The replacement of calcite ($CaCO_3$) by cerussite ($PbCO_3$)

Ke Yuan[1*], Sang Soo Lee[1], Vincent De Andrade[2], Neil C. Sturchio[3], Paul Fenter[1]

1. Chemical Sciences and Engineering Division, Argonne National Laboratory. 9700 South Cass Avenue, Argonne, IL 60439;

2. Advanced Photon Source, Argonne National Laboratory. 9700 South Cass Avenue, Argonne, IL 60439;

3. Department of Geological Sciences, University of Delaware. Newark, DE 19716.

*Corresponding author. Tel: +1 630-252-1787; Fax: +1 630-252-9570; Email: kyuan@anl.gov

Abstract (≤ 200 words)

The mobility of toxic elements, such as lead (Pb) can be attenuated by adsorption, incorporation, and precipitation on carbonate minerals in subsurface environments. Here, we report a study of the bulk transformation of single-crystal calcite ($CaCO_3$) into polycrystalline cerussite ($PbCO_3$) through reaction with acidic Pb-bearing solutions. This reaction began with the growth of a cerussite shell on top of calcite surfaces followed by the replacement of the remaining calcite core. The external shape of the original calcite was preserved by a balance between calcite dissolution and cerussite growth controlled by adjusting the Pb^{2+} concentration and pH. The relation between the rounded calcite core and the surrounding lath-shaped cerussite aggregates was imaged by transmission X-ray microscopy, which revealed preferentially elongated cerussite crystals parallel to the surface and edge directions of calcite. The replacement reaction involved concurrent development ~100 nm wide pores parallel to calcite *c*-glide or $(1\bar{2}0)$ planes, which may have provided permeability for chemical exchange during the reaction. X-ray reflectivity measurements showed no clear epitaxial relation of cerussite to the calcite (104) surface. These results demonstrate Pb sequestration through mineral replacement reactions and the critical role of nanoporosity (3% by volume) on the solid phase transformation through a dissolution-recrystallization mechanism.

Introduction

Lead (Pb) contamination in groundwater aquifers and soils poses a significant threat to the safety of drinking water[1, 2]. Carbonate minerals are ubiquitous on Earth. Lead sequestration by carbonate minerals, particularly calcite, has been observed by mechanisms of adsorption, incorporation and precipitation[3-9]. Most studies of the interaction of Pb^{2+} with calcite have focused on phenomena occurring at mineral surfaces. However, relatively few studies have been done to examine heavy metal sequestration into bulk solid phases through coupled dissolution/crystallization reactions (i.e., mineral replacement reactions). Although bulk reactions can be slow, they can be much more effective than surface reactions in terms of the net sequestration of heavy metal contaminants per unit volume of solid.

The characteristic feature of a mineral replacement reaction is the transformation of a reactant mineral phase into a secondary product phase having a distinct structure and composition while preserving the original dimensions of the reactant phase (i.e., a pseudomorph)[10, 11]. The shape preservation indicates that the reaction front proceeds inward from the original solid-liquid interface. Such conversion of both mineral structure and composition are well known to occur under hydrothermal and metamorphic conditions at high temperature and pressure[12-17]. At low temperature, such replacement reactions can play an important role in controlling the compositions of both solid and fluid phases, which can influence the mobility of toxic elements and radionuclides in groundwater aquifers. For example, the replacement of calcite by solid phases sharing the same cation (Ca^{2+}) but different anions (CaF_2[18, 19], $CaSO_4$[20], and CaC_2O_4[21]) has been reported. Two critical factors that determine the equilibrium shape of a replaced crystal are the relative solubilities and reaction rates of both dissolution and growth of the reactant and product phases[11, 22]. In addition, the development of porosity is essential for promoting the advancement of a reaction front from the solid-liquid interface to the interior of a crystal[10, 11].

In this study, we explored the replacement of single crystals of calcite ($CaCO_3$) by polycrystalline cerussite ($PbCO_3$). The objectives of this study were to investigate the spatial coupling between the dissolving calcite crystal and the growing cerussite crystals both temporally and spatially, and to resolve the size and spatial distribution of the pores that enable mass transport to the reacting interface. Multiple *ex situ* and *in situ* techniques were used to observe and understand the mineral replacement process. Optical microscopy was used to record

the replacement reaction *in situ*, with complementary *ex situ* scanning electron microscopy (SEM) images to further characterize the associated morphological changes. Full-field transmission X-ray microscopy (TXM) was used to resolve the three-dimensional spatial distributions of calcite, cerussite, and the pore space distribution within a partially reacted calcite crystal. X-ray powder diffraction (XRD) was used to record the amount of $PbCO_3$ (cerussite) as a function of time, and X-ray reflectivity (XR) was used to analyze the interfacial structure during the initial growth of cerussite on the calcite (104) surface. The results of this investigation yield new insights into the detailed nature of the mineral replacement reaction, the structural relation between the calcite and the cerussite, and the role of nanoscale porosity.

Materials and Methods

Optical microscopy and scanning electron microscopy

The morphological changes of calcite replaced by cerussite were observed *in situ* by using an optical microscope with a magnification of 448× (Nikon Optiphot) equipped with a digital camera and an image recording system. The calcite crystals were grown on 18 mm × 18 mm × 0.25 mm borosilicate glass plates using the ammonium diffusion method[23, 24]. An in-house constructed fluid cell having an internal volume of 4.2 mL was made by sealing two pieces of transparent glass onto a PEEK cell. The cell was filled with a $Pb(NO_3)_2$ reaction solution (either 1 mM or 5 mM prepared in equilibrium with atmospheric CO_2) (Sigma Aldrich) at pH ranging from 2.8 to 5.2 (Accumet Basic AB15 pH meter). Acidic pH promotes the dissolution of calcite. Following the reactions, the samples were rinsed gently with deionized (DI) water, dried under flowing N_2, and coated with Au for imaging by using the Hitachi S4700 SEM.

X-ray diffraction

XRD patterns were measured using a Bruker D8 Advance diffractometer. The step size was 0.005° with a measurement time of 1 s per step using Cu Kα radiation ($\lambda = 0.15418$ nm). A series of 0.03 g calcite samples (Chihuahua, Mexico) with size between 90 and 106 μm (similar to the size of the crystals observed under the optical microscope) were selected by sieving, and placed in Teflon bottles filled with 100 ml of 5 mM $Pb(NO_3)_2$ solution of pH = 2.8 in air. These powder samples were reacted for 0.5 to 23 h and the solids were separated by filtration. The samples were gently washed with DI water, dried and further ground using pestle and mortar for powder

XRD measurements. Each sample weighed about 20 mg, and was back loaded into the sample holder to minimize preferred orientation effects. Semi-quantitative phase analysis was accomplished using the reference intensity ratio (RIR) method (see supporting information). The RIR values for calcite and cerussite are 2.0 and 6.7 based on PDF 05-0586 and PDF 47-1734, respectively.

Transmission X-ray microscopy

Transmission X-ray microscopy measurements were performed at beamline 32-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory. The X-ray energy was 8 keV with a field of view of 51 µm × 51 µm. The sample (See SI for sample preparation) was imaged in 721 projection directions spanning over 180° of rotation angle with an exposure time of 1s per image and a spatial resolution of 60 nm[25]. Data reconstruction was processed by using Tomopy[26]. The acquired images were segmented using Drishti 2.6[27], and further analyzed and visualized in Fiji ImageJ[28-30].

X-ray reflectivity

The specular XR measurements were performed at beamline 33-ID-D of APS using incident photon energy of 18.0 keV. The reflectivity signal with the associated background was measured by using an area detector (Pilatus) as a function of vertical momentum transfer, q ($Å^{-1}$). A calcite crystal (Chihuahua, Mexico) about 10 mm × 8 mm × 2 mm in size was cleaved along the (104) plane and immediately placed within seconds in a thin-film cell sealed with a Kapton window. The calcite was reacted with ~2 mL of 5mM Pb^{2+} solution of pH = 2.8 for 20 min, and then the solution was drained leaving a few µm thick liquid layer between the calcite surface and the Kapton film held by capillary force. The d_{104} spacing of the calcite unit cell is 3.035 Å with a surface unit cell area of A_{uc} = 20.198 $Å^2$. Details regarding these experimental methods can be found elsewhere[9, 31, 32].

Results

Observing the replacement of calcite by cerussite using optical microscopy and SEM

Morphological changes of the calcite crystals were observed *in situ* by using optical microscopy and structural details were further investigated by using SEM. Two different Pb^{2+}

replacement solutions of 1 mM and 5 mM of initial pH = 2.8 were used as reactants with calcite. The calcite crystals, grown on a glass substrate, are observed to have multiple growth planes, and therefore various crystallographic orientations with respect to the substrate surface[33]. The calcite crystals chosen for this optical microscopic study exhibited rhombohedral shapes with exposed (104) surfaces orientated perpendicular to the viewing direction (Figure 1a). The *c*-glide plane can be identified from the diagonal passing through the two obtuse corners (dashed lines in Figure 1a).

During the earliest stage of the reaction (1 to 2 h), the top (104) surface roughened and precipitation occurred primarily on the four side surfaces (Figure 1a and 1b). The growth of a new phase was indicated by the expansion of the darker regions in the optical image (Figure 1a). SEM images show that this new phase formed aggregates on the side surfaces of the calcite, and the crystals within these aggregates on a given surface appeared to be aligned (Figure 1b, 0.5 h image). XRD analysis revealed that the secondary phase was cerussite ($PbCO_3$, Figure 2). Thermodynamic calculations using Geochemist's Workbench 9.0 also predicted the presence of a single solid phase as cerussite (Table S1).

The advancement of a polygon-shaped reaction boundary on the top (104) surface of the calcite crystal was observed upon further reaction in the Pb^{2+} solutions, especially for calcite in the 5 mM solution (Figure 1a, 5 mM Pb^{2+}; SI, Video S1). The progression of the darker areas is attributed to the precipitation of cerussite on the top calcite (104) surface and a formation of a cerussite shell around the calcite. The reaction front was composed of four straight edges, and advanced into the middle of the calcite crystal. Of the four reaction fronts, two were observed to move faster as indicated by arrows in Figure 1a. As a result, the converging point of the four edges was not centered on the (104) surface, but deviated to the lower right corner (Figure 1a, 5 mM Pb^{2+} 4.7 h and Figure 1b, 5 h images).

There are a number of differences in the reaction at the two Pb concentrations. The size of the product crystal in the 5 mM Pb^{2+} was larger than that in the 1 mM Pb^{2+} solution (Figure 1a, 1mM Pb^{2+} 15h image and 5 mM Pb^{2+} 4.7 h image). Although the corners of the replaced crystal became rounded in the 1mM Pb^{2+} solution, the rhombohedral shape of calcite could still be recognized. The time required to completely cover the top calcite (104) surface by cerussite was

also different: the reaction time in 5 mM Pb^{2+} solution was 5 hours which was shorter than that in the 1 mM Pb^{2+} solution (15 hours) (Figure 1a).

The evolution of the area of the calcite (104) surface covered by cerussite (i.e., dark areas) shown in Figure 1a is plotted as a function of time, which reflects the two-dimensional growth rate of the cerussite shell in two different Pb solutions (Figure S1). Notably, the dark area was caused by the rapid growth of a cerussite shell on the top (104) surface of calcite and the complete replacement of the bulk calcite crystal was expected to take a longer time. The slopes were 771 $\mu m^2/h$ and 1800 $\mu m^2/h$ in the 1mM and 5 mM Pb^{2+} solution, respectively. In the 1 mM Pb^{2+} solution, the calcite crystal started to decrease in size after 9.7 h, corresponding to the dissolution of calcite and the precipitated cerussite.

The pH of the initial solution has a dramatic impact on the reaction. At initial pH = 4.0, the calcite surface roughness increased during the first six hours of reaction, but the formation of a cerussite shell and advancement of a reaction front were not observed (Figure S2a). Increase of the initial solution pH resulted in the growth of different product phases (Table S2 and S3). At least two types of crystal phases can be recognized (Figure S2b), including needle-shaped cerussite and hexagonal crystals tentatively identified as hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, (having a $R\bar{3}c$ symmetry) based on the shape. Mixed cerussite and hydrocerussite phases have been found to precipitate on surfaces of calcite and aragonite at pH = 5-7 [34]. The needle-shaped cerussite preferentially grew on the corners of calcite. Well-crystallized hydrocerussite crystals were readily recognized on both the glass substrate and on the calcite surfaces (Figure S2b), implying a homogeneous nucleation process.

Quantifying the phase evolution by XRD

A series of *ex situ* XRD patterns were measured for calcite powders reacted for up to 23 h in 5 mM Pb^{2+} solutions with initial pH = 2.8, while the evolution of the solution pH was recorded as a function of time. Calcite and cerussite were identified as the two phases present during the entire reaction period. Within the first 0.5 h, new reflections were found at 2θ = 24.79°, 25.48° and 43.47°, corresponding to the Bragg diffraction peaks from cerussite (111), (021), and (221), respectively (Figure 2). Semi-quantitative phase analysis showed that the amount of cerussite increased at the rate of ~ 4 wt.% per hour in the first 7 hours (Figure S3). The amount of

cerussite remained constant at ~28 wt.% from 7 h to 23 h. At the same time, the solution pH increased abruptly within one hour from 2.8 to 4.0, and then stabilized at pH around 4.5 after 7 h (SI, Figure S3), about the time when the amount of cerussite stopped increasing.

Imaging a partially replaced calcite crystal by TXM

Transmission X-ray microscopy was used to probe the structural relations between the parent calcite crystal and the cerussite growth layer, including the orientation of the cerussite crystals, and the sizes and spatial distribution of the pores in a calcite sample reacted in a 5 mM Pb^{2+} solution of an initial pH = 2.8 for 15 hours. In the reconstructed TXM images (Figure 3), the brightness is proportional to the local density of the material. Consequently, dark areas between the grains correspond to the pores. Sharp boundaries between the cerussite (bright) and calcite (grey) were observed (Figure 3). The high contrast between calcite and cerussite is caused by the large difference in the X-ray attenuation length for $CaCO_3$ and $PbCO_3$. The absence of a compositional transition region within each phase and the presence of pore spaces (results shown later) between these two phases are consistent with the replacement of calcite by cerussite via an interface coupled dissolution/precipitation process rather than a solid state diffusion reaction[35, 36].

The shape of the cerussite crystals resembles the lath-shaped cerussite observed under SEM. A primary calcite core was observed, which is surrounded by small, isolated calcite remnants within the cerussite replacement rim (Figure 3; Figure 4, $CaCO_3$). The triangular shaped bottom plane is the calcite surface that was initially in contact with the glass substrate (Figure 4, $PbCO_3$ bottom view and Figure S4a; see SI, Figure S5 and S6 for the determination of crystallographic orientation of the calcite). There should be seven corners (in addition to the one truncated by the glass substrate) and six surfaces left on the replaced calcite. Other than the three surfaces associated with the triangular growth plane truncated by the glass substrate, most surfaces were modified due to the growth of cerussite, but the original boundaries of the calcite can be identified by edges and corners. Cross-sectional views of three surfaces associated with one vertex (Figure S4b, the converging point of the three red lines) indicate preferred orientation of cerussite crystals. The crystals form aggregates of parallel laths on the two side surfaces (Figure S4b, b-1 & b-2). On the top surface, however, the crystals tend to elongate along the four edge directions (Figure S4b-3). The angle between two cerussite crystals found on the edges is 104°, close to the obtuse step angle (101.6°) on the calcite (104) surface.

An additional structural feature observed was pore space between the calcite core and the growing cerussite. This appears to have provided space for fluid to allow the dissolution of calcite and diffusion of CO_3^{2-} to the growing cerussite (Figure 3). The thickness of the pores primarily ranged from 92 to 112 nm (Figure 5a). Analysis of the distribution of diameters of the pores showed that the mean Feret diameter of the pores was 230 nm, but a few disk-shaped pores had a diameter larger than 6 μm (Figure 5b), which corresponded to the gap spaces distributed continuously on one side of the calcite core (Figure 4, Pore; Figure S7, pore indicated by the arrow). Pores were parallel to the $(1\bar{2}0)$ or the *c*-glide plane of calcite, which cut through the diagonal edges connecting the two obtuse corners (Figure 4, Model). The alignment of cerussite crystals along the diagonal direction was also observed in SEM images of the calcite surfaces (Figure 1b, 2 h image). The total volume of $PbCO_3$ after reaction was about 50% larger than that of $CaCO_3$, where 98% of the $CaCO_3$ volume was in the residual unreacted core. The observed pore space corresponded to 3% of the total volume of the replaced crystal (Table S4). Pores were apparently isolated (Figure S7) although they may have been interconnected by grain boundary porosity that was smaller than 60 nm resolution (associated with the instrumental limit).

Structural controls of calcite on cerussite: X-ray reflectivity

We investigated the potential ordering of the $PbCO_3$ precipitates and sorbed Pb^{2+} ions at the calcite surface during the initial growth of cerussite by using specular X-ray reflectivity of a calcite (104) surface in a 5mM Pb^{2+} solution at initial pH = 2.8, reacted for 20 min. Previous study has shown that Pb can be incorporated into calcite in the presence of EDTA[9]. Our X-ray reflectivity (XR) data show no indication of the ordering of Pb^{2+} or cerussite precipitates at the calcite (104) surface. The electron density profile obtained through fitting the reflectivity data is in agreement with our earlier results for the pristine calcite/water interface[32] (Figure S8 and Table S5).

The only evidence from XR for the growth of the cerussite phase was found in the background signals (See SI, Figure S9 for background integration method). The two-dimensional detector images revealed several "powder rings" in the background region at momentum transfers of q = 1.45, 1.74, 2.53, and 2.86 $Å^{-1}$ (Figure S10). These positions matched the most intense Bragg peaks in the XRD pattern of cerussite (Table S6). The observation of the cerussite diffraction pattern as powder rings instead of localized spots on the detector, along with the lack

of any cerussite signals in the XR signal, indicates that the cerussite crystals had no structural relationship with the calcite (104) surface. X-ray reflectivity results are therefore consistent with cerussite formation through a dissolution-recrystallization mechanism, rather than direct epitaxial growth on the calcite (104) surface. Our XR data did not provide insight into the formation of any metastable amorphous $PbCO_3$ phase on the calcite surface. Further investigations are needed to study the possible phase transformation from an amorphous lead carbonate to crystalline cerussite under the current experimental conditions.

Discussion

Effects of the molecular-scale reactivity of calcite (104) surface

A mineral replacement reaction occurs via dissolution of the surface layers of a mineral which leads to an interfacial fluid layer that is supersaturated with respect to a replacing solid phase[11]. Therefore, the stability of surface sites (e.g., step vs. terrace) is a crucial factor in controlling the reaction process. Here, we observed asymmetrical movements of reaction fronts (i.e., fast *vs.* slow moving edges) during the initial formation of the cerussite shell on the top (104) surface of calcite, which likely were controlled by the anisotropic dissolution process that has been found previously on the calcite surface. It is known that the dissolution of calcite occurs through step retreat along the $[48\bar{1}]$ and $[\bar{4}41]$ directions of the rhombohedral etch pits[37-41]. Because of the symmetry of the *c*-glide plane, steps associated with the four edges of the rhombic etch pits can be grouped into obtuse ($[48\bar{1}]_+$, $[\bar{4}41]_+$) and acute ($[48\bar{1}]_-$, $[\bar{4}41]_-$) steps[42]. Previous AFM studies showed that the dissolution of calcite results in rounding at one corner, which is caused by the retreating of the structurally open $[48\bar{1}]_+$ and $[\bar{4}41]_+$ steps, while the opposing acute $[48\bar{1}]_-$ and $[\bar{4}41]_-$ steps remain sharp[43, 44]. It is likely that the fast dissolving steps of the etch pit were oriented as shown in the 0.5 h sample (Figure 1b), corresponding to the two fast moving reaction fronts where the fast growth of cerussite appears to be facilitated by preferential dissolution along the two obtuse $[48\bar{1}]_+$ and $[\bar{4}41]_+$ steps.

Size change of the replaced crystal reflects spatial coupling

The coupling between the dissolution and precipitation can be inferred from changes in size of the product crystal. The area (calculated from two-dimensional optical images in Figure 1a) of the top calcite (104) surface reacted in 1 mM Pb^{2+} solution for 15 h was 17% smaller than that of

the original calcite (Figure 1a). The size decrease indicated that the precipitation of cerussite was the rate-limiting step and the dissolution rate of calcite should have been faster than the precipitation of cerussite. In contrast, the size of the product crystal reacted in 5 mM Pb^{2+} solution was similar to that of the original calcite crystal (Figure 1a, 5mM Pb^{2+}). Here, the calcite dissolution was likely the rate-limiting step, or the dissolution rate of calcite and precipitation rate of cerussite could have been similar. In addition, the calculated equilibrium pH in 5 mM Pb^{2+} solution increased to around 4.6 as a result of the buffering effects of the dissolved inorganic carbon species (Table S1). This indicates that the replacement reaction was self-limited because of the declining dissolution rate of calcite at higher pH as shown in the XRD phase quantification results (Figure 2 and Figure S3).

Pore development

Generation of pores during the mineral replacement reaction is influenced by the differences in both solubility and molar volume between the host and secondary phases[45]. Calcite is more soluble than cerussite ($K_{sp(CaCO3)} = 10^{-8.48}$ *vs.* $K_{sp(PbCO3)} = 10^{-13.23}$)[34,46], and dissolution of calcite will result in a higher amount of $CaCO_3$ dissolving than $PbCO_3$ precipitating at close to equilibrium conditions. However, with the relatively high concentration Pb^{2+} solutions (1~5 mM) used in this work, the dissolution of trace amounts of CO_3^{2-} leads to supersaturation with respect to cerussite, which favors the nucleation and growth of cerussite. The molar volume of cerussite (40.63 cm^3/mol) is slightly larger than that of calcite (36.93 cm^3/mol), thus cerussite may occupy the space left by the dissolving calcite and inhibit the development of porosity[10, 11]. However, cerussite has the aragonite structure and tends to crystallize into tabular shapes, which are different from the rhombohedral calcite shapes. In our TXM image, the unreacted calcite was composed of a central calcite core and remaining small calcite crystals trapped between cerussite grains (Figure 4), indicating that cerussite may have caused fractures in calcite during the replacement. This suggests that the differences in crystal structure and crystallization habit between cerussite and calcite may be the primary factors that allowed the development of porosity (Figure 3 and Figure 4). Although pores sizes less than 60 nm cannot be resolved in these images due to the finite instrumental spatial resolution, interconnected nm-scale pores likely connect the apparently distinct pores found here. The similar orientations of pores and cerussite crystals along the $(1\bar{2}0)$ plane indicate that the pores were distributed mainly on the

boundaries between cerussite crystals, and between cerussite and remaining calcite grains. The pore volume comprised only about 3% volume of the sample, but it appears to have been essential for the progress of the reaction, by providing permeability for chemical mass transport during the replacement.

Environmental Implications

The spontaneous replacement of calcite by cerussite under acidic conditions reveals insights into the spatial coupling between dissolution kinetics, crystal growth, and porosity development within a confined space. The advancement of the rhombohedral-shaped reaction front during the initial growth of the cerussite shell reflects the influence of dissolution at molecular scale on the kinetics of the macroscopic crystallization process. In natural environments of circumneutral pH conditions, adsorption and precipitation of Pb on calcite surfaces are expected. However, high Pb concentration (~100 mg/kg) soils and sediments have been found in abandoned lead and zinc mines, where Pb leaches from mine tailings caused by acid mine drainage[47]. Because the replacement reaction observed here is relatively fast at even ambient conditions, calcite minerals present in the tailings are a potential sink for Pb by conversion to cerussite in the presence of acidic Pb-bearing fluid. Ultimately, the presence of phosphate in solutions could alter the final Pb phase from lead carbonate into less-soluble Pb-phosphate phases such as pyromorphite[48], depending on phosphate concentration. Understanding the entire sequence of potential replacement mechanisms may benefit the development of alternative approaches for sequestering lead and other toxic heavy metal elements in specific environmental conditions.

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Supporting Information

Growth rate of the cerussite shell on the calcite (104) surface (Figure S1), thermodynamic simulations of the equilibrium pH and solid phases (Table S1, Table S2 and Table S3), optical images of replacement experiments performed at pH 4.0 and 5.2 (Figure S2), XRD phase quantification methods and results (Figure S3), determination of the orientation of the cerussite partially-replaced calcite (Figure S4, Figure S5, and Figure S6), pore distribution (Figure S7), volume of the cerussite, calcite and pores (Table S4), Electron density profile obtained by fitting the X-ray reflectivity data (Figure S8 and Table S5), X-ray reflectivity background integration method and results (Figure S9, Figure S10 and Table S6).

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