A New Concept of Calcium Carbonate Concrete using Demolished Concrete and CO₂

Ippei Maruyama1*, 2, Wataru Kotaka3, Bui Ngoc Kien4, Ryo Kurihara4, Manabu Kanematsu5, Hikotsugu Hyodo6, Hiroshi Hirao7, Ryoma Kitagaki8, Masaki Tamura9, Masato Tsujino10, Satoshi Fujimoto11 and Takafumi Noguchi1

Received 14 June 2021, accepted 21 September 2021 doi:10.3151/jact.19.1052

Abstract

Countermeasures against carbon dioxide emissions are a concern in the construction field as well as in society. To solve this problem, a concept for new calcium carbonate concrete is proposed, and this concept is validated experimentally. In the proposed concept, calcium carbonate comprising Ca originating from demolished concrete or other Ca-containing industrial wastes and HCO₃⁻ from CO₂ gas collected from the air or emitted by industrial plants acts as a binder for aggregates, which can be natural rocks or crushed demolished concrete. This short paper describes the details of the process of making calcium carbonate concrete and discusses future perspectives.

1. Introduction

Portland cement is the most mass-produced human-made material on earth. Portland cement reacts with water and binds natural rocks as aggregates to form concrete. Since the invention of Portland cement, it has become an indispensable material for buildings and civil infrastructures, and it is now the cornerstone of modern society.

Carbon dioxide emitted by the cement industry is estimated to account for approximately 7% of the world's total emissions (IEA 2018), and has played a role in global warming since the Anthropocene. Portland cement emits approximately 770 kg-CO₂/t of cement during production, of which 480 kg/t is due to the calcination of limestone (JCA 2020). The total amount of Portland cement produced globally since the beginning of the 20th century is approximately 110 billion tons (Andrew 2018), and the total amount produced in Japan is approximately 4 billion tons (Hyodo et al. 2021). In contrast, the cumulative amount of CO₂ emitted by the calcination of limestone for cement production is estimated to exceed 2 billion tons (in Japan), and this amount is still increasing.

In contrast, the calcium retained as hydrate in concrete can be defined as a potential resource that can fix CO₂ through carbonation. This potential resource has the ability to fix up to 2 billion t-CO₂ in Japan and 55 billion t-CO₂ worldwide. It is thus possible to immobilize an amount corresponding to 2.0% of the total amount of CO₂ in the atmosphere [28000 billion tons (NAOJ 2021)]. The amount of concrete accumulated in Japan is estimated to be approximately 100 billion tons (Tanaka et al. 2013), based on the production volume of cement and the amount of demolition. The annual amount of concrete waste generated by demolition in Japan is 40 to 100 million tons (MLIT 2018), which means that 1.8 to 4.8 million tons of potential CO₂ fixation capacity is unused as roadbed material or backfill material (MLIT 2018). Under these circumstances, the reuse of calcium in concrete waste is of great importance.

Based on this background, in this study, we propose a new calcium carbonate concrete (CCC) comprising a binder of calcium carbonate and aggregate from concrete waste; a prototype reaction to create a small, hardened CCC specimen is also demonstrated. This process is inspired by the calcite concretion naturally observed at the seabed (Yoshida et al. 2015), which is formed by bicarbonate ion from corroded organ and calcium ion from the sea. This is evidence that calcium carbonate is possible to bind aggregate particles. Previously, calcium
carbonate precipitation is widely studied, but there is no trial to make calcium carbonate precipitate between aggregate particles to bind them for making construction materials.

2. Experiment

2.1 Materials

To imitate demolished concrete materials, carbonated hardened cement paste and silica sand were used. Ordinary Portland cement was used to prepare hardened cement paste (hcp) specimens. The chemical composition, mineral composition and material properties of the ordinary Portland cement used are shown in Tables 1 and 2, respectively. The water-to-cement ratio for the hcp was 0.40, and deionized water was used. Water and cement were mixed using a vacuum mixer (Twister, Renfert) for two minutes. Then, the fresh paste was poured into a stainless bowl and re-mixed for five hours until a creamy consistency was obtained. A mold with dimensions of 40 × 40 × 160 mm was used. After 3 d, the hcp specimens were demolded and cured in saturated conditions at 40°C for 28 d. Then, the hcp specimens were crushed into particles with diameters of less than 300 µm, and an accelerated carbonation process was applied to imitate the carbonation process of concrete in nature. The accelerated carbonation was carried out under conditions of a 5% CO₂ concentration by volume, relative humidity of 60% RH, and 20°C for more than one week.

Silica sand was produced by Ube Sands Industries, Ltd. (Hirano, Yamaguchi Prefecture). The density was 2.60 g/cm³, and a content of 96% SiO₂ was confirmed by X-ray fluorescence analysis. No. 5A grade was used after removing particles with diameters of greater than 0.6 mm by sieving.

Deionized water and CO₂ gas (purity higher than 99.5%) were mixed with limestone powder to produce a calcium bicarbonate solution at approximately 4°C. The limestone powder was made from limestone fine aggregate from Torigatayama, Kochi Prefecture. The density was 2.65 g/cm³, and a content greater than 55 mass% of CaO was confirmed.

2.2 Processing

A schematic of the proposed processing method is shown in Fig. 1. First, limestone powder is placed in the “(a) Reservoir” as a calcium source and mixed with deionized water and CO₂ gas to produce a calcium bicarbonate solution whose temperature is maintained at about 4°C by a heat extractor. Second, the “(b) Mold” is filled with carbonated hcp powder (2.24 g) or silica sand (2.67 g), and the outside of the mold is heated to 70°C. The mold and reservoir are connected by pipes to create a circulation system so that the calcium bicarbonate solution can be circulated by a pump. It is possible that calcium carbonate will precipitate in the mold. After the solution can no longer pass through the mold, the pump is switched off, and the hardened sample is removed from the mold.

The internal mold size is φ10 × 20 mm, and it is made of stainless steel with a thickness of approximately 2.0 mm.

---

Table 1 Mineral composition and properties of cement.

| Chemical composition (mass%) | Mineral composition (mass%) |
|-----------------------------|-----------------------------|
| LOI (%)                     | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂O | K₂O | Cl⁻ | Total |
| 1.88                        | 20.4 | 5.22  | 2.78  | 64.7| 1.16| 0.26| 0.31 | 0.014| 97.46 | 100.0 |

Table 2 Chemical composition and properties of cement.

---

H₂O – Solution

Ca(HCO₃)₂ – Solution

Ca/Mg-source (Limestone powder)

Heat extractor

Fig. 1 Schematic illustration of the proposed processing method.
2.3 Analysis
Several analyses were conducted to characterize the precursor materials and resultant CCC sample.

For the compressive strength, a universal loading machine (Autograph AGS-X, SHIMADZU) was used. The loading rate was 0.6 MPa/min. After the loading experiment, a portion of the specimen was ground to obtain a powder with particle diameters of less than 75 μm. The powder specimen was then heated at 105°C for several hours. Thermogravimetry (TG) and differential scanning calorimetry (DSC) (STA449F5 Jupiter, NETZSCH) were conducted to quantify the amount of calcium carbonate in the sample. The heating rate was 10°C/min, and the temperature range was from room temperature (approx. 30°C) to 900°C. Nitrogen gas was used at a flow rate of 50 ml/min. Powder X-ray diffraction (XRD) and Rietveld analyses were conducted using a RIGAKU Mini Flex diffractometer. α-corneundum was mixed with the sample powder such that 10 mass% of the total powder was α-corneundum. The measurement conditions were as follows: an X-ray source with a tube voltage of 40 kV, tube current of 15 mA, scanning range of $2\theta = 5°$ to $70°$, step width of 0.02°, and scanning speed of 2°/min. The primary and secondary solar slit sizes were 2.5°. Rietveld analyses were performed using TOPAS (Ver. 6.0, Bruker). The presence of alite, belite, tricalcium aluminate phase, calcium alumino-ferrite phase, bassanite, gypsum, anhydrite, periclase, calcite, aragonite, vaterite, magnesite, dolomite, hydrogarnet, hemicarboaluminate, monocarboaluminate, ettringite, monosulfate, and portlandite was analyzed and quantified. Three specimens were used for each analysis.

In addition, a thin-section sample (with a thickness of ca. 10 μm) was prepared, and polarized micrographs were obtained. Scanning electron micrographs (SEM) and energy-dispersive X-ray spectrometry (EDS) mapping (Hitachi, TM-4000 Plus and Oxford, AZTEC ONE) were obtained using fragments of the specimen with an acceleration voltage of 15 kV.

3. Experimental results
After the processing described in Section 2.2 and Fig. 1, hardened CCC specimens were obtained after 24 h. A photograph of the obtained samples is shown in Fig. 2. In the case utilizing silica sand, the specimen is fragile, and some parts are broken. A specimen with a height of approximately 10 mm is shown in Fig. 2. However, the specimens obtained utilizing the carbonated hcp powder are hardened. Therefore, additional measurements were performed on these specimens.

The average compressive strength of the three specimens was 8.6 MPa, with a standard deviation of 0.65 MPa. This strength is sufficiently hard to make a brick, but it is not comparable to the compressive strength of modern Portland cement concrete.

The TG results are shown as differential TG data in Fig. 3. In the carbonated hcp powder, portlandite, vaterite and/or aragonite, and calcite peaks were observed, while the CCC specimen exhibited a vaterite and/or aragonite peak and sharp calcite peak. According to these data, the carbonated hcp powder fixed 25.6 mass% CO$_2$ per ignited mass, whereas the CCC specimen fixed 39.0 mass% CO$_2$ per ignited mass.

![Fig. 2 CCC specimens obtained using carbonated hcp powder (left) and silica sand (right).](image)

![Fig. 3 Differential TG results for the carbonated hcp powder and CCC specimen.](image)
Figure 4 shows the XRD patterns of carbonated hcp powder and CCC samples; in both cases, calcite and aragonite were the major phases of the calcium carbonate. Because dolomite and magnesite accounted for less than 0.5 mass% and many peaks overlapped with other phases, they were not included in the quantification. The results of the quantification are shown in Fig. 5. First, the carbonated hcp powder phases were quantified using the TG results and XRD/Rietveld analysis. The same procedure was then applied to the data for the CCC specimen. To estimate the calcium carbonate used as the binder of the CCC specimen, the calcium alumino-ferrite phase was used for normalization. The calcium alumino-ferrite phase was selected because it has the lowest rate of hydration, and thus little reaction is expected to occur at 70°C in one day. Based on the results, it was estimated that approximately 13% of the calcium carbonate in the original mass of carbonated hcp powder was used as the binder to cement carbonated hcp particles. In Fig. 5, the amorphous phase, which is mainly calcium silicate hydrate (C-S-H), decreased in the CCC specimen. This could be attributed to the leaching of calcium to form calcium carbonate. When one mole of calcium carbonate is precipitated from the calcium bicarbonate solution, one mole of CO₂ is produced, and this CO₂ is expected to react with Ca from C-S-H, which is unstable at the corresponding pH (5 to 8) (Kojima et al. 1992). Simultaneously, the Ca/Si atomic ratio of C-S-H will decrease, and the silicate chain in C-S-H will increase.

Regarding the calcium carbonate, the amount of aragonite and calcite increased dramatically in the CCC specimen, while the amount of vaterite decreased. Pre-
vious studies have reported that aragonite is stable, while vaterite and calcite are unstable above 50°C (Plummer and Busenberg 1982; Ogino et al. 1987; Weiss 2014). Therefore, an increase in aragonite is expected, whereas an increase in calcite is not expected at this temperature.

The SEM images are shown in Fig. 6. As shown in Fig. 6(a), the pores or spaces between the carbonated hcp particles were mainly filled by needle-shaped crystals. Based on the quantified XRD (QXRD) data, these needle-shaped crystals are aragonite. The needle-shaped crystals have diameters of 1 to 3 µm and a length of less than about 10 µm. Blocks are confirmed to be present behind the needles, and these might be calcite based on the morphology and QXRD data.

Figure 7 shows the SEM-EDS mapping of the CCC specimen for silicon, calcium and carbon. It should be noted that the surface is not polished, and the EDS reflects the volume with a diameter of more than 1 µm behind the electron-hit area; the data are thus considered qualitative. As the original carbonated hcp powder contains silicon in C-S-H, the clouds in the silicon EDS image reflect the original position of the carbonated hcp powder. In contrast, carbon is distributed mainly in the space between the silicon clouds. This indicates that calcium carbonate crystals or amorphous calcium carbonate have precipitated in the spaces between the carbonated hcp particles.

Polarized micrographs were also obtained, and typical results are shown in Fig. 8, in which the left figure shows the image with the open Nicol configuration, and the right one shows the image with the crossed Nicol configuration.
configuration. The colored areas in Fig. 8(b) represent areas where calcium carbonate (mainly calcite or aragonite) crystals were precipitated, and brown areas show the carbonated hcp particles. The results also suggest that the spaces between the carbonated hcp particles were filled mainly by calcite and aragonite.

4. Discussion

4.1 Strength
The nominal density (including pores) of the CCC specimen was about 1.48 g/cm³. Assuming that the solid is composed of calcium carbonate (the densities of aragonite, calcite, and vaterite are 2.91, 2.71, and 2.54 g/cm³, respectively) and C-S-H (with a density of 2.60 g/cm³) (Jennings 2000, 2008), the estimated pore volume of the CCC specimen was calculated to be about 46%. The compressive strength of hcp specimens with the same water-to-cement ratio of 0.40 obtained in a previous study is plotted as a function of porosity (the drying state is assumed to be 105°C) calculated based on QXRD data (Maruyama and Igarashi 2014) in Fig. 9 and compared with the current CCC data. The CCC specimen appears below the hcp trend lines. This might be due to the nature of calcium carbonate, which does not have a layered structure, while the C-S-H sheets can be bound by charge-balancing calcium ions in the interlayer spaces. For a deeper discussion and confirmation, further compilation of data is necessary.

4.2 Consumed solution
Based on a previous study (Plummer and Busenberg 1982), calcite solutions using high-concentration CO₂ gas showed about 13.2 mM-total Ca/kg-solution at 4°C and about 3.6 mM-total Ca/kg-solution at 70°C, while aragonite solutions using high-concentration CO₂ gas showed about 15.3 mM-total Ca/kg-solution at 4°C and about 4.0 mM-total Ca/kg-solution. Based on these results, the solubility of aragonite is always higher than that of calcite in the temperature range of the present experiment, and the major precipitated phase is aragonite, which is consistent with previous studies (Ogino et al. 1987; Chen and Xiang 2009; Weiss 2014). By changing the temperature of a calcium bicarbonate solution, the degree of supersaturation can be changed by a factor of 2.3 to 2.8. If the calcium carbonate solution is under the general pCO₂ condition, the degree of supersaturation can be changed by a factor of more than 70 (Kojima et al. 1992), and thus a relatively rapid procedure (less than 24 h in this study) can be realized. Temperature change assists to increase the amount of precipitation. By considering the mass of calcium carbonate consumed in the capsule and the precipitated amount of calcium carbonate calculated by the difference in solubilities at 4°C and 70°C, 256 g of solution is theoretically needed, which is comparable to the obtained experimental results of 160 to 190 g of solution. This is 150 times the volume of solution needed to produce the CCC material. The packing ratio of the powder, flow rate, and temperature have a significant influence on the final product and required
amount of solution. In the next procedure, optimization is necessary to build larger and harder materials.

4.3 Perspective
The proposed process is shown in Fig. 10; the process is inspired by the calcite concretion that is naturally observed at the seabed. Calcium carbonate concretion of tusk shells was found in the clayey sea bed in the Kurosedani Formation of the Yatsuo Group, which is distributed in Toyama Prefecture, Central Japan (Yoshida et al. 2015). In the case of concretion formation, \( \text{HCO}_3^- \) originates from a fatty acid from the putrefying organs of the tusk shell, and the source of \( \text{Ca}^{2+} \) ions is seawater. The fatty acid is diffused from the mouth of the shell to the surrounding clayey matrix, and calcium carbonate is precipitated after the fatty acid contacts the seawater accompanied by a sudden drop in pH [the inverse relation can be found in Morse and Berner (1972) and in other references]. Even though all of these phenomena are governed by the diffusion-precipitation process, the process of calcite concretion formation (diameter 14 to 17 mm) is expected to occur on the timescale of weeks to months (Yoshida et al. 2015). In the proposed process, both \( \text{Ca}^{2+} \) ions and \( \text{HCO}_3^- \) are present in the solution mixed with \( \text{CO}_2 \) gas and calcite powder. The driving force of calcium carbonate precipitation in the proposed process is the temperature change and high concentration of the related elements in solution; with a large temperature change, \( \phi10 \times 20 \text{ mm} \) specimens can be obtained in 24 h.

As shown in Fig. 9, aggregates can be general inorganic materials, which allows the precipitation of calcium carbonate on the surface of the materials. Based on the present study, crushed demolished concrete lump can be used as the aggregate. In the present study, calcium carbonate is formed on the surface of carbonated hcp preferably rather than the quartz surface. Therefore, the appropriate surface condition should be studied further. For the calcium source, it is possible to use carbonated concrete or calcium carbonate rocks. It is also possible to use calcium-containing industrial waste, such as gypsum. Regarding the bicarbonate source, gas emissions from industrial factories and plants containing high \( \text{CO}_2 \) concentrations are likely sources; ultimately, air with a bubbling process in solution is also possible. Because buildings and other infrastructure made of concrete are a type of calcium source that is mined and de-carbonated, the present study may contribute to the efficient reuse of calcium from demolished concrete by carbonation. It should be mentioned that with the proposed process, there is no need for high-temperature processes such as cement clinker production.

In the case of natural calcite concretion, the porosity was only 25% (Yoshida et al. 2015). Therefore, idealistically, it is possible to obtain a porosity of 25% using the proposed process. Optimization to reduce the remaining porosity is the next challenge that needs to be investigated.

As for the energy consumption, although it is a very primitive process, a rough estimate is presented here for the future study. In the forming process, a silicon code heater and a pump were used. Based on the value given in the specifications, 30 W/m and 26 W were used at the maximum for the silicon code heater and the pump, respectively. Based on these values, the energy used was estimated as 0.0091 kWh (heater) and 0.026 kWh (pump). In Japan, 444 g-CO\(_2\)/kWh of electricity (FEPC 2020) was used, in this sense, 15.58 g-CO\(_2\) is emitted and this value is higher than the captured 0.6 g-CO\(_2\) per specimen. Although actual values were not monitored during processing, but based on this value, the pumping process should be revised or optimized to make a car-

Fig. 10 Schematic of the calcium carbonate concrete process inspired by carbonate concretion formation.
bon-negative construction material.

At the same time, once this technology is developed, the calcium element will be recyclable. From a sustainability point of view, this technology will open the door to a calcium-closed construction society with low carbon emissions. Finally, a similar process can be applied to other carbonates such as magnesite and dolomite, and carbonate rocks as well as the possibility of the presence of water ice have been found on Mars (Bibring et al. 2004; Ehlmann et al. 2008), it would be interesting to investigate expanding the proposed process for extraplanetary buildings.

5. Conclusion

A new concept of calcium carbonate concrete is proposed. The concept was validated by an experiment using carbonated hardened cement paste powder/silica sand and calcium bicarbonate solution made from pure CO₂ gas and calcite powder. The obtained strength was only 8.6 MPa with a porosity of 46%. An approximately 100 times larger volume of solution was required to make the target material. The major binding phase of calcium carbonate was needle-shaped aragonite, which has the highest density among calcium carbonate polymorphs. Further basic studies and research on optimization are necessary. By optimizing the energy consumption of the processing, there is a possibility to make a carbon negative construction material. The proposed technique will open the door to a calcium-closed sustainable construction society with low carbon emissions.

Acknowledgements

This research was funded by the NEDO Moonshot Research and Development Project, "Calcium Carbonate Circulation System for Construction" (Project manager: Prof. Taka-fumi Noguchi, The University of Tokyo).

References

Andrew, R. M., (2018). “Global CO₂ emissions from cement production.” Earth System Science Data, 10(1), 195-217.

Bibring, J. P., Langevin, Y., Poulet, F., Gendrin, A., Gondet, B., Berthé, M., Soufflot, A., Drossart, P., Combes, M., Bellucci, G., Moroz, V., Mangold, N., Schmitt, B., Erard, S., Forni, O., Manaud, N., Pouilleau, G., Encenzat, T., Fouchat, T., Melchiorri, R., Altieri, F., Formisano, V., Bonello, G., Fonti, S., Capaccioni, F., Cerroni, P., Coradini, A., Kottsov, V., Ignatiev, N., Moroz, V., Titov, D., Zasova, L., Mangold, N., Pinet, P., Schmitt, B., Sotin, C., Hauber, E., Hoffmann, H., Jaumann, R., Keller, U., Arvidson, R., Mustard, J., Duxbury, T. and Forget, F., (2004). “Perennial water ice identified in the south polar cap of Mars.” Nature, 428(6983), 627-630.

Chen, J. and Xiang, L., (2009). “Controllable synthesis of calcium carbonate polymorphs at different temperatures.” Powder Technology, 189(1), 64-69.

Ehlmann, B. L., Mustard, J. F., Murchie, S. L., Poulet, F., Bishop, J. L., Brown, A. J., Calvin, W. M., Clark, R. N., Des Marais, D. J., Milliken, R. E., Roach, L. H., Roush, T. L., Swayze, G. A. and Wray, J. L., (2008). “Orbital identification of carbonate-bearing rocks on Mars.” Science, 322(5909), 1828-1832.

Hyodo, H., Hoshino, S., Hirao, H. and Nomura, K., (2021). “A study on calculating CO₂ uptake due to carbonation during concrete cycle.” Cement Science and Concrete Technology, 74(1), 333-340. (in Japanese)

IEA, (2018). “Technology roadmap: Low-carbon transition in the cement industry.” Paris: International Energy Agency.

JCA, (2020). “Outline of LCI data of cement industry [online].” Tokyo: Japan Cement Association. Available from: <https://www.jcassoc.or.jp/cement/4pdf/jg1_01.pdf>. (in Japanese)

Jennings, H. M., (2000). “A model for the microstructure of calcium silicate hydrate in cement paste.” Cement and Concrete Research, 30(1), 101-116.

Jennings, H. M., (2008). “Refinements to colloid model of C-S-H in cement: CM-II.” Cement and Concrete Research, 38(3), 275-289.

Kojima, Y., Sadotomo, A., Yasue, T. and Arai, Y., (1992). “Control of crystal shape and modification of calcium carbonate prepared by precipitation from calcium hydrogencarbonate solution.” Journal of the Ceramic Society of Japan, 100(1165), 1145-1153. (in Japanese)

Maruyama, I. and Igarashi, G., (2014). “Cement reaction and resultant physical properties of cement paste.” Journal of Advanced Concrete Technology, 12(6), 200-213.

MLIT, (2018). “Construction by-product fact-finding survey [online].” Tokyo: Ministry of Land, Infrastructure, Transport and Tourism. Available from: <https://www.mlit.go.jp/sogoseisaku/region/recycle/d02status/index_0201status.htm>. (in Japanese)

Morse, J. W. and Berner, R. A., (1972). “Dissolution kinetics of calcium carbonate in sea water-I, A kinetic origin for the lysocline.” American Journal of Science, 272(9), 840-851.

NAOJ, (2021). “Chronological scientific tables. [online].” Tokyo: National Astronomical Observatory of Japan. Available from: <https://www.rikenanpyo.jp/kaisetsu/chronolog.html> (in Japanese)

Ogino, T., Suzuki, T. and Sawada, K., (1987). “The formation and transformation mechanism of calcium carbonate in water.” Geochimica et Cosmochimica Acta, 51(10), 2757-2767.

Plummer, L. N. and Busenberg, E., (1982). “The solubilities of calcite, aragonite and vaterite in CO₂-H₂O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O.” Geochimica et Cosmochimica
Tanaka, K., Hayakawa, Y., Okuoka, K., Sugimoto, K. and Tanikawa, H., (2013). “Time-series estimation of the material stock of buildings and infrastructure of all prefectures in Japan.” Journal of Japan Society of Civil Engineers, Ser. G (Environmental Research), 69(6), II_25-II_34. (in Japanese)

FEPC, (2020). “Energy and environment [online].” Tokyo: The Federation of Electric Power Companies of Japan. Available from: <https://www.fepc.or.jp/library/pamphlet/pdf/20_environment.pdf>. (in Japanese)

Weiss, C. A., Torres-Cancel, K., Moser, R. D., Allison, P. G., Gore, E. R., Chandler, M. Q. and Malone, P.G., (2014). “Influence of temperature on calcium carbonate polymorph formed from ammonium carbonate and calcium acetate.” Journal of Nanotechnology and Smart Materials, 1, Article ID 105.

Yoshida, H., Ujihara, A., Minami, M., Asahara, Y., Katsuta, N., Yamamoto, K., Sirono, S. I., Maruyama, I., Nishimoto, S. and Metcalfe, R., (2015). “Early post-mortem formation of carbonate concretions around tusk-shells over week-month timescales.” Scientific Reports, 5, Article ID 14123.