcium carbonate polymorph precipitation in spring systems**

11 Brian Jones

12 Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton,

13 Alberta, T6G 2E3, Canada

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17 E-mail address: Brian.Jones@ualberta.ca

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19   ABSTRACT

20   Many spring deposits throughout the world are characterized by spectacular deposits of calcium

21   carbonate that are formed of various combinations of aragonite and calcite, and in very rare cases

22   vaterite. The factors that control the precipitation of the aragonite and calcite have been the

23   subject of considerable debate that has been based on natural precipitates and information gained

24   from numerous laboratory experiments. Synthesis of this information indicates that there is

25   probably no single universal factor that controls calcite and aragonite precipitation in all springs.

26   Instead, the reason for aragonite as opposed to calcite precipitation should be ascertained by

27   considering the following ordered series of possibilities for each system. First, aragonite,

28   commonly with calcite as a co-precipitate, will form from spring water that has a high CO_2

29   content and rapid CO_2 degassing, irrespective of the Mg:Ca ratio and scale of precipitation.

30   Second, aragonite can be precipitated from waters that have low levels of CO_2 degassing

31   provided the Mg:Ca ratio is high enough inhibit calcite precipitation. Third, the presence of

32   biofilms may lead to the simultaneous precipitation of aragonite and calcite (irrespective of CO_2

33   degassing or Mg:Ca ratio) either within the different microdomains that develop in the biofilm or

34   because of diurnal changes in various geochemical parameters associated with the biofilm.

35   Although the precipitation of calcite and aragonite has commonly been linked directly to water

36   temperature, there is no clear evidence for this proposition. It is possible, however, that

37   temperature may be influencing another parameter that plays a more direct role in the

38   precipitation of these $CaCO_3$ polymorphs. Despite the advances that have been made, the factors

39   that ultimately control calcite and aragonite are still open to debate because this long-standing

40   problem has still not been fully resolved.

41   Keywords: Calcite; Aragonite; Vaterite, $CaCO_3$ polymorphs; springs; biofilms

1. Introduction

Many spring systems throughout the world are characterized by spectacular, varicoloured discharge aprons that are formed largely of calcium carbonate precipitated from the flowing spring waters. Prime examples of such deposits include those at Pamukkale in the Denizli Basin, Turkey (Kele et al., 2011; Özkul et al., 2013), Mammoth Hot Springs in Yellowstone National Park, U.S.A. (Fouke et al., 2000; Chafetz and Guidry, 2003), and Huanglong in Siuchuan Province, China (Lu et al., 2000; Wang et al., 2014). These deposits, as well as those associated with smaller springs, may be formed entirely of calcite, entirely of aragonite, or mixtures of both polymorphs. As noted by Sun et al. (2015), precipitation of the stable phase of a mineral is commonly preceded by precipitation of a metastable phase. Although it has long been understood that calcite is the stable $CaCO_3$ polymorph, the reasons why metastable aragonite is precipitated in spring systems has been the subject of debate since Suganuma (1928) questioned the conclusions offered by Meigen (1901) and Warth (1902). Vaterite, the third polymorph of $CaCO_3$, has only been reported from an unusual supraglacial spring located on northern Ellesmore Island, Arctic Canada (Grasby, 2003).

The factors that control precipitation of the different $CaCO_3$ polymorphs is important in many other aspects of geology, including marine deposits, organisms that form their skeletons of calcite and/aragonite, cave precipitates, and lake deposits (e.g., Goto, 1961; Hill and Forti, 1997). Geological investigations into this question have used interpretations of natural samples as well as various experiments to try and resolve the problem (e.g., Kitano, 1962b; Folk, 1994; Pentecost, 2005). Over the last 10-15 years, considerable interest in $CaCO_3$ polymorphs has arisen in the areas of material science and chemical materials as calcite, aragonite, and vaterite have become widely used in many different industrial applications (e.g., Meldrum, 2003; Sand et

65   al., 2012; Declet et al., 2016). In these areas of science, numerous experiments using many

66   different types of reagents and many different techniques have been undertaken in an effort to

67   gain an understanding of the factors that control calcite, aragonite, and vaterite precipitation.

68   Despite the innumerable studies that have focused on various aspects of the calcite-

69   aragonite problem, it is still difficult to identify any universal factor(s) that control the

70   precipitation of aragonite in any given situation. For spring deposits, aragonite precipitation has

71   been variously linked to water temperature, pH, the presence or absence of various elements such

72   as Mg and Sr, the presence of microbes, the level of supersaturation, and the rate of precipitation

73   (e.g., Loste et al., 2003; Jones and Renaut, 2010; Kanellopoulos, 2012). Collectively, this

74   suggests that the calcite – aragonite precipitation problem is extremely complex and that

75   variations in virtually any parameter may trigger aragonite precipitation.

76   This review paper, which synthesizes the vast amount of data and ideas that have been

77   derived by many different studies, is designed to summarize the work that has been done to date,

78   discuss the different parameters that have been deemed important in $CaCO_3$ precipitation, and

79   offer some ideas that might help to resolve this complex issue. This paper is presented in five

80   parts: (1) a review of the existing data and information regarding the factors that may control

81   precipitation of the $CaCO_3$ polymorphs, (2) the spatial relationships between calcite and

82   aragonite precipitates evident in spring deposits throughout the world, (3) comparison of calcite

83   and aragonite in spring deposits with calcite and aragonite in cave speleothems, (4) examination

84   of the models that have been proposed for calcite and aragonite precipitation in spring deposits,

85   and (5) discussion of the results of the review and ideas for resolution of the problem. Although

86   a definitive answer is not yet possible, this review should provide some focus on the problem and

87   perhaps point the way forward.

2. Controls of CaCO$_3$ polymorph precipitation

It is evident from the vast literature that deals with CaCO$_3$ polymorph precipitation, both in natural settings and laboratory experiments, that many different parameters can influence calcite and aragonite precipitation. In evaluating the underlying causes for precipitation of the different polymorphs it immediately becomes clear that part of the complexity arises because the physical and chemical parameters may act independently or in tandem. In other words, a change in one parameter may trigger a change in another parameter that then causes precipitation of one polymorph or another. Parameters like the saturation level, which is a function of many variables, is a prime example. Herein, each parameter that has been implicated in the precipitation of the different CaCO$_3$ polymorphs in natural settings and laboratory experiments are evaluated independently in order to clarify the basic issues associated with each one.

2.1. Water temperature

Rose (1837) suggested that a temperature (T) higher than 30° (unit not specified) was needed for aragonite precipitation. The idea that T played an important role in the precipitation of aragonite and calcite was subsequently supported by Meigen (1901), Linck (1903), Johnstone et al. (1916), Kohlschütter and Egg (1925), Saylor (1927), Faive (1946), Togari and Togari (1955), and Zeller and Wray (1956). The exact relationship between T and aragonite precipitation has, however, proven difficult to define with precision and some studies have even suggested T does not control the polymorph that is precipitated (e.g., Curl, 1962; Siegel and Reams, 1966; Hill and Forti, 1997; Rowling, 2004).

Some studies have suggested that the change from calcite to aragonite precipitation occurs once a critical T has been reached. Specific examples include (1) Suganuma (1928) who found that calcite formed at < 50°C, whereas aragonite formed if T > 50°C, (2) Goto (1961), who

111   suggested that aragonite forms when T > 60°C, (3) Roques and Girou (1974) who experimentally

112   demonstrated that the $CaCO_3$ phase changed from vaterite to calcite to aragonite as T increased,

113   (4) Chakrabarty and Mahapatra (1999), who argued that vaterite formed if T < 15°C, calcite at

114   room T, and aragonite when T > 70°C, (5) Nebel and Epple (2008) who proposed that vaterite

115   was precipitated at low T, calcite at room T, and aragonite at high T, (6) Chen and Xiang (2009)

116   who suggested that vaterite formed at 30-40°C and that at a T of 50°C increased aragonite

117   precipitation occurred, (7) Rosa et al. (2011) who argued that vaterite formed at 25°C, calcite at

118   30°C, and aragonite at 37°C, and (8) Burton and Walters (1987) who suggested that calcite and

119   aragonite precipitation was controlled mainly by T. Other laboratory experiments (e.g., Wray

120   and Daniels, 1957; Zhou and Zheng, 2001; Hu and Deng, 2004; Meldrum and Cölfen, 2008)

121   have also supported the idea that high T will lead to aragonite precipitation.

122   The notion that aragonite precipitation is directly related to a critical T has, however, been

123   disputed by other studies. Faive (1946), for example, showed that aragonite precipitation

124   reached a maximum at T = 60° (scale not specified but assumed to be Celsius) but then

125   decreased as T further increased (Fig. 1A). Similarly, Kitano (1955) suggested that aragonite

126   forms when T > 55°C, but noted that this is not always the case and Kitano and Hood (1962)

127   showed that with increased T, the amount of aragonite increased but never resulted in aragonite

128   alone. Similarly, Togari and Togari (1955) showed that calcite formed at T < 30°C and that the

129   amount of aragonite increases up to 70°C, but thereafter there was equal amounts of calcite and

130   aragonite. Atlay et al. (2007) also argued that the amount of aragonite increased when T > 50°C.

131   In caves, T does not seem to be a controlling factor (Gonzalez and Lohmann, 1987;

132   Rowling, 2004) and Hill and Forti (1997) noted that aragonite appears to be more common in

133   high latitude, cold caves (T ~ 0°C) than in warm, low-latitude caves. Curl (1962), in

134   commenting on the same issue, argued that T may trigger secondary effects by influencing other

135   variables such as reaction rates, diffusion rates, and ion availability.

136   *2.2. Water pH*

137   The exact role that pH may play in the precipitation of aragonite and calcite is based almost

138   entirely on experimental work. Even so, the issue of pH on $CaCO_3$ precipitation is poorly

139   understood because most information comes from incidental comments offered as other

140   parameters are being considered.

141   Matsumoto et al. (2010), based on experiments whereby CO_2/NH_3 microbubbles are passed

142   through the reagent mixture, noted the following relationships: (1) vaterite if pH < 9; (2) calcite

143   if pH > 11; and (3) aragonite if pH was 9.7 to 10.5. They also noted, however, that with a pH of

144   9.7, the rate of aragonite crystallization accelerated if the CO_2/NH_3 molar ratio and average

145   bubble size of the CO_2 gas were decreased. Similarly, Tai and Chen (1998) used experiments to

146   argue that $CaCO_3$ polymorph precipitation was controlled by various parameters, including pH

147   with precipitation of (1) calcite if pH > 12; (2) vaterite if pH < 10, and (3) aragonite if pH = 11

148   when the experiments were run at room T. At higher T, however, aragonite became a major

149   component at pH < 11 but calcite still formed at higher pH. Hu and Deng (2004, their Fig. 6)

150   also noted that aragonite precipitation was highest at 70°C when the pH was 11.

151   Although Weiss et al. (2014) precipitated vaterite and calcite in their experiments, they

152   suggested that the lack of aragonite was due to the pH of ~ 8.4, which is far lower than that

153   associated with other experiments.

154   *2.3. CO₂ content and degassing*

155   Rose (1860), Credner (1870), and Adler (1897) argued that aragonite forms from hot water

156   when it is saturated with CO_2. Kitano (1962b, his Figs. 1, 2) used various experiments to show

157   that when CO_2 was bubbled through solutions there was a radical change in the proportions of

158   calcite, aragonite, and vaterite precipitated over a temperature range of 0 to 100°C (Fig. 1B, C).

159   In a subsequent paper, he pointed out that aragonite is the dominant precipitate in Japanese

160   springs where CO_2 degassing is the highest (Kitano, 1963). Yagi et al. (1984) also used

161   experiments to show that CO_2 influenced aragonite precipitation. In recent years, many

162   experiments have produced calcite and aragonite by bubbling CO_2 through various mixtures of

163   reagents (Dickinson et al., 2002; Matsumoto et al., 2010; Bang et al., 2011). Such experiments

164   not only showed that CO_2 can cause such precipitation but also demonstrated that other factors

165   such as the average bubble size and the CO_2/NH_3 molar ratio also influence polymorph

166   precipitation (Matsumoto et al., 2010).

167   Folk (1994), while arguing that T and Mg were the main controls over calcite and aragonite

168   precipitation in springs, noted that high CO_2 degassing can override those controls. For various

169   springs in Yunnan Province of China, Jones and Peng (2012, 2014a, 2016) also suggested that

170   CO_2 degassing was the primary control over the precipitation of calcite and aragonite.

171   According to Kawano and Obokata (2007), the water in Anraku Hot Spring in Japan is

172   supersaturated with respect to calcite and aragonite due to abiotic CO_2 degassing and CO_2 loss

173   resulting from cyanobacteria photosynthesis. Based on laboratory experiments using this spring

174   water, they argued that the presence of microbial mats led to a significant increase in the

175   precipitation rate of $CaCO_3$ (by 1.9 to 3.2 times), and an increase in the percentage of aragonite.

176   *2.4. Saturation levels*

177   A prerequisite for calcite and aragonite precipitation is that the parent fluids must be

178   supersaturated with respect to both ploymorphs (Curl, 1962). Supersaturation is, however, a

179   complex parameter that is controlled by many different parameters, including T, rate of supply of

180   solution, rate of evaporation or loss of CO_2, initial concentrations of reactants, and the rate of

181   precipitation (Curl, 1962). Similarly, Roques and Girou (1974) suggested that supersaturation

182   levels were not the only parameter that controlled polymorph precipitation because the presence

183   of various foreign ions can also control which polymorph is precipitated.

184   Numerous studies have argued that supersaturation levels commonly determine the $CaCO_3$

185   polymorph that will be precipitated. Holland et al. (1964), based on the analysis of cave waters,

186   argued that high supersaturation levels caused by rapid CO_2 degassing led to aragonite

187   precipitation and that this parameter was more important than the Mg content of the water. Ahn

188   et al. (2005) used experimental data to suggest that the precipitation of aragonite, calcite, and

189   vaterite was related to low, medium, and high supersaturation levels, respectively. This is

190   reflected in other studies where precipitation has been attributed to supersaturation levels as well

191   as other parameters such as T, the presence of additives, and cooling (Meldrum, 2003; Wang et

192   al., 2013).

193   De Choundens-Sánchez and González (2009) used experiments to demonstrate that the

194   precipitation of $CaCO_3$ polymorphs was controlled by supersaturation levels and the Mg/Ca ratio

195   of the fluid (Fig. 1D). They argued that as the Mg/Ca ratio increased, progressively higher

196   supersaturation levels are needed for calcite precipitation because the change in the Mg/Ca ratio

197   causes a decrease in growth rate of calcite while the aragonite growth rates stay unaffected.

198   Thus, aragonite is dominant in solutions with high Mg/Ca ratios and low supersaturations.

199   *2.5. Alkali metals*

200   Experimental studies by Okumura and Kitano (1986) showed that (1) the alkali metal ions

201   (Li^+, Na^+, K^+, Rb^+) easily co-precipitate with aragonite, but not with calcite, (2) the amount of

202   alkali metal ions co-precipitated with calcite increases as Mg increases, and (3) Na in aragonite

203 reduced the amount of Li^+, K^+, and Rb^+ that is incorporated. Nevertheless, there was no

204 indication that any of these ions determined which polymorph was precipitated. Sawada (1998)

205 and Meldrum (2003) suggested, however, that Li retards the growth of calcite. Ogino et al.

206 (1990) argued that the presence of Li retarded the transformation of aragonite or vaterite to

207 calcite.

208 *2.6. Divalent ions*

209 Divalent ions, including Mg^{2+}, Sr^{2+}, Fe^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, have commonly been

210 implicated as the underlying cause of aragonite as opposed to calcite precipitation. Credner

211 (1870), for example, argued that the presence of Sr, Ba, or Pb favoured aragonite precipitation.

212 This notion was subsequently supported by Bauer (1890), Johnston et al. (1916), Faust (1950),

213 Zeller and Wray (1956), and Wray and Daniels (1957). Harada and Goto (1957) and Goto

214 (1961), however, argued that the presence of Sr, Ba, Pb, or Mg was not needed to force aragonite

215 precipitation.

216 *2.6.1. Magnesium*

217 Leitmeier (1909) suggested that the presence of Mg favoured aragonite precipitation. Since

218 then, the notion that the presence of Mg inhibits calcite precipitation while promoting aragonite

219 precipitation has been substantiated by theoretical calculations, many different types of

220 experiments, and analysis of natural precipitates (Lippmann, 1960; Kitano, 1962a, 1962b;

221 Bischoff, 1968; Katz, 1973; Berner, 1975; Reddy and Nancollas, 1976; Kitano et al., 1979;

222 Reddy and Wang, 1980; Mucci and Morse, 1983; Yoshida, 1987; Deleuze and Brantley, 1992;

223 Rushdi et al., 1992; Falini et al., 1994; Heywood and Mann, 1994; Tai and Chen, 1995; Wada et

224 al., 1995; Gutjahr et al., 1996; Falini et al., 1997; Berndt and Seyfried, 1999; Davis et al., 2000;

225 Zhang and Dawe, 2000; Zhou and Zhang, 2000; Tsukamoto et al., 2001; Meldrum, 2003;

226   Sunagawa et al., 2007; Xie et al., 2007). Lin and Singer (2009), however, suggested that the

227   precipitation of aragonite as opposed to calcite was related mainly to the Mg/Ca molar ratio

228   rather than the actual amount of Mg. Based on their experiments, Togari and Togari (1955)

229   argued that more aragonite was formed as T or the amount of Mg increases. Lin and Singer

230   (2009) also suggested that Mg incorporation increases as T rises. The growth rate of calcite is

231   known to decrease as the concentration of dissolved Mg in the parent solution increases (Reddy

232   and Wang, 1980; Mucci and Morse, 1983; Deleuze and Brantley, 1992). Conversely, an increase

233   in the Mg/Ca ratio may lead to an increase in aragonite precipitation.

234   The exact role that Mg plays in the precipitation of aragonite as opposed to calcite has been

235   widely debated. The most commonly expressed idea is that Mg inhibits the growth of calcite and

236   thereby allows aragonite to grow rapidly (e.g., Bischoff, 1968; Bischoff and Fyfe, 1968; Berner,

237   1975; Fernández-Díaz et al., 1996; De Choudens-Sánchez and González, 2009). Inhibition of

238   calcite growth is generally attributed to "poisoning" of the growth sites on the calcite crystal

239   faces by Mg ions that are more strongly hydrated than the Ca ions (Lippmann, 1960; Bischoff,

240   1968; Reddy and Nancollas, 1976; Nancollas and Sawada, 1982; Hill and Forti, 1997; Meldrum,

241   2003; Rowling, 2004). Mg does not have the same effect on aragonite because it cannot be

242   incorporated into its lattice as easily (Berner, 1975; Mucci and Morse, 1983; Meldrum, 2003;

243   Jiménez-López et al., 2004). Nancollas and Sawada (1982) suggested that the inhibition of

244   calcite growth by Mg was related to surface-controlled processes, including Mg (1) acting as a

245   surface poison, (2) causing strain in the calcite lattice with concomitant increase in solubility of

246   the solid phase that, in turn reduces the supersaturation levels, and (3) preferentially poisoning of

247   crystal growth in directions perpendicular to *c* axis of the crystal.

248   Sun et al. (2015), based on thermodynamic considerations, argued that the inhibition of

249   calcite nucleation following inclusion of Mg is due to an increase in the surface energies. They

250   also suggested that for seawater, a Mg:Ca ratio > 2 and supersaturation levels > 18 were needed

251   for aragonite precipitation.

252   *2.6.2. Strontium*

253   Based largely on laboratory experiments, it has been proposed that Sr can lead to the

254   precipitation of aragonite (Kitano and Kawasaki, 1958; McCauley and Roy, 1974; Wada et al.,

255   1993, 1995). Kitano (1962a) used experiments to show that the amount of aragonite increased as

256   the amount of Sr increased, but only up to a certain limit where after the amount of aragonite

257   decreased. Buerger (1971) suggested that Sr, like Mg, inhibited calcite growth and thereby

258   promoted precipitation of aragonite. Sunagawa et al. (2007) supported this contention after

259   examining a succession of alternating calcite and aragonite laminae that had been precipitated

260   from spring waters in a fracture through a serpentine mass found at Kashio in Japan.

261   In contrast, Curl (1962) argued that the higher concentrations of Sr in aragonite, relative to

262   calcite, reflected a Sr partition coefficient that was more favorable to aragonite. Aragonite will

263   readily accept Sr into its lattice (up to 14% $SrCO_3$ – Radha and Navrotsky, 2013) and forms an

264   isomorphic series with strontianite (Speer and Hensley-Dunn, 1976). In terms of aragonite-

265   calcite precipitation, it is highly unlikely that the Sr ions will act in the same manner as Mg

266   because of the differences in the ionic radii of Sr (1.12 Å) and Mg (0.66 Å) relative to Ca (0.99

267   Å). These differences in size mean that the Sr ion will not enter the calcite lattice whereas it will

268   freely be incorporated into the aragonite lattice. Given this situation, it seems unlikely that Sr

269   will have any influence on the precipitation of aragonite as opposed to calcite.

270   *2.6.3. Barium*

271   The role that Ba plays in the precipitation of the $CaCO_3$ polymorphs is open to debate.

272   Some studies have suggested that its presence leads to calcite precipitation (Kitano, 1962a),

273   whereas other studies have shown that it leads to the precipitation of vaterite (McCauley and

274   Roy, 1974; Kitano et al., 1979; Wada et al., 1993).

275   *2.6.4. Other divalent metals and rare earths*

276   Various experiments have shown that other elements, including Fe, Ni, Co, Zn, and Cu also

277   promote aragonite precipitation (Wada et al., 1993, 1995; Tai and Chen, 1995; Meldrum, 2003),

278   whereas Mn, Cu, and Pb favour calcite precipitation (Tai and Chen, 1995). Rowling (2004)

279   suggested that calcite precipitation can be affected by many inhibitors, including heavy metals

280   and rare earths (Cu, Sc, Pb, La, Y, Cd, Au, Zn, Ge, Mn, Ni, Ba, Co), sulfate, and phosphate.

281   *2.7. Additives*

282   Over the last 10-15 years, numerous experiments have been undertaken in an effort to

283   determine the parameters that can assure precipitation of any one of the three $CaCO_3$

284   polymorphs. One of the strategies used to control such precipitation has involved additives that

285   are mixed with the reagents used in the experiments (e.g., Meldrum and Cölfen, 2008). Among

286   the vast array of additives that have been used for this purpose are ethylene glycol (Flaten et al.,

287   2009), urea and various acids (Wang, 2008), polysaccharides, polyacrylamide (PAM) and

288   polyacrylic acid (PPA) (Matahwa et al., 2008), Mg/DL-asparitic or L-tyrosine (Xie et al., 2007),

289   poly(diallyldimethylammonium (PDDA), cetyltrimethylammonium (CTAB), and

290   ethylenediaminetetraacetic acid (EDTA) (Atlay et al., 2007), glycine (Hou and Feng, 2005),

291   alcohol (Sand et al., 2012), and glutamic acid (Manoli and Dalas, 2000). This abbreviated list of

292   additives amply demonstrates the vast number of different chemical substances that have been

293   used in the experimental precipitation of vaterite, calcite, and aragonite. The primary focus in

294   most of these studies has been production of a given polymorph and relatively little attention has

295   been given to the reasons that control that precipitation. Xyla et al. (1991) argued that the

296   presence of additives retarded precipitation rates. Meldrum and Hyde (2001) suggested,

297   however, that the additives may retard crystal growth because the additives complex the cations

298   that are in solution and thereby change supersaturation levels and the activity of the ions, or

299   reduce crystal growth rates by binding to the growth sites.

300   **3. Spatial relationships between $CaCO_3$ polymorphs in spring deposits**

301   Calcite and aragonite are common in spring systems throughout the world. To date,

302   however, vaterite has only been recorded from a supraglacial spring on the northern part of

303   Ellesmere Island (Arctic Canada) where it occurs with calcite, gypsum, and native sulfur

304   (Grasby, 2003). According to Grasby (2003), vaterite exists there because of the extremely cold

305   environment and the high-pH waters.

306   Aragonite and/or calcite precipitates have been reported from many springs, including

307   those in Italy (Guo and Riding, 1992; Folk, 1994; Guo and Riding, 1998), northern Euboea and

308   Eastern Central Greece (Kanellopoulos, 2012), Japan (Okumura et al., 2012), Indonesia

309   (Okumura et al., 2012; Sugihara et al., 2016), China (Jones and Peng, 2014a, 2014b, 2016),

310   Kenya Rift Valley (Jones and Renaut, 1996; Renaut and Jones, 1997), Turkey (Özkul et al.,

311   2013), and the U.S.A. (Fouke, 2011) These selected examples clearly illustrate that aragonite

312   and calcite are common worldwide and not restricted to any specific areas. Any assessment of

313   the factors that control the precipitation of these two polymorphs in these settings must be

314   applied relative to the known spatial and temporal relationships between the two minerals in

315   those settings (Figs. 2, 3).

316   *3.1. Spatial and temporal relationships between aragonite and calcite*

317   The following examples have been selected to specifically illustrate the spatial and

318   temporal relationships that exist between aragonite and calcite in spring deposits.

319   *3.1.1. Temporal variation in aragonite-calcite precipitation*

320   Travertines at Rakuenso in the Myoken hot spring area of southwest Japan, are

321   characterized by light coloured laminae (150-2509 μm thick) formed of calcite dendrite crystals

322   that alternate with dark-coloured (50-100 μm thick) aragonite laminae (Okumura et al., 2013a).

323   A similar alternation of aragonite and calcite micro-laminations has also been documented from

324   spring deposits at Rapolano, Italy (Guo and Riding, 1992). Alternating aragonite and calcite

325   laminae of similar style are also evident in spring deposits from Gongxiaoshe, Yunnan Province,

326   China (Fig. 2A).

327   At Jifei, located in Yunnan Province, China (Jones and Peng, 2014a), deposits precipitated

328   from spring water that flowed over a cliff face are formed of alternating aragonite and calcite

329   layers that are each up to 3 cm thick (Fig. 3A). The fact that the layers are thicker than those in

330   the deposits described by Okumura et al. (2013b) and Guo and Riding (1992) and found at

331   Gongxiaoshe (Fig. 2A) implies that the physiochemical conditions did not change with the same

332   frequency as those associated with other springs in Japan, Italy, and China.

333   *3.1.2. Geographic variation in individual spring systems*

334   On Angel Terrace in the Mammoth Hot Spring system of Yellowstone National Park, the

335   distribution of calcite and aragonite changes downstream from the spring vents (Fouke et al.,

336   2000). In that system, aragonite forms at temperatures > 40°C, calcite and aragonite are co-

337   precipitated at T of 30 to 43°C, and calcite is found where T is < 30°C (Fouke et al., 2000). This

338   distribution pattern, however, is complicated by (1) mixtures of calcite and aragonite that

339   precipitate at the air-water interface in the higher-T ponds and aragonite shrubs that form on the

340   floors of high-T ponds, and (2) mixtures of calcite and aragonite in the downstream sites that

341   reflect, as least in part, the downflow transportation of some $CaCO_3$ crystals (Fouke et al., 2000).

342   *3.1.3. Geographic variation between springs*

343   Some spring systems are characterized by calcite alone whereas others are dominated by

344   aragonite. Examples of spring deposits formed entirely of calcite include those from Shuzhishi

345   Spring (Fig. 3B) in the Rehai geothermal area, Tengchong (Jones and Peng, 2012), the Clinton

346   deposits in British Columbia, Canada (Jones and Renaut, 2008), Waikite Springs, New Zealand

347   (Jones et al., 1996, 2000), and Lýsuhóll, Iceland (Jones et al., 2005).

348   Examples of spring deposits formed solely of aragonite are relatively rare but include those

349   documented by Folk (1994, his Fig. 2) and Pentecost (2005, his Fig. 37). Other examples where

350   aragonite is the dominant polymorph includes the Azuaje Travertine found on Gran Canaria

351   Island, Spain (Rodríguez-Berriguete et al., 2012).

352   At many springs, aragonite and calcite are intermixed in varying proportions. Specific

353   examples of mixed calcite-aragonite deposits include those found at Chemurkeu on the shores of

354   Lake Bogoria, Kenya (Jones and Renaut, 1996; Renaut and Jones, 1997), in modern hot springs

355   at Shiqiang (Stone Wall) in Yunnan Province, China (Jones and Peng, 2016), the Myoken hot

356   spring area of southwest Japan (Okumura et al., 2013a), and in spring deposits at Rapolano, Italy

357   (Guo and Riding, 1992). Likewise, at Pamukkale (Turkey), some of the vertically banded

358   travertines in the Çukurbağ fissure ridge are formed of alternating laminae of fibrous aragonite

359   and calcite (Özkul et al., 2013, their Fig. 11).

360   *3.1.4. Microscale relationships between aragonite and calcite crystals*

361   In many spring systems, like those at Jifei (Jones and Peng, 2014a) and Shiqiang (Jones

362   and Peng, 2016) in Yunnan Province, China, the spring deposits include (1) calcite and aragonite

363   that grew alongside each other in the same laminae (Fig. 2B, C), (2) aragonite crystals that are

364   rooted on the top of calcite crystals (Fig. 2D, E), and (3) aragonite crystals that are encased by

365   calcite crystals (Fig. 2F).

366   **4. Comparison of CaCO$_3$ polymorph precipitation in cave speleothems and springs**

367   Many speleothems in caves throughout the world are formed of aragonite and/or calcite

368   (e.g., Cabrol, 1978; Bar-Matthews et al., 1991; Hill and Forti, 1997; Frisia et al., 2002; Rowling,

369   2004; Rossi and Lozano, 2016). In those settings, aragonite precipitation from freshwater occurs

370   at temperatures ranging from 2.4°C to 20°C, but is most common where T > 12°C (Frisia et al.,

371   2002). The temperature in caves, however, seems to play no role in dictating the precipitation of

372   calcite as opposed to aragonite (Gonzalez and Lohmann, 1987; Frisia et al., 2002).

373   The spatial and temporal relationships between aragonite and calcite in cave speleothems,

374   which are essentially the same as in spring deposits, includes (1) alternation of aragonite and

375   calcite laminae at variable scales, (2) lateral changes from aragonite to calcite along individual

376   laminae, and (3) some speleothems being formed entirely of calcite whereas others are formed

377   solely of aragonite (e.g., Wassenburg et al., 2012).

378   As with spring deposits, the alternation between calcite and aragonite precipitation has

379   been attributed to many different parameters, including (1) supersaturation levels (Rossi and

380   Lozano, 2016), (2) CO$_3$ concentrations (Riechelmann et al., 2014), (3) nucleation effects related

381   to substrate mineralogy (Fairchild and Baker, 2012), (4) high Zn concentrations in drip waters

382   (Caddeo et al., 2011), (5) drip rates that affect CO$_2$ degassing rates (Holland et al., 1964; Hill and

383 Forti, 1997; Frisia et al., 2002), and (6) Mg/Ca ratio of the drip waters (Rossi and Lozano, 2016).

384 The situation with respect to supersaturation levels is unclear because aragonite precipitation is

385 associated with low supersaturation levels in some caves, whereas in other caves it has been

386 linked to high supersaturation levels (Railsback et al., 1994; Denniston et al., 2000). Murrray

387 (1954), based on examination of cave waters, cave deposits, and experiments concluded that the

388 factors that favoured aragonite precipitation in caves included (1) high T, (2) low concentrations

389 of calcium bicarbonate, and (3) high concentrations of Mg, Sr, and Pb. He also noted, however,

390 that the pH, and the presence of Mn, Ba, or sulfate ions had little impact on this issue. In

391 essence, this contradicts most of the parameters that Fisher (1962) and Curl (1962) considered

392 critical for determining the precipitation of aragonite and calcite in caves.

393   Wassenburg et al. (2012), based on aragonite-calcite speleothems in caves in Morocco,

394 suggested that decreased rainfall led to precipitation of aragonite, with more aragonite being

395 precipitated in the dolostone cave, where the Mg/Ca ratio of drip water was higher, than in the

396 limestone cave. Although this explained the temporal changes, they were unable to explain the

397 lateral aragonite-to-calcite transitions. Despite not finding a clear correlation between the Mg:Ca

398 ratio and calcite-aragonite precipitation, Gonzalez and Lohmann (1987), noted that aragonite

399 only forms if the Mg:Ca ratio is greater than 1.5.

400   Hill and Forti (1997) in their review of calcite and aragonite precipitation in caves offered

401 the following conclusions on the problem: (1) T does not seem to be a controlling factor in caves

402 because aragonite commonly forms in caves at high latitudes where T is commonly ~ 0°C and in

403 caves with higher T in the tropical areas, (2) aragonite precipitation generally arises where

404 calcite growth is inhibited by high Mg content in the fluids (3) Sr does not seem to be a critical

405 issue, (4) pH does not seem to affect precipitation, (5) the degree of supersaturation is critical as

406   it controls the rate of precipitation that dictates nucleation and growth rate; at low

407   supersaturation, aragonite nucleation is higher than for calcite, and (6) aragonite precipitation is

408   favoured in areas of caves where CO_2 levels are high.

409   **5. Models for calcite-aragonite precipitation in spring systems**

410   If it is assumed that spring precipitates have formed from the waters that are now flowing

411   over them, it should be possible to correlate the constituent minerals with some aspect(s) of their

412   environmental setting. Folk (1994, his Fig. 2) and Pentecost (2005, his Fig. 37) used this

413   approach when they tried to correlate the precipitation of aragonite and/or calcite with the water

414   T, Mg content, and Mg:Ca ratio (Fig. 4). On the basis of his diagram (Fig. 4A), Folk (1994, p.

415   235) argued that (1) aragonite forms if water T > 40-45°C, regardless of fluid composition, (2) if

416   the molar Mg/Ca ratio is > 1:1, aragonite forms regardless of water T, and (3) calcite forms if T

417   < 40°C and the water is Ca-rich. Critically, he noted that there are two exceptions to these

418   general rules, namely (1) in areas with rapid CO_2 degassing, aragonite will form even if the

419   conditions favor calcite precipitation, and (2) if ion transportation is slow because of viscous

420   fluids or mucus films, calcite can form even in hot waters (cf., Buczynski and Chafetz, 1991).

421   Pentecost (2005), while agreeing that T and Mg content were the most important controls, also

422   argued that the situation can be complicated by (1) kinetic effects given that Kitano (1963) had

423   suggested that aragonite dominates in Japanese springs where the rate of CO_2 degassing is high,

424   (2) the presence of organic matter because numerous studies, including those by Murray (1954)

425   and Lowenstam and Wiener (1983), had demonstrated that all three $CaCO_3$ polymorphs can form

426   in the presence of organic matter at room temperature, and (3) the presence of Sr that can lead to

427   the precipitation of aragonite as suggested by Malesani and Vannucchi (1975).

428   In some springs, aragonite precipitation is clearly associated with small-scale variations in

429   CO_2 degassing. At Futamata Spring, Japan, Kitano (1962b) noted that calcite was precipitated in

430   flowing water whereas aragonite was precipitated from the same water as it splashed onto rock

431   surfaces. He suggested that the aragonite precipitated because of the rapid CO_2 degassing

432   triggered by agitation of the splashing water. Chafetz et al. (1991) attributed the formation of

433   aragonite around gas bubbles in pools in a small spring system in SW Colorado, USA, to rapid

434   CO_2 degassing that produced very high levels of supersaturation.

435   Many springs that are located in volcanically active areas are characterized by gas

436   emissions that have a high CO_2 content. Intergrown calcite and aragonite precipitates are, for

437   example, a feature of the hot springs at Chermukeu on the shores of Lake Bogoria in the Kenyan

438   Rift Valley (Jones and Renaut, 1996; Renaut and Jones, 1997). There, the spring waters have

439   been characterized by constant water chemistry over last 30 years, and have very low Mg content

440   with a Mg:Ca ratio never above 1:1, a Sr content of < 350 ppb, and no evidence of microbial

441   control (Renaut and Jones, 1997). Gases emitted with the spring waters at Chermukeu, as for

442   other springs in the Kenyan Rift Valley, have a high CO_2 content that is, in some cases, up to

443   98% (McCall, 1967; Darling et al., 1995). Renaut and Jones (1997) concluded that the

444   temporally-irregular alternation between aragonite and calcite precipitation was related to

445   temporal changes in the PCO_2 and CO_2 degassing.

446   There are numerous springs in Yunnan Province, China, which is a tectonically active area

447   that experiences numerous earthquakes. Spring deposits, including those at La Xin (Jones and

448   Peng, 2014b), Jifei (Jones and Peng, 2014a), Eryuan (Peng and Jones, 2013), and Shiqiang

449   (Jones and Peng, 2016) are characterized by both aragonite and calcite precipitates that are

450   integrated at all scales. Water in these springs, with T ranging from 57 to 88°C and pH from 6.6

451   to 8.5, are characterized by low Mg levels and low Mg:Ca ratios (Jones and Peng, 2016, their

452   Table 1). At Shiqiang, for example, the Mg:Ca ratio is 0.35 (based on ppm) or 0.63 (molar

453   ratio). In most of these springs, there are thriving microbial mats and there is clear evidence that

454   microscale variations in the distribution of calcite and aragonite is related to precipitation that

455   has taken place in the microdomains in those mats (Peng and Jones, 2013). It has, however,

456   proven impossible to relate the aragonite and calcite precipitation to T, pH, Mg content or any

457   other parameter of the water chemistry. CO_2 can form up to 90% of the gas emissions associated

458   with the springs in the Tengchong geothermal area (Du et al., 2006; Cheng et al., 2014) and the

459   CO_2 content is known to vary with time. At Dagunguo, the CO_2 content in the gases has varied,

460   somewhat irregularly, from 49.7% in 1980 to 99.7% in 2000 (Du et al., 2006, their Table 4). The

461   temporal changes in the CO_2 gas has been linked to earthquake activity (Ren et al., 2005),

462   hydrothermal explosions (Shangguan et al., 2005), and/or variations in the source of the gas (Du

463   et al., 2005). For hot springs in western Sichuan Province, increases in CO_2 emissions typically

464   occurs following major earthquakes (Zhou et al., 2015). Thus, Jones and Peng (2016) suggested

465   that variations in the amount of CO_2, and hence its rate of degassing, were probably responsible

466   for the changes between aragonite and calcite precipitation.

467   There is clear evidence that the presence of microbes and microbial mats can influence

468   precipitation of the $CaCO_3$ polymorphs, especially at a small scale. At Pancuran Pitu in central

469   Java, Indonesia, there is a travertine mound formed exclusively of aragonite that is characterized

470   by well-developed microbial mats (Okumura et al., 2012). Downstream, the water T ranges from

471   51.8° to 32.9°C but the Mg:Ca molar ratio is > 1.7 throughout. Although Okumura et al. (2012)

472   argued that the microbial mats controlled development of the aragonite crystals, they suggested

473   that aragonite was being precipitated because of the high Mg:Ca ratio. Aragonite precipitates

474   found around Nagano-yu Hot Spring in southwest Japan (Okumura et al., 2011) are characterized

475   by sub-millimeter laminae that were attributed to diurnal variations in the activity of the biofilms

476   associated with that deposit. In some biofilms, neighbouring microdomains only microns apart

477   can be the sites of aragonite and calcite precipitation that take place at the same time (Peng and

478   Jones, 2013). These examples clearly illustrate that biofilms can have a pronounced effect on

479   precipitation of the $CaCO_3$ polymorphs.

480   Greer et al. (2015), based on a sample collected from Shiqiang (exact location not

481   specified), argued that "aragonite rods" formed as a result of phase transformation from the

482   associated Mg-calcite. It seems highly unlikely, however, that the metastable aragonite would

483   evolve from the stable calcite. Furthermore, Greer et al. (2015) did not consider the possibility

484   of co-precipitation of the two phases or that the aragonite crystals may have been precipitated

485   first and then subsequently entombed by calcite crystals. Thus, the proposal offered by Greer et

486   al. (2015) is not considered viable.

487   After describing spring deposits formed of aragonite and calcite in Northern Euboea and

488   eastern central Greece, Kanellopoulos (2012) suggested, based on previous studies, that the

489   precipitation of the different polymorphs was potentially controlled by (1) temperature, (2) Sr

490   content, (3) Mg/Ca ratio, (4) pCO_2$, and (5) precipitation rates.

491   **6. Discussion**

492   Numerous studies based on natural spring systems and laboratory experiments have shown

493   that precipitation of aragonite as opposed to calcite can be attributed to many different

494   parameters. Collectively, the experimental studies have demonstrated that precipitation of the

495    $CaCO_3$ polymorphs can be controlled by virtually any parameter, including some that are

496   unrealistic in the context of natural spring systems. Boulos et al. (2014), for example, argued

497 that the angle of tilt of the Vortex Fluidic Device that they used in their experiment was one

498 parameter that affected the nature of the $CaCO_3$ precipitate. Nevertheless, the parameters that

499 are most commonly associated with the precipitation of aragonite as opposed to calcite include

500 water T, inhibition of calcite growth by "poisoning" of the calcite crystal growth surfaces, the

501 pCO_2 and the rate of CO_2 degassing, microbial activity, and/or saturation levels. Any

502 parameter(s) deemed to be important in this respect must, however, be operative at all scales

503 given that the aragonite–calcite precipitation varies from the microscale to the megascale.

504 The link between T and polymorph precipitation has commonly been regarded as a primary

505 control (Folk, 1994; Pentecost, 2005), with the idea that aragonite generally forms at higher

506 temperatures. This notion, however, is not universally applicable as demonstrated by the

507 following examples:

508 • In many spring vent pools in the Kenyan Rift Valley and throughout Yunnan Province,

509 China, aragonite and calcite (Figs. 2, 3) have been precipitated from the same parent fluid, at

510 the same temperatures, and at the same time (Renaut and Jones, 1997; Jones and Peng,

511 2016). In these examples, it is important to stress that precipitation is taking place in the

512 vent pool where the water has undergone only minimal cooling and there has been no

513 opportunity for downslope changes in water T, pH, or chemistry.

514 • In caves, aragonite is generally more common in cold, high latitude caves than in the

515 warmer, low latitude caves (Hill and Forti, 1997). Even in warmer caves, the T is generally

516 only ~ 26°C and hence much cooler than water found in the high-T springs in places like the

517 Kenyan Rift Valley and Yunnan Province, China.

518   • Although there are spring systems where polymorph precipitation appears to be linked to

519   water T, the correlation is never perfect, and as noted by Folk (1994) and Fouke et al. (2000)

520   there are always exceptions.

521   Considerations like these indicate that there is no direct linkage between water T and

522   polymorph precipitation. It is entirely possible, however, that T may be controlling or

523   influencing another parameter (e.g., supersaturation level) that exerts a more direct role in

524   dictating which polymorph is precipitated.

525   The notion that aragonite precipitation is a result of calcite growth inhibition has commonly

526   been advanced as the underlying reason for precipitation of this unstable polymorph, irrespective

527   of where it is found (e.g., Meldrum, 2003; Rowling, 2004). The underlying premise is that

528   elements, such as Mg^{2+}, "poisons" the growth surfaces on the calcite crystals that, in turn, allows

529   aragonite to precipitate because those elements do not inhibit aragonite precipitation.

530   Application of this model to aragonite found in spring deposits, however, needs to be used with

531   caution for the following reasons:

532   • Models for "poisoning" the growth surfaces of calcite are based on the assumption that the

533   crystals are growing via the "classical crystal growth model" with surface controlled

534   processes being operative (e.g., Nancollas and Sawada, 1982). It is, however, becoming

535   increasingly clear that calcite crystal growth in spring systems commonly involves "non-

536   classical crystal growth models" whereby mesocrystals develop through the addition of

537   nanocrystals in a common crystallographic register (e.g., Meldrum and Cölfen, 2008; Jones,

538   in press). As yet, it is not clear if the presence of Mg or any other element inhibits the

539   growth of calcite mesocrystals.

540 • Many springs in the Kenyan Rift Valley (e.g., Renaut and Jones, 1997) and Yunnan

541   Province, China (e.g., Jones and Peng, 2016) have waters with very low Mg content and

542   Mg:Ca ratios that are commonly < 1:1. Despite this, aragonite is a common precipitate.

543 • The premise that Sr may inhibit calcite growth in the same way as Mg is not accepted

544   because Sr will not substitute readily into the calcite lattice, whereas it will readily enter into

545   the aragonite lattice. This cannot be considered as reliable evidence for inhibition of calcite

546   growth.

547   The presence of CO_2 in spring waters has frequently been implicated in the precipitation of

548 the $CaCO_3$ polymorphs with clear supporting evidence coming from study of natural systems

549 like those in the Kenyan Rift Valley (e.g., Renaut and Jones, 1997) and Yunnan Province, China

550 (e.g., Jones and Peng, 2016) and laboratory experiments (e.g., Kitano, 1962b). Springs that are

551 located in volcanically and tectonically active areas, for example, are commonly supercharged

552 with CO_2, which may be derived from magma chambers, decarbonation of subsurface carbonate-

553 silicate rocks, and/or heating of organic matter (e.g., Pentecost, 2005). CO_2 in these spring

554 systems are known to be temporally variable with seismic activity commonly triggering an

555 increase in CO_2 gas emissions (Sorey et al., 1998; Zhou et al., 2015). In some cases, CO_2

556 degassing can reach levels that are harmful to local vegetation (Sorey et al., 1998). Spring water

557 generally has a higher CO_2 content than the atmosphere, especially in situations where it has

558 been super-charged with CO_2, and this typically leads to degassing as the CO_2 in the water tries

559 to equilibrate with the air (cf., Chafetz et al., 1991). Such degassing causes an increase in

560 supersaturation levels in the water may then lead to the precipitation of calcite and/or aragonite.

561 Critically, this can happen at all scales, ranging from $CaCO_3$ precipitation around gas bubbles

562 (e.g., Schreiber et al., 1981; Chafetz et al., 1991), to rafts that form at the water-air interface

563 (e.g., Black, 1953; Taylor et al., 2004), to large scale deposits at cascades or waterfalls where

564 water agitation significantly increases CO_2 degassing (e.g., Zhang et al., 2001). The potential

565 control that CO_2 content and degassing has on $CaCO_3$ polymorph precipitation is significant

566 because available evidence clearly illustrates that this process can (1) vary through time in

567 accord with natural variations in CO_2 flux, and (2) control processes that operate at all scales

568 ranging from micro- to mega-scale.

569 Biofilms generated by various microbial populations are common features of many spring

570 systems, irrespective of water temperature. The biofilms serve to isolate the substrates from the

571 spring water (Decho and Lopez, 1993; Decho, 2000, 2010), and are characterized by numerous

572 microdomains (Decho, 2010). As noted by Peng and Jones (2013) this means that different

573 conditions can exist in each microdomain with all having physiochemical conditions that are

574 different than those in the overlying spring water. Thus, aragonite, calcite, and even amorphous

575 calcium calcite (ACC) may develop at the same time in the same biofilm (Peng and Jones, 2013).

576 Similarly, Okumura et al. (2013b) demonstrated that diurnal variations associated with biofilms

577 can lead to alternating calcite and aragonite laminae. In most cases, it appears that the microbes

578 have, in one way or another, modified the physiochemical condition in the microdomains of the

579 biofilms to favor precipitation of the different polymorphs. Given that this can take place at

580 scales of $< 1 \ \mu m$ it has, so far, proven impossible to monitor and clearly demonstrate how this is

581 achieved.

582 The debate concerning the factors that control aragonite as opposed to calcite precipitation,

583 irrespective of where it is taking place, is typically based on the premise that there is one

584 universal feature that explains the process. The fact that no universal cause has yet been

585 identified suggests that many different parameters may be involved and that each one may be site

586   specific. This was already implied by Folk (1994) who noted exceptions to his notion that the

587   precipitation of calcite and aragonite were controlled largely by water T and/or the Mg:Ca ratio.

588   In any assessment of the underlying causes of calcite and aragonite precipitation, care should be

589   given to separating parameters into those that have a direct or indirect impact on polymorph

590   precipitation. It is, for example, clear that very high levels of CO_2 degassing will invariably lead

591   to the precipitation of aragonite. Conversely, T does not seem to play a direct role in polymorph

592   precipitation but it may influence other parameters (e.g., saturation levels) that do control

593   precipitation.

594   The factors that control aragonite and calcite precipitation in spring systems has been a

595   subject of considerable debate and controversy ever since the question was first posed by Meigen

596   (1901) and Warth (1902). This long-standing debate probably reflects the complexity of the

597   problem and the fact that there is no universal control that is applicable in all situations. It seems

598   evident that resolution of this problem will require a change in research approach that may

599   include: (1) detailed on-site micro-scale monitoring of spring systems with the view of

600   correlating active precipitation with precise physiochemical characteristics of the parent solute,

601   (2) establishing criteria for recognizing the presence of biofilms in situations where physical

602   evidence of their presence is missing because they were not calcified, (3) further investigation

603   and resolution of the role that biofilms play in $CaCO_3$ precipitation, and (4) integration of

604   information derived from spring systems and laboratory experiments while recognizing that there

605   are significant differences between the two approaches in terms of scale, time, and the number of

606   active variables involved. In the context of spring systems, it seems unlikely that the calcite-

607   aragonite precipitation problem will be resolved unless there is a radical change in the manner in

608   which these systems are examined.

609 **7. Conclusions**

610   Synthesis of information available from numerous studies of natural spring systems and

611 countless laboratory experiments considered relative to natural occurrences of aragonite and

612 calcite in spring systems suggests that the causes for precipitation of aragonite at a particular

613 location should be viewed from hierarchical perspective, whereby an ordered series of

614 possibilities are considered for each system. The following points are critical.

615   • Aragonite, commonly with calcite as a co-precipitate, will form from spring water that has

616   a high CO_2 content and rapid CO_2 degassing. Under this situation, a high Mg content or a

617   high Mg:Ca ratio are not required for aragonite precipitation. This can happen from the

618   microscale (e.g., around air bubbles) to megascale (e.g., laminae/bed production). In all

619   situations, the precipitation is driven by the very high supersaturation levels that result from

620   rapid CO_2 degassing.

621   • Aragonite will be precipitated from waters that have low levels of CO_2 degassing provided

622   the Mg:Ca ratio is high. The critical level of the Mg:Ca ratio that triggers aragonite

623   precipitation is generally thought to be somewhere in the range of 1 (Folk, 1994) to 2 (Sun

624   et al., 2015). Aragonite precipitation takes place because the Mg inhibits growth of the

625   calcite.

626   • Aragonite–calcite–ACC may be precipitated at the same time within the microdomains that

627   develop within biofilms that are commonly found in spring systems. Such precipitation

628   can take place irrespective of CO_2 levels and the Mg:Ca ratio in the spring water. Similar

629   processes associated with the diurnal changes in the behaviour of the biofilms may also

630   cause diurnal variations in the precipitation of calcite and aragonite.

631   The co-precipitation of aragonite and calcite can only take place if the water is

632   supersaturated with respect to both polymorphs. In each spring, various factors will control the

633   supersaturated levels in the spring water, which is the ultimate driver of calcite and aragonite

634   precipitation irrespective of scale.

643
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1067

FIGURE CAPTIONS

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1069   **Fig. 1.** (A) Percentage of aragonite in $CaCO_3$ as a function of fluid temperature (scale not

1070   specified but assumed to be Celsius) from experiments by Favire (1946, p. 46). (B)

1071   Percentages of aragonite, calcite, and vaterite as a function of temperature in experiments

1072   by Kitano et al. (1962, their Fig. 1). (C) Percentages of aragonite, calcite, and vaterite as a

1073   function of temperature in experiments with CO_2 being bubbled through the parent fluid

1074   (Kitano, 1962b, his Fig. 2). (D) Precipitation of aragonite and calcite as a function of the

1075 Mg/Ca_{aq} ratio and saturation levels based on experiments by De Choudens-Sánchez and

1076   González (2009, their Fig. 4).

1077   **Fig**. **2.** SEM photomicrographs showing microscale relationships between calcite and aragonite

1078   in various hot spring deposits in Yunnan Province, China. Panel A from Gongxioshe,

1079   LaXin (see Jones and Peng, 2014b, for description of site); panels B, C, E, F from

1080   Sqhiqiang (see Jones and Peng, 2016, for description of site); and panel D from Jifei (see

1081   Jones and Peng, 2014a, for description of site). (A) Alternating laminae of aragonite and

1082   calcite. (B) Calcite crystals overlying aragonite laminae. Note small clusters of aragonite

1083   needles between some of the calcite crystals. (C) Clusters of aragonite crystals growing

1084   between calcite crystals. (D) Aragonite cluster nucleated on top of a calcite crystal. (E)

1085   Intermixed calcite and aragonite crystals. (F) Clusters of aragonite crystals encased by

1086   calcite crystals.

1087   **Fig. 3**. (A) Alternating beds of calcite (light coloured) and aragonite (dark coloured) at Jifei,

1088   Yunnan Province, China formed by spring waters flowing down a cliff face (see Jones and

1089   Peng, 2014a, for descriptions of site). (B) Spring deposits at Shuzhishi Spring, Rehai

1090   Geothermal area, Tengchong, Yunnan Province, China. Succession of calcite spring

1091 deposits (no aragonite) with each bed formed of calcite dendrites (see Jones and Peng,

1092 2012, for description of site).

1093 **Fig. 4.** Proposed relationships between precipitation of calcite and aragonite in high spring

1094 systems with water T, Mg content, and Mg:Ca ratios as proposed by (A) Folk (1994, his

1095 Fig. 2) and (B, C) Pentecost (2005, his Fig. 37). For these graphs from Pentecost (2005),

1096 the temperature and Mg:Ca and Mg content axes have been transposed in order to facilitate

1097 easier comparison with the Folk's graph that is shown in panel A.
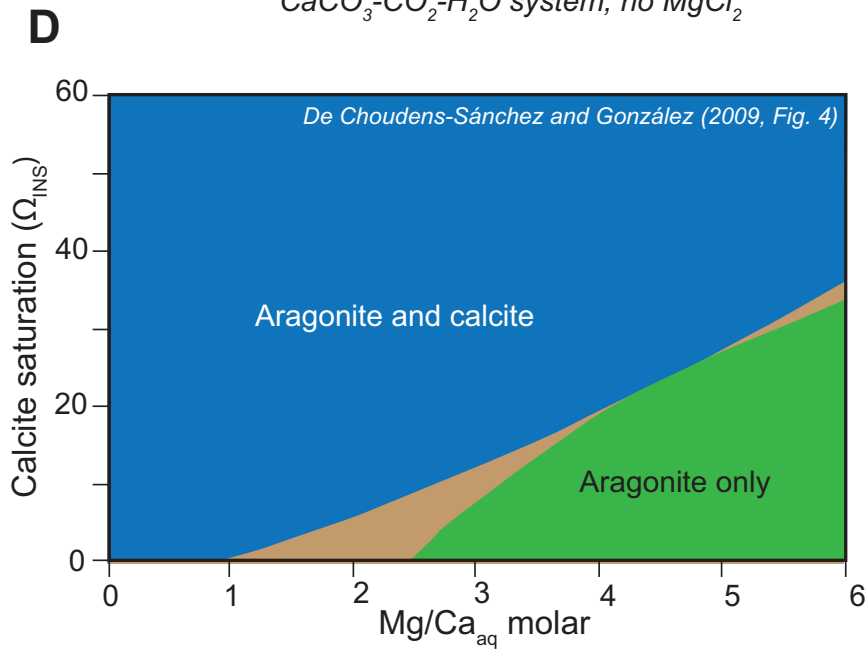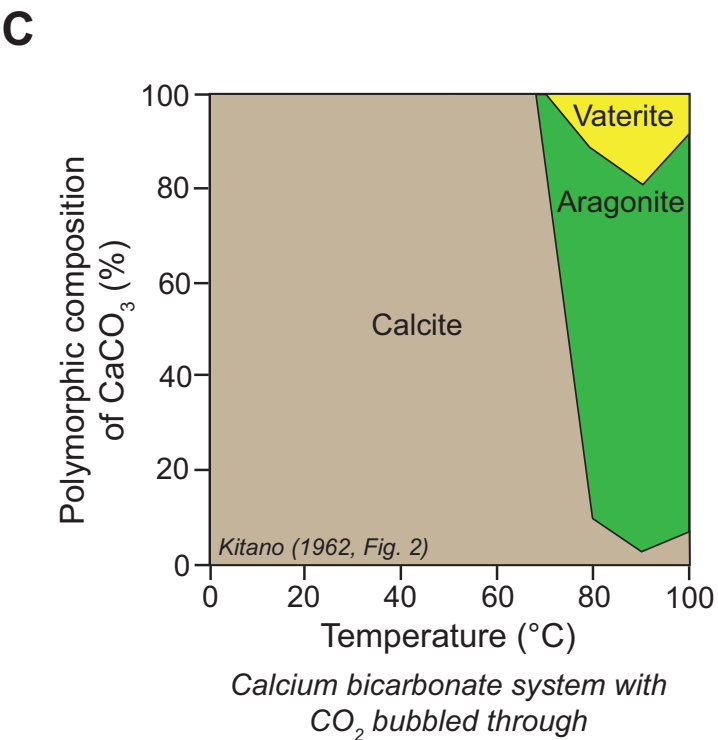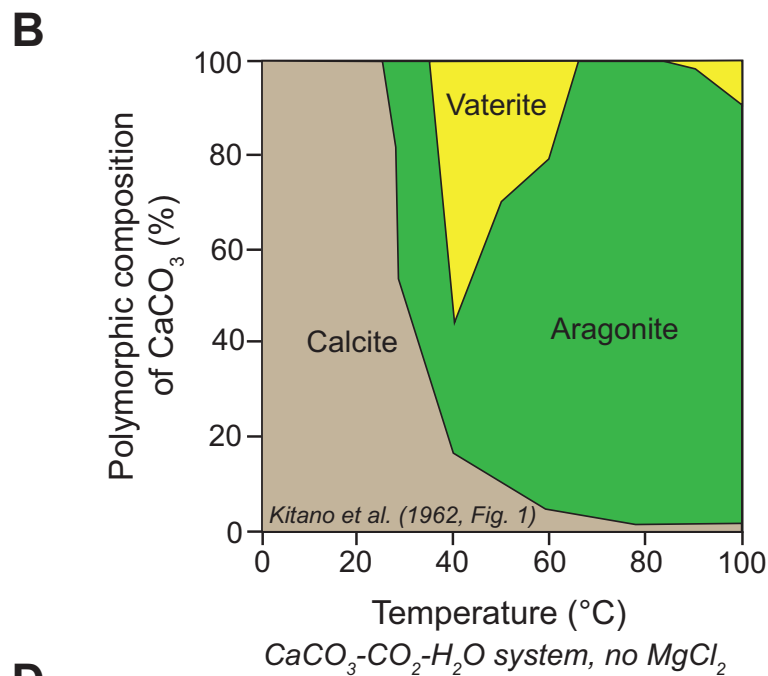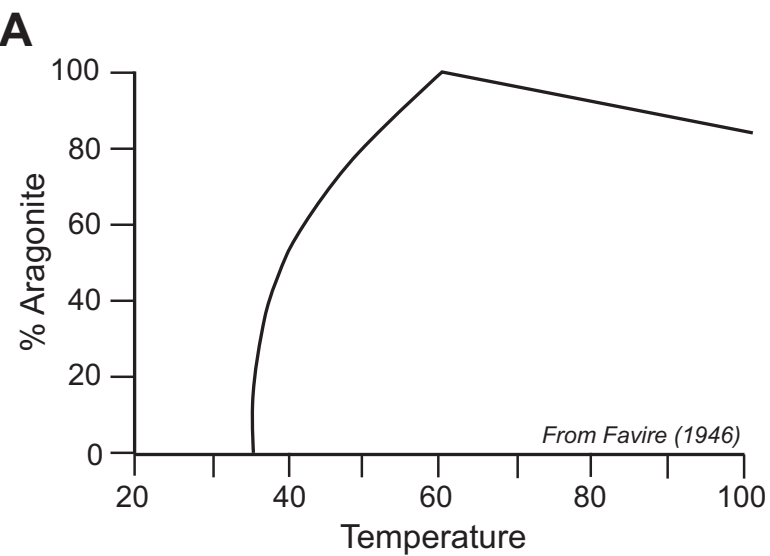
Figure 1

A

% Aragonite vs Temperature

From Favire (1946)

B

Polymorphic composition of CaCO$_3$ (%) vs Temperature (°C)

Calcite, Vaterite, Aragonite

Kitano et al. (1962, Fig. 1)

CaCO$_3$-CO$_2$-H$_2$O system, no MgCl$_2$

C

Polymorphic composition of CaCO$_3$ (%) vs Temperature (°C)

Calcite, Vaterite, Aragonite

Kitano (1962, Fig. 2)

Calcium bicarbonate system with CO$_2$ bubbled through

D

Calcite saturation (Ω_{INS}) vs Mg/Ca$_{aq}$ molar

Aragonite and calcite, Aragonite only

De Choudens-Sánchez and González (2009, Fig. 4)

Figure 2
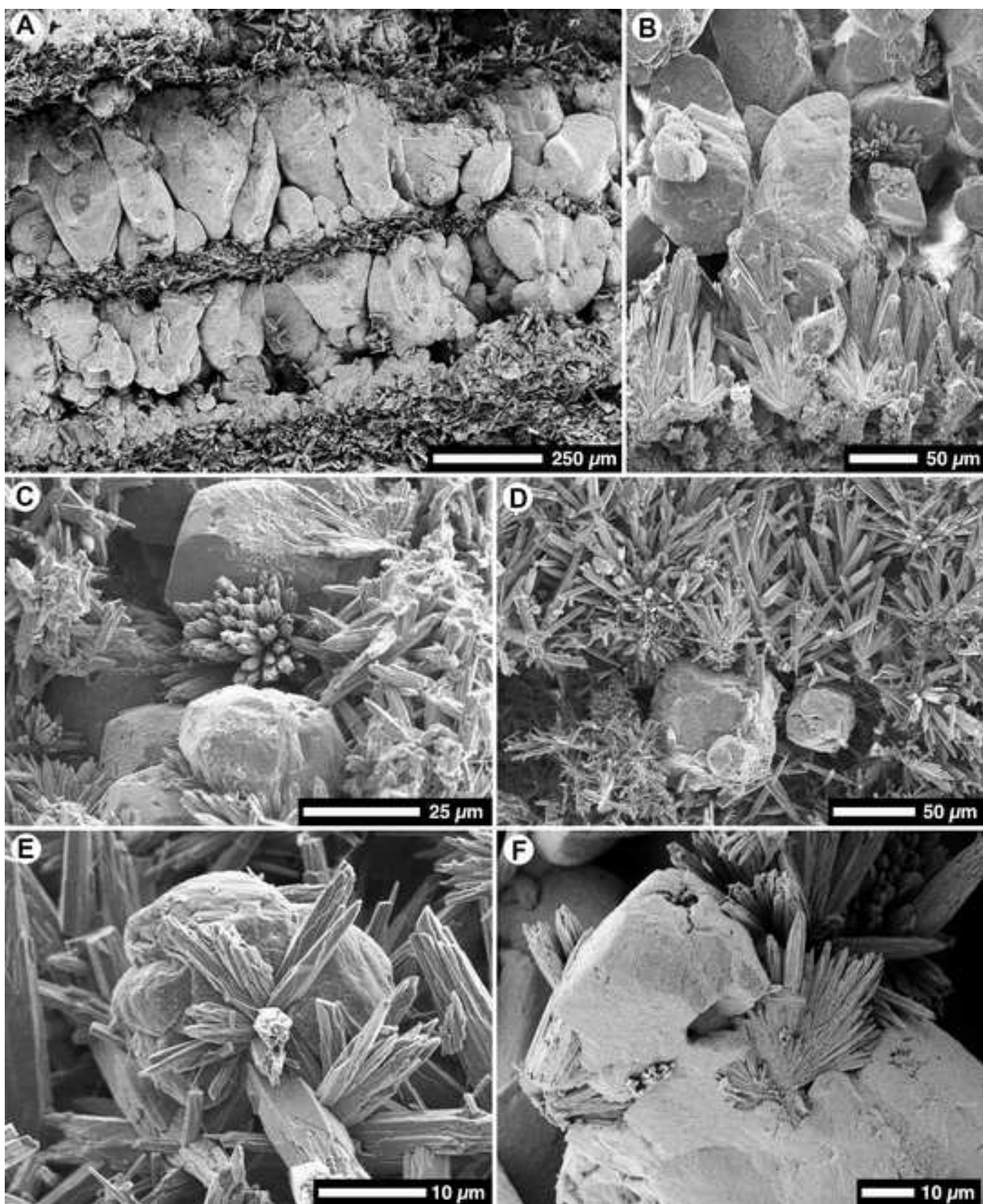**Click here to download high resolution image**

Figure 3
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Figure 4