

1 Sequestration of antimony on calcite observed by
2 time-resolved nanoscale imaging

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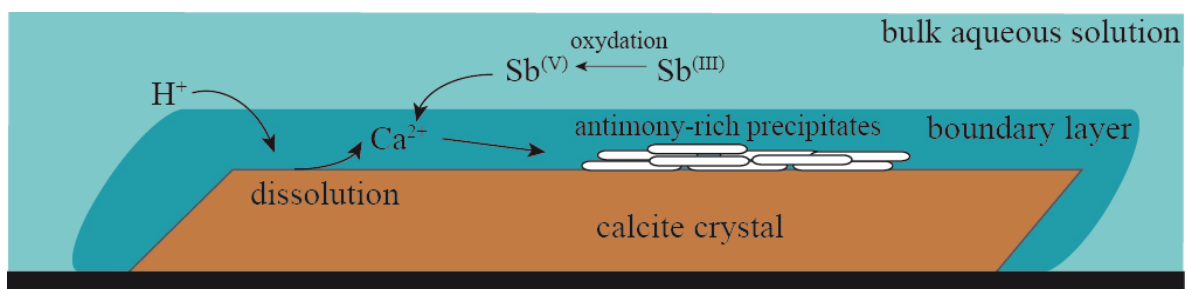
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17 ABSTRACT. Antimony, which has damaging effects on the human body and the ecosystem, can
18 be released into soils, ground- and surface waters either from ore minerals that weather in near
19 surface environments, or due to anthropogenic releases from waste rich in antimony, a
20 component used in batteries, electronics, ammunitions, plastics and many other industrial
21 applications. Here, we show that dissolved Sb can interact with calcite, a widespread carbonate
22 mineral, through a coupled dissolution-precipitation mechanism. The process is imaged in-situ,
23 at room temperature, at the nanometer scale by using an atomic force microscope equipped with
24 a flow-through cell. Time-resolved imaging allowed following the coupled process of calcite
25 dissolution, nucleation of precipitates at the calcite surface and growth of these precipitates.
26 Sb(V) forms a precipitate, whereas Sb(III) needs to be oxidized to Sb(V) before being
27 incorporated in the new phase. Scanning-electron microscopy and Raman spectroscopy allowed
28 identification of the precipitates as two different calcium-antimony phases ($\text{Ca}_2\text{Sb}_2\text{O}_7$). This
29 coupled dissolution-precipitation process that occurs in a boundary layer at the calcite surface
30 can sequester Sb as a solid phase on calcite, which has environmental implications as it may
31 reduce the mobility of this hazardous compound in soils and groundwaters.



32

33 **Introduction**

34 The environmental presence and behavior of antimony (Sb), a hazardous substance as a solid
35 or in solution, is gathering increased attention due to its increasingly extensive use in various
36 products and its fate in the environment. The use of Sb includes applications as flame retardant
37 in plastics, rubbers, textiles, brake pads, pigments, paints, ceramics, and semiconductor materials
38 such as GaSb and InSb in electronic devices. In addition, it is present as a lead alloy in storage
39 batteries and ammunitions. Substantial Sb emissions are related to mining and smelting activities
40 and spent ammunitions at shooting ranges^{1,2}. Its widespread use results in high concentrations
41 present in waste, including air pollution control residues (i.e., ashes of flue gas treatment) from
42 waste incineration³. Consequently, soils can show significant concentrations of Sb^{4,5}, leading to
43 elevated levels in soil pore water and groundwater⁵.

44 Antimony can be found in four oxidation states (-III, 0, III, and V), of which Sb(III) as neutral
45 antimonite ($\text{Sb}(\text{OH})_3$) and Sb(V) as antimonate ($\text{Sb}(\text{OH})_6^-$) oxyanion are the most common
46 species in natural environments⁶. In oceans, the concentration of dissolved antimony is around
47 $0.2 \mu\text{g L}^{-1}$. In non-polluted freshwater⁷ it is usually below $0.2 \mu\text{g L}^{-1}$ but can sometimes reach 5
48 $\mu\text{g L}^{-1}$, while the average concentration in world rivers^{6,8} is close to $1 \mu\text{g L}^{-1}$. Comparatively high
49 concentrations of up to $95 \mu\text{g L}^{-1}$ antimony have been recorded in polluted groundwater and
50 soils, where the antimony source was either natural, such as volcanic glass⁹, or anthropogenic
51 e.g., contaminated soil and other industrial wastes⁶. Groundwater flowing out of an abandoned
52 antimony mine near Goesdorf, Luxemburg⁸ was found to contain Sb at a concentration of up to
53 2.2 mg L^{-1} at pH 7-8. The concentration in alkaline groundwater (pH~8) near an active mine in
54 the Hunan province in China¹⁰ was found to reach 11.4 mg L^{-1} ; and all dissolved antimony was

55 in the form of Sb(V). Laboratory leaching of similar mining impacted soils¹ showed water
56 extractable concentrations of up to 748 mg kg⁻¹ of soils and concentrations in water of up to 103
57 mg L⁻¹ after 7 days contact time, for a pH range between 5 and 7.

58 In calcium (Ca) rich environments as calcareous soils and alkaline waste materials, Ca is
59 suggested as an important sink for Sb. Calcium antimonates (Ca[Sb(OH)₆]₂ and Ca_{1+x}Sb₂O₆OH₂₋
60 _{2x}) belong to the family of roméite minerals¹¹. The solubility of roméite at room temperature¹²
61 and pH 8 is of the order of 4 mg L⁻¹. The solubility product of roméite varies as this mineral may
62 contain vacancies and crystallographic defects that affect dissolution¹³. Solubility between 10^{-3.4}
63 and 10^{-4.8} mol L⁻¹ at 25°C has been proposed, with a factor 60 difference between extreme
64 values¹³. In several industrial waste systems, the solubility product of a hydrated calcium
65 antimonate indicates this mineral should precipitate¹⁴. Based on XANES spectroscopy and
66 equilibrium calculations, it has been proposed that this mineral controls the solubility of
67 antimony in soils near active antimony mines in China¹ or during the leaching of bottom ash
68 from incinerated municipal waste¹⁴. However, to our knowledge, no direct evidence of the
69 presence of roméite or another calcium antimony phase was provided in these studies, such as
70 Raman spectroscopy or X-ray diffraction identification.

71 The dissolution-precipitation reaction of roméite at calcite interfaces could contribute to long-
72 term spatial and temporal storage of antimony in carbonate-rich environments. The main
73 objectives of the present study are to 1) characterize the coupling between calcite dissolution and
74 precipitation of Ca - Sb phase(s); 2) quantify the spatial and temporal evolution of the precipitate
75 nuclei; 3) hypothesize if a coupled dissolution-precipitation process could immobilize Sb at the
76 calcite surface.

77 **Materials and methods**

78 A calcite crystal (Iceland spar, Vizcaya, Mexico) was obtained from the Natural History
79 Museum in London. ICP-OES (inductively coupled plasma - optical emission spectroscopy)
80 analyses indicate the high purity of the calcite crystal, with trace amounts of Mn (31 ppb), Mg
81 (2.8 ppb) and Sr (11.4 ppb). Fresh calcite fragments (ca. 3 x 2 x 1 mm) were prepared directly
82 before each experiment by cleaving the calcite crystal parallel to the {10-14} plane.

83 The calcite surfaces were scanned in a room with controlled temperature (22 ± 1 °C) and
84 humidity (40%) using a Bruker Multimode Atomic Force Microscope (AFM) operating in
85 contact mode (Supporting Information). At the beginning of each experiment, deionized water
86 was injected over the calcite surface for several minutes, to observe any reaction or dissolution.
87 Then, antimony-free solutions and solutions with a controlled amount of Sb (Sb(III) or Sb(V)),
88 with the same constant ionic strength (0.05 M) and various controlled pH values between 2 and
89 8, were injected (Table S1). Several solutions with identical compositions were used to test the
90 reproducibility of the obtained results.

91 The same procedure described below was followed in each experiment to ensure results could
92 be compared between experiments. Firstly, deionized water was injected for 10 minutes and 5
93 images were acquired. Secondly, a solution without Sb and at the desired constant pH was
94 injected for another 10 minutes and 5 images were acquired. Thirdly, solutions with increasing
95 Sb concentrations were injected, with 5 images acquired at 1.5 minute intervals, then the AFM
96 tip was lifted for 10 minutes after which another image was acquired, then the AFM tip was
97 lifted for 1 hour and a further series of AFM images were acquired. Following this procedure,
98 calcite dissolution was followed in the AFM for several hours. As a consequence, the injection

99 was intermittent, with an average flow rate of $22 \mu\text{L}\cdot\text{s}^{-1}$ and residence time between 1.5 minute
100 and several hours (Supplementary Information). Then the sample was removed from the flow-
101 through cell, left in contact with the solution for 12 to 20 hours to allow sufficient time for
102 reaction, and then imaged again. The same samples were used for scanning electron microscopy
103 imaging and Raman spectroscopy characterization (Supporting Information).

104 **Results**

105 *Dissolution at calcite surface:* The cleaved calcite {10-14} surface is characterized by the
106 presence of steps (Figure S1a). Direct in situ observations showed that in contact with water and
107 aqueous solutions the calcite surface dissolves along steps that retreat, as well as through the
108 formation of etch pits with typical rhombohedral shapes (Figure S1b). Etch pit steps were
109 typically one unit cell (3.1 \AA) high, before deepening. These pits spread sideways to merge and
110 remove successive unit-cell heights layer by layer. The average spreading rate $v_{\text{avg}}=(v_+ + v_-)/2$
111 was measured from etch pits spreading between two successive AFM scans. Here, v_+ and v_- are
112 the velocities of the obtuse and acute steps of etch pits, respectively¹⁵. At pH below 4, the
113 dissolution was so fast that it was not possible to measure etch pit spreading rates. At pH
114 between 4.5 and 8, spreading rates and their standard deviation could be calculated from multiple
115 measurements and found to fall in the range $v_{\text{avg}} = 2.6\pm 1.3$ to $4.1\pm 0.5 \text{ nm}\cdot\text{s}^{-1}$, a range of values
116 previously reported for calcite¹⁵. No clear effect of Sb on the overall etch pit spreading rate could
117 be observed. However, in all experiments where Sb(V) was injected, the shape of the initial
118 rhombohedral etch pits evolved within minutes to show a rounding curve at the obtuse corner
119 that seemed to be pinned (Figure S1c, d).

120 *Formation of precipitates:* The precipitates initially formed as small “spots”, with an average
121 height of a few nanometers, just within the limits of AFM recognition under the given fluid
122 conditions and contact mode. They were distributed at kink sites on the calcite surface (Figure 1)
123 and showed low adhesion, as they were easily moved by the scanning AFM tip at the initial stage
124 of precipitation. With time, they tended to localize near step edges (Figure 1) or near deep etch
125 pits (Figure 2b) or, close to locations where dissolution was more intense. This means that
126 dissolution sites where more calcium was released control the nucleation process of the
127 precipitates. Initially the precipitates nucleated as individual particles with a rounded shape
128 (Figure S2a). Then these particles either piled up or aggregated to form larger particle clusters
129 (Figure S2 b-d). They grew in size into larger rounded structured aggregates until they covered
130 the whole calcite surface (Figure 2a). Even at this stage, they were weakly attached to the
131 surface, as successive scans on the same area showed that fewer particles were present than in
132 the surroundings (Figure 2a), which we interpret by the displacement of particles by the scanning
133 AFM tip.

134 The shape and size of these precipitates could be measured in all experiments where they were
135 observed and all showed that they formed patches with a more or less circular perimeter, a low
136 height to diameter aspect ratio (Figure S3), and no evidence of crystallographic facets at the
137 onset of precipitation. We have chosen to measure particles whose diameter is larger than 100
138 nanometers, the spatial resolution of the AFM technique used here. With time, some of these
139 particles developed facets (Figure S2d). Images were collected at different times, under different
140 conditions, and over differing areas of observation. Under all these conditions the precipitated
141 particles presented rounded perimeters. At the scale of the AFM observations tip-shaped
142 convolutions would therefore be minimal. The height and diameter of the precipitates measured

143 for all experiments (Figure 3) show that initially particles were quite flat (~ 10 nm), with a
144 diameter in the range 100-200 nm. These particles formed within 2 minutes after the injection of
145 Sb. With time, particles tended to grow in height, while keeping a maximum diameter smaller
146 than 800 nm and within the range 300-800 nm. During this stage, particles aggregated or merged
147 together and then grew in height to 20-120 nm. For three experiments the same particles could be
148 followed in a time sequence and their height to diameter ratio showed a positive trend with time
149 (Figure S3), demonstrating that particles first grew laterally (by the merging of smaller particles),
150 as thin discs and then grew more continuously in height. In one experiment, a linear fit of the
151 particle height with time could be performed and gives a growth rate of $0.016 \text{ nm}\cdot\text{s}^{-1}$ (Figure
152 S4b), whereas the diameter of the precipitates did not change significantly (Figure S4a). With
153 time the calcite surface became covered by these particles that produced several layers of
154 precipitates (Figure 2a). These observations were seen for acidic fluids in the presence of Sb; the
155 lower the pH, the faster the calcite dissolved and more particles precipitated. Many more
156 particles nucleated and grew in the presence of Sb(V) as compared to Sb(III).

157 *Identification of the precipitates:* Evidence for dissolution of the calcite surface and
158 precipitation of a new phase was also observed in the SEM (Figure 4a) on calcite samples left 24
159 hours in the Sb solutions. In the 200 ppm Sb(V) solutions at pH 5 the calcite surface was covered
160 in precipitates along with rhombohedral etch pits seen in Figure 4b. The precipitates were
161 between 5 and 25 μm width. These particles had clear crystal facets indicating a crystalline
162 structure and showed a consistent dipyramidal form (Figure 4b). Incorporation of Sb into the
163 particles was confirmed by comparison of the EDX spectra for the particles, which showed peaks
164 for Ca $K\alpha$, $K\beta$ and Sb $L\alpha$ $L\beta$ in the spectral region between 3 to 5 keV, and the underlying
165 calcite surface (Figure 4c). Raman spectroscopy of the precipitates produced spectra (Figure 4d)

166 with peaks listed in Table S2. The small, sharp band at 1086 cm^{-1} is consistent with the
167 symmetrical stretch of carbonate in the underlying calcite crystal¹⁶, as are the smaller peaks at
168 156 , 283 and 711 cm^{-1} . The rest of the peaks therefore originate from the precipitate itself. The
169 dominant peak in the spectrum at 624 cm^{-1} and the smaller peak at 384 cm^{-1} correspond well
170 with previously published synthetic $\text{Ca}_2\text{Sb}_2\text{O}_7$ Raman spectra¹⁷. This mineral was also observed
171 to form in hydrothermal experiments where calcite was left in contact with dissolved Sb¹⁸.
172 However, the strong Raman peak documented for synthetic $\text{Ca}_2\text{Sb}_2\text{O}_7$ at 472 cm^{-1} is not present
173 in the spectra obtained from the precipitates. Similarly the published spectra do not show
174 evidence for peaks around 500 cm^{-1} that are visible in Figure 4d. This could be related to crystal
175 orientation, which is known to change the relative intensities of peaks within the Raman
176 spectra¹⁹. However, it may also be related to the precipitate chemistry or mixed phase as Raman
177 spectra²⁰ from the natural mineral oxycalcioroméite ($\text{Ca}_2\text{Sb}_2\text{O}_6\text{O}$) with a more varied
178 composition and cubic structure show dominant peaks around 500 cm^{-1} .

179 **Discussion**

180 *Dissolution-precipitation in a boundary layer:* The interactions of calcite with oxyanions, such
181 as arsenic or selenium, were reported in previous studies^{21,22,23}, where it was shown that etch pit
182 corners could be pinned during dissolution to result in etch pit shapes deviating from normal
183 rhombohedral etch pits, characteristic of calcite dissolving in water¹⁵. In the present study, a
184 similar effect was observed, demonstrating that Sb interacts with kink sites in etch pits and
185 slightly modify the dissolution process. However, this pinning does not have a measurable effect
186 on the etch pit dissolution rate that remained within the average rate for calcite in pure water ($2\text{-}4$
187 $\text{nm}\cdot\text{s}^{-1}$).

188 During dissolution of calcite, ions are released such that the fluid-mineral boundary layer
 189 becomes increasingly saturated with Ca^{2+} and CO_3^{2-} ions, this last species being protonated into
 190 HCO_3^- at neutral and low pH. When the calcite surface is in contact with the Sb-bearing solution,
 191 the interfacial fluid becomes supersaturated with a new Ca-Sb phase that can then precipitate. It
 192 is now well-established, using real-time phase-shift interferometry and ion-specific micro-
 193 electrodes, that interfacial mineral-fluids can become supersaturated with a new phase when the
 194 bulk solution is undersaturated²⁴. This interface-coupled dissolution-precipitation process^{25,26} is
 195 summarized in the graphical abstract and involves the dissolution of the calcite substrate,
 196 releasing Ca^{2+} , followed simultaneously by the nucleation of precipitates, initially only less than
 197 10 nanometers in diameter. The small rounded precipitate particles grew in diameter, until they
 198 reached a size in the range 300-800 nm, and then grew in height to 20-120 nanometers.
 199 Observations indicate that the initial particles merged with adjacent particles (Figures 3c; S2b,
 200 S2d). With time the calcite surface became covered by these particles that produced several
 201 layers of precipitates (Figure 2a). There is therefore a balance between nucleation of new
 202 precipitates and growth of existing ones.

203 *Mechanism of dissolution precipitation:* The interface coupled dissolution-precipitation
 204 reactions at the calcite surface can be schematically represented as follows:



207 The appearance of tiny (few nm) particles on the dissolving calcite surface and their
 208 subsequent merging with adjacent particles tends to indicate a heterogeneous growth process that
 209 may be initiated as pre-nucleation clusters within the calcite-fluid boundary layer. The growth of

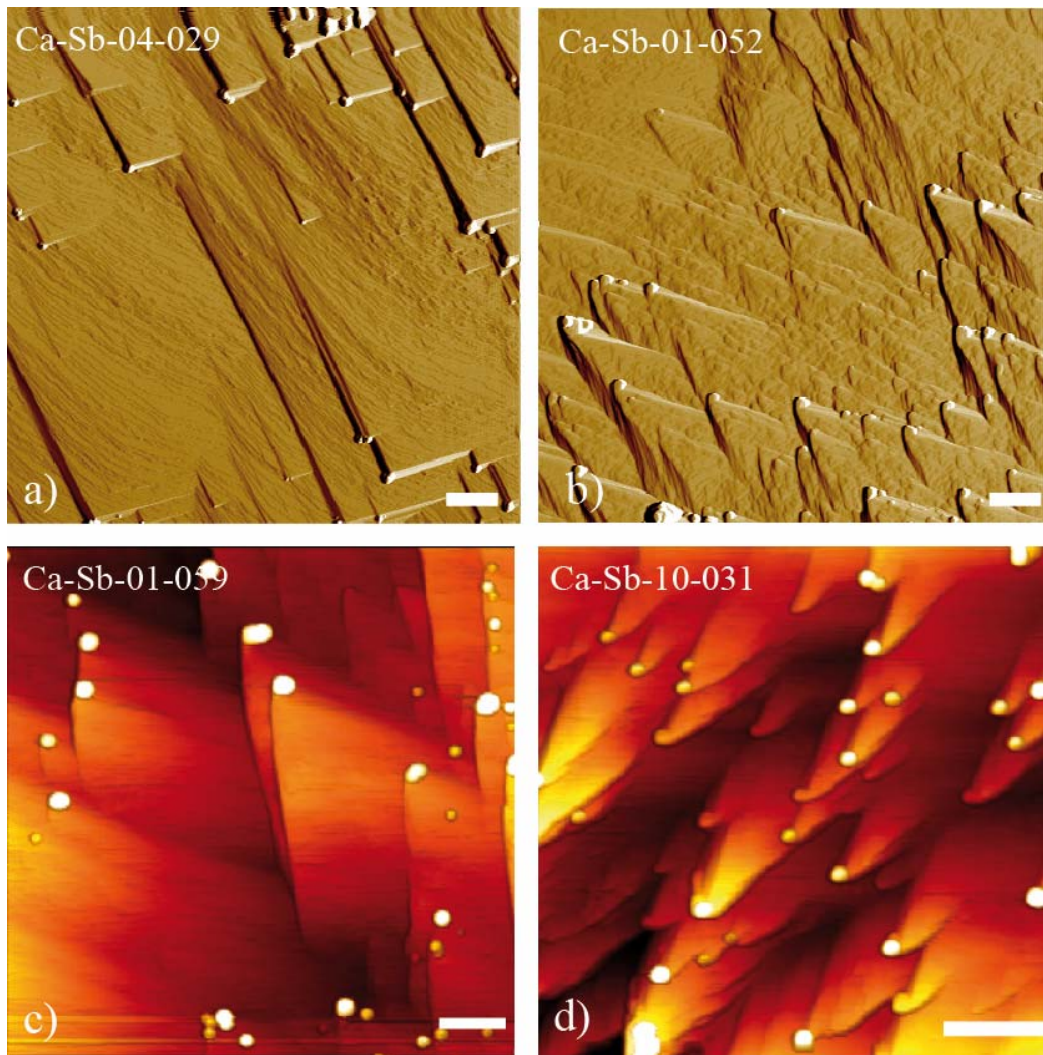
210 the precipitate does not follow a classical homogeneous mechanism²⁷ that would require the
211 addition of growth building ionic species to step edges and kink sites. Instead, given the
212 limitations of our AFM observations, the first particles already with a diameter of a few
213 nanometers appeared within seconds and at most within 1.5 minutes during one scan on the
214 dissolving calcite surface. To do this, it could be assumed that some ionic species association had
215 already occurred within the fluid boundary layer. Gebauer et al.²⁸ have shown that stable pre-
216 nucleation ion clusters of calcium carbonate form even in undersaturated solutions. In our case
217 the Sb-bearing solution is undersaturated with respect to any possible Ca-phase but precipitation
218 is clearly observed on a dissolving surface. The current understanding of the mechanism of phase
219 separation allowing for the initial formation of solid particles is an active topic of research²⁸
220 because of the application to many geochemical systems including biomineralisation. However,
221 the formation of stable pre-nucleation clusters can be explained in terms of equilibrium
222 thermodynamics that would promote some form of structural orientation between ions in solution
223 resulting in an association of ionic species forming the initial denser cluster form. From our
224 AFM observations it is not clear whether the initial 1-2 nanometer particles nucleate directly on
225 the calcite surface or arrive at the surface already as “clusters” that have formed as pre-
226 nucleation clusters within the near-surface boundary fluid layer. The latter scenario seems highly
227 likely, given that the observations showed immediate precipitation of particles as soon as the
228 calcite surface was in contact with a Sb-bearing solution.

229 The precipitation of the new phase was observed to increase with a decrease in pH, which is
230 consistent with a faster dissolution rate of calcite at lower pH and therefore a faster release of
231 Ca^{2+} ions required for the precipitation of the new phase. Therefore we could reasonably expect
232 that a Ca-antimonate phase is likely to precipitate at the calcite surface. Initially, these

233 precipitates have a disc shape and do not show facets. With time, they develop facets (Figures
234 S2d and 4). $\text{Ca}_2\text{Sb}_2\text{O}_7$ has an orthorhombic crystal structure similar to weberite ($\text{Na}_2\text{MgAlF}_7$)²⁹,
235 and often forms with a dipyramidal habit unlike oxycalcioroméite, which is isometric. Therefore,
236 the formation of dipyramids in combination with the dominant Raman band at 624 cm^{-1} indicates
237 that the precipitated phase is dominantly orthorhombic $\text{Ca}_2\text{Sb}_2\text{O}_7$. However, additional bands at
238 500 cm^{-1} in the Raman spectrum indicate some of the isometric phase is also present in the
239 precipitates. The structure of the Ca-antimonate has been shown to be sensitive to the presence of
240 ions such as F^- , where increase in these ions within the crystal structure encourages the formation
241 of the isometric rather than the orthorhombic form³⁰. Whether the mixed phase is due to a phase
242 transformation during or after the experiment is unclear from the ex-situ data. As Sb-rich fluid is
243 injected in the AFM flow-through cell, the release of Ca ions at the calcite surface, will be more
244 concentrated near active dissolution sites such as at the bottom of etch pits or kinks. Here
245 precipitates are initially more numerous (Figures 1, 2b). At these locations, the concentration
246 products of $\text{Ca}_2\text{Sb}_2\text{O}_7$, and probably oxycalcioroméite, are large enough to reach supersaturation
247 with respect to these minerals and result in their subsequent precipitation. The precipitates grow
248 initially as disc-shaped particles; that agglomerate into larger particles, evolving towards fully
249 crystallized $\text{Ca}_2\text{Sb}_2\text{O}_7$ and oxycalcioroméite crystals. Such a coupled dissolution-precipitation
250 process on carbonates has also been reported for the precipitation of a Ca arsenate phase on
251 calcite²³ and the formation of a Ca-selenate phase on calcite²². These examples provide a
252 mechanism of possible sequestration of environmentally harmful elements. More generally, such
253 coupled replacement reactions are widespread in mineral-water systems³¹ whenever the release
254 of ions from the dissolving mineral is coupled to the precipitation of a new phase at the surface
255 of a dissolving mineral.

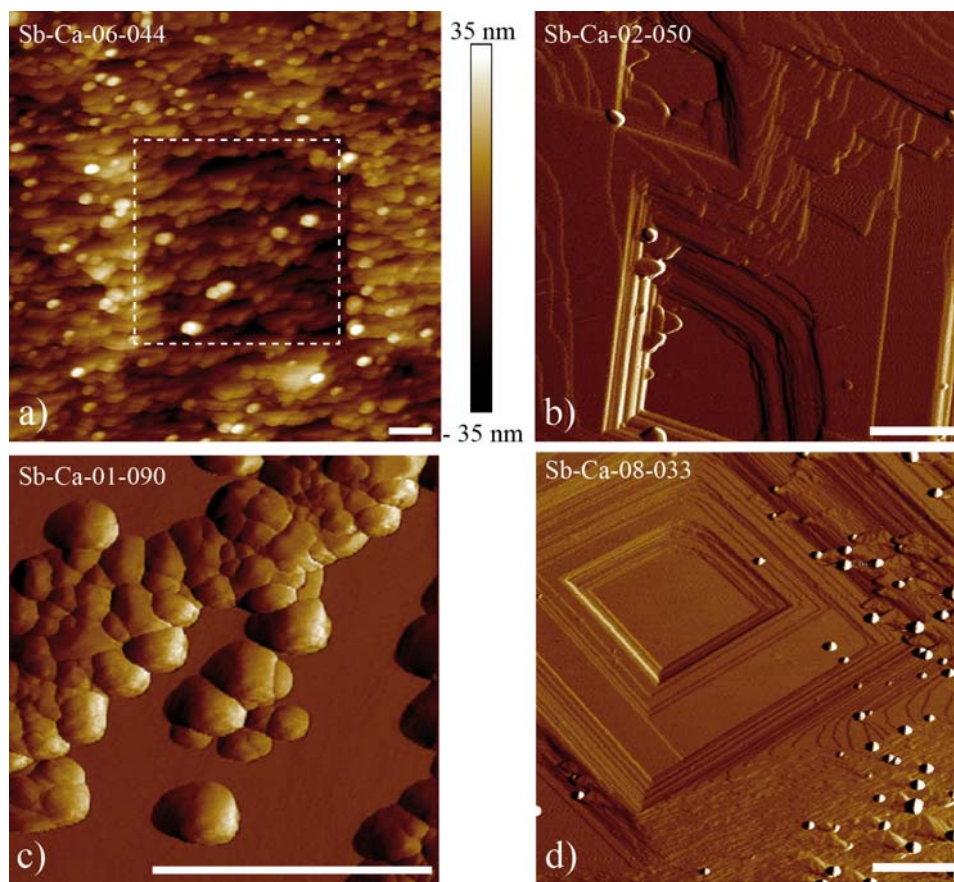
256 *Environmental implications:* The present results show that coupled to calcite dissolution, Ca -
257 Sb phases precipitate as nanometer size particles on the calcite surface (heterogeneous
258 nucleation). Primary nanoparticles are then self-assembled into rounded aggregates that coalesce
259 to form larger particle aggregates averaging 130-220 nm wide and up to 80 nm high that cover
260 the carbonate surface. There are much fewer particles at high (8) than low (2.5) pH and fewer
261 particles in the presence of Sb(III) than in the presence of Sb(V). As confirmed by Raman
262 spectroscopy, these particles are predominately $\text{Ca}_2\text{Sb}_2\text{O}_7$ (and probably minor
263 oxycalcioroméite). Furthermore, we could not find any evidence for the formation of the
264 hydrated romeite crystalline salt $\text{Ca}[\text{Sb}(\text{OH})_6]_2$, that has been suggested to explain unexpectedly
265 low Sb concentrations in extracts of alkaline soils^{1,12,32}. This phase may possibly form at higher
266 pH values that could be consistent with ground water in alkaline soils. If this phase was present
267 in the experiments, it could not be detected in the Raman data.

268 As a consequence of the interaction of calcite surfaces with Sb-bearing solutions, antimonate
269 can be sequestered in a solid form on calcite surfaces by a coupled dissolution-precipitation
270 process in a boundary fluid layer. These results provide a mechanistic understanding of
271 environmental studies where a Ca-antimonate phase was proposed to form, but could not
272 previously be observed in-situ^{1,4,12}. Therefore, it is reasonable to suggest that calcite or other
273 soluble Ca-bearing surfaces could provide a realistic environmental remediation strategy in the
274 case of elevated Sb concentrations related to acid mine drainage systems, contaminated shooting
275 range soil and ashes from waste incineration.

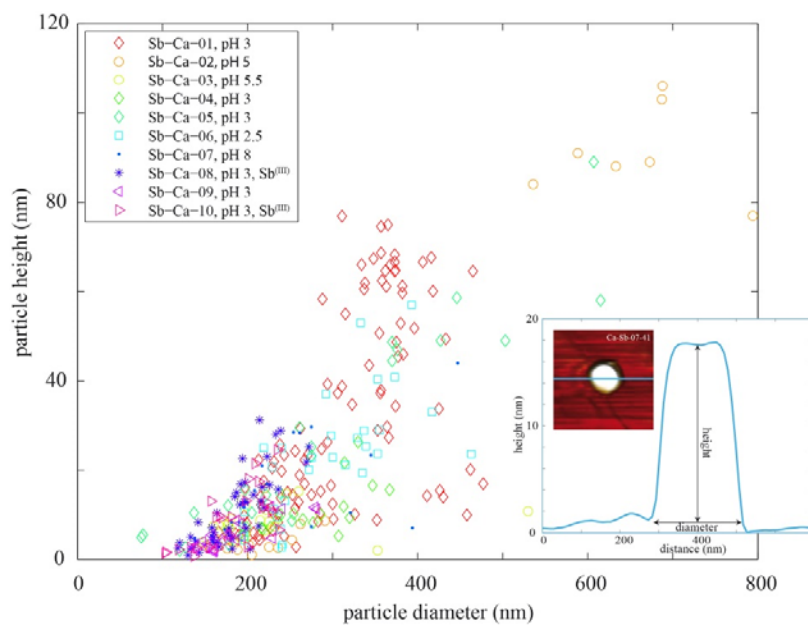


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277 Figure 1. AFM images showing nucleation of precipitates (white spots) at step kinks on a calcite
 278 surface. a-c) 2D images in deflection mode. c-d) 3D rendering in height mode. Solution
 279 compositions are: a) 50 ppm Sb(V), pH 3.2. b-c) 200 ppm Sb(V), pH 3; d) 5 ppm Sb(III), pH 3
 280 (here probably the Sb(III) oxidized into Sb(V)). These data demonstrate that the antimony-rich
 281 precipitates nucleate near step kinks where supersaturation with respect to the new phase is also
 282 most likely. Deposits pin the steps at those points and thus inhibit dissolution locally as the steps
 283 dissolve around them, hence the appearance of the finger-like morphology emanating from these
 284 pinned points. Scale bar 1 μm .



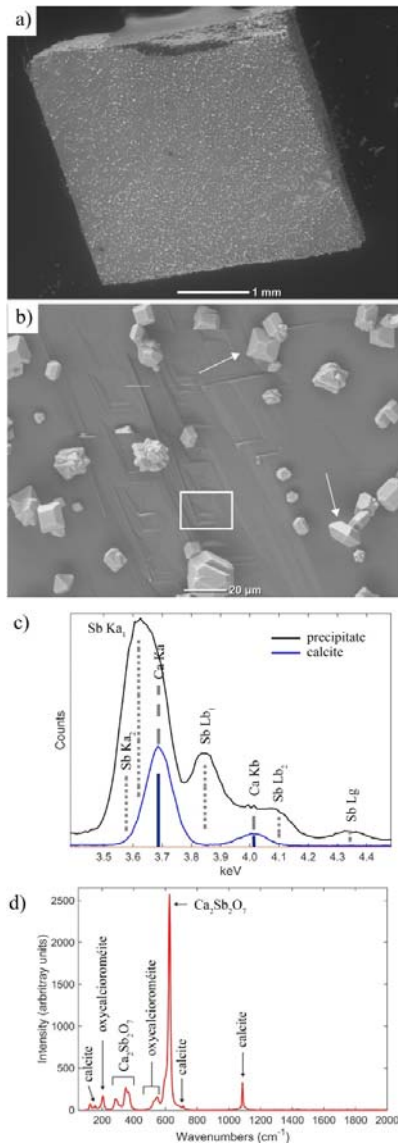
285
 286 Figure 2. AFM images (deflection mode) of calcium-antimony precipitates on a calcite surface.
 287 Scale bar: 1 μm for all images. a) Calcite surface, $10 \times 10 \mu\text{m}^2$, covered with calcium-antimonate
 288 precipitates. The central area, outlined by a dashed square, corresponds to a $5 \times 5 \mu\text{m}^2$ area
 289 scanned previously and contains less precipitates. This demonstrates that precipitates are weakly
 290 attached as some are removed by the AFM tip during scanning. Solution Sb(V) 200 ppm, pH 2.5.
 291 b) Etch pits on calcite surface with precipitates along actively dissolving edges. The location of
 292 the precipitates is related to the location of higher dissolution. Solution Sb(V) 200 ppm, pH 5.1.
 293 c) Image (deflection mode) of a calcite surface after 12 hours in solution Sb(V) 200 ppm, pH 3
 294 showing precipitates of calcium-antimonate that form individual patches that then agglomerate.
 295 d) Image (deflection mode) of a calcite surface in solution Sb(III) 10 ppm pH 3, with very few
 296 precipitates of calcium-antimonate demonstrating that Sb(III) form much fewer precipitates.



297

298 **Figure 3.** Height versus diameter of Ca-Sb nanoparticles in all AFM experiments. Inset: Height

299 profile across a nanoparticle and definition of the height and diameter.



300

301 **Figure 4.** SEM images and EDX and Raman spectra of Ca-Sb precipitates. a) SEM image of the
 302 calcite surface with precipitates at the surface (exp. Sb-Ca-5). b) Higher resolution image of the
 303 precipitates showing their typical dipyramidal structures (white arrows) and the presence of etch
 304 pits on the underlying calcite surface (white box). c) EDX spectra focused on the region between
 305 3.4 and 4.5 eV showing the overlapping Sb, Ca peaks (blue: underlying calcite surface, grey:
 306 precipitate). d) Typical Raman spectrum of the precipitate with phases labelled based on
 307 published spectra for oxycalcioroméite²⁰ and Ca₂Sb₂O₇ (Ref. 17).

308

309 ASSOCIATED CONTENT

310 **Supporting Information.** The supplementary Information file (pdf file) contains: Text
311 (Experimental conditions), Figure S1; Figure S2; Figure S3; Table S1; and Table S2.

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316 **Author Contributions**

317 CVP and FR performed the experiments and wrote the manuscript. HK acquired and interpreted
318 the Raman and SEM data. GMH, GB and GO participated to the interpretations of the
319 experimental data and their consequences for the environment. All authors have given approval
320 to the final version of the manuscript.

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