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Using ikaite and other hydrated carbonate minerals to increase ocean alkalinity for carbon dioxide removal and environmental remediation

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Introduction

Removing large volumes of CO₂ from the atmosphere may be required to meet the goals of the Paris Agreement in addition to rapid and deep emissions reductions. This has catalysed recent attention on carbon dioxide removal (CDR) approaches that can remove more CO₂ from the atmosphere than they emit. The oceans absorb approximately 25% of the CO₂ that is emitted to the atmosphere causing acidification, which adds to the stress experiences by some shell forming organisms. Some proposals have been put forward to remove additional CO₂ by increasing ocean alkalinity that may also help to ameliorate the impact of ocean acidification by converting CO₂ to bicarbonate (HCO₃⁻) ions that remain in the ocean >10⁵ years (often termed 'ocean alkalinity enhancement', OAE¹).

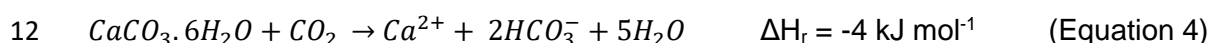
The first OAE proposal involved calcining limestone to create lime (Equation 1), and then dissolving it in the ocean² (Equation 2). The process consumes thermal energy in the chemical transformation of the material and would only be carbon negative if the process emissions were captured and stored³. The energy released during carbonation (Equation 2) in the ocean is impossible to recover. As such techno-economic assessments suggest an energy penalty of 1-7 GJ_{primary} and a cost \$70-160 per net tonne of CO₂ removed from the atmosphere³ (enthalpy is used in Equation 1 and 2 to reflect process energy requirements, although given inefficiencies within processing equipment, actually energy requirements are usually much greater).



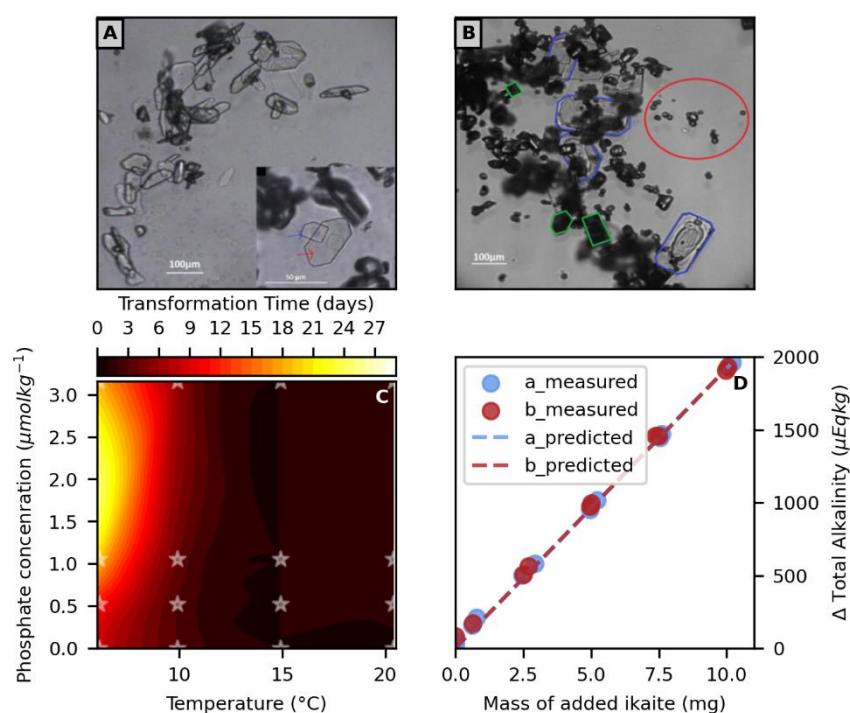
Given that the surface ocean is supersaturated with respect to calcium carbonate minerals (e.g., calcite), it is not possible to sequester atmospheric CO₂ by spreading these minerals directly into the ocean. Increasing the partial pressure of CO₂ (>1,000 ppmv at 1 atm) in a seawater/limestone reactor would induce carbonate mineral dissolution⁴, but this may require a large reactor, 2-2.5 GJ of electricity per gross tonne of CO₂⁵, and would require direct air capture systems for atmospheric CO₂ removal. Some hydrated carbonate minerals will spontaneously dissolve in seawater at ambient partial pressures (Figure S1, Supplementary Text 1). These minerals are rare, and thus cannot be extracted from natural deposits in sufficient quantity to make a meaningful climate impact. However, it may be possible to create them specifically for addition to the ocean.

1 Producing hydrated mineral carbonates for ocean alkalinity enhancement

2 One promising candidate is ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) which is a naturally occurring, metastable
 3 hydrated calcium carbonate mineral⁶ that forms in cold ($<15^\circ\text{C}$), alkaline, nutrient-rich waters⁷.
 4 In these conditions ikaite precipitation is favoured over anhydrous calcium carbonate (e.g.,
 5 calcite), which eventually dehydrates into calcium carbonate or dissolves upon changes in
 6 solution chemistry, pressure, or temperature⁶. As such, it is possible to precipitate synthetic
 7 ikaite⁸. The enthalpy of reaction is exothermic (Equation 3), although its precipitation is not
 8 naturally spontaneous for most earth surface temperature/pressures due to the change in
 9 entropy ($\Delta S_r = -0.14 \text{ kJ mol}^{-1} \text{ K}^{-1}$). Subsequently, the energy 'lost' through carbonation in the
 10 ocean is lower than that when using lime (Equation 4).



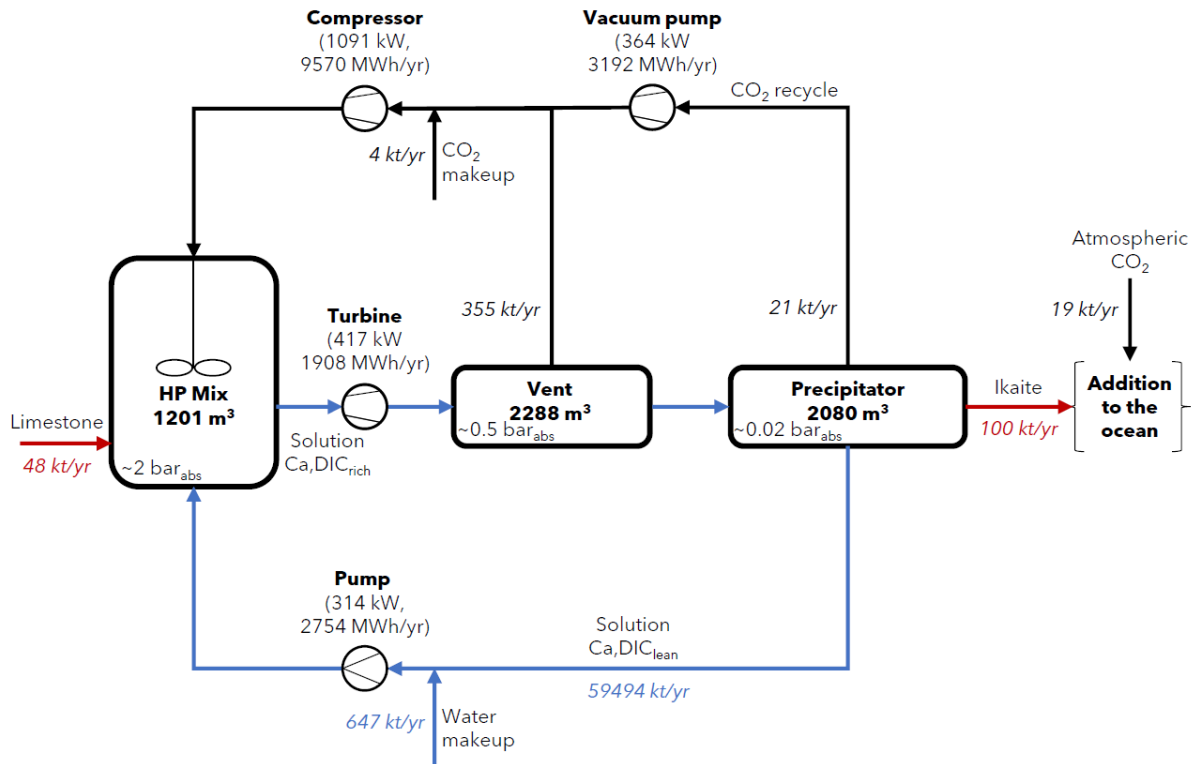
13 The feasibility of using ikaite, or other hydrated minerals, for OAE requires that the produced
 14 mineral remains stable for sufficient time to be added to the ocean and dissolve. If ikaite were
 15 to transform into calcite before addition, it would have no effect on alkalinity, or possibly a
 16 reduction of alkalinity by seeding additional carbonate precipitation⁹. Experimental work
 17 suggests that synthetic ikaite (Figure 1A and B) can be stable for days at low temperature
 18 (sufficient time to be added to the ocean, Figure 1C), and that it dissolves in seawater and
 19 stoichiometrically increases alkalinity (Figure 1D).



20

21 Figure 1: Optical characterization of powder that was interspersed with different crystal habits
 22 of ikaite showing a) morphologies that often characterize ikaite crystals¹⁰ b) and assemblage
 23 of ikaite (blue edges), vaterite (red circle) and calcite (green edges). c) A stability matrix of
 24 ikaite showing presence within the solution over time for a given temperature (interpolated
 25 between the marked datapoints) d) Measured and dissolved total alkalinity (TA) from
 26 dissolution of ikaite in two natural seawaters (a/b). (See Supplementary Text 2)

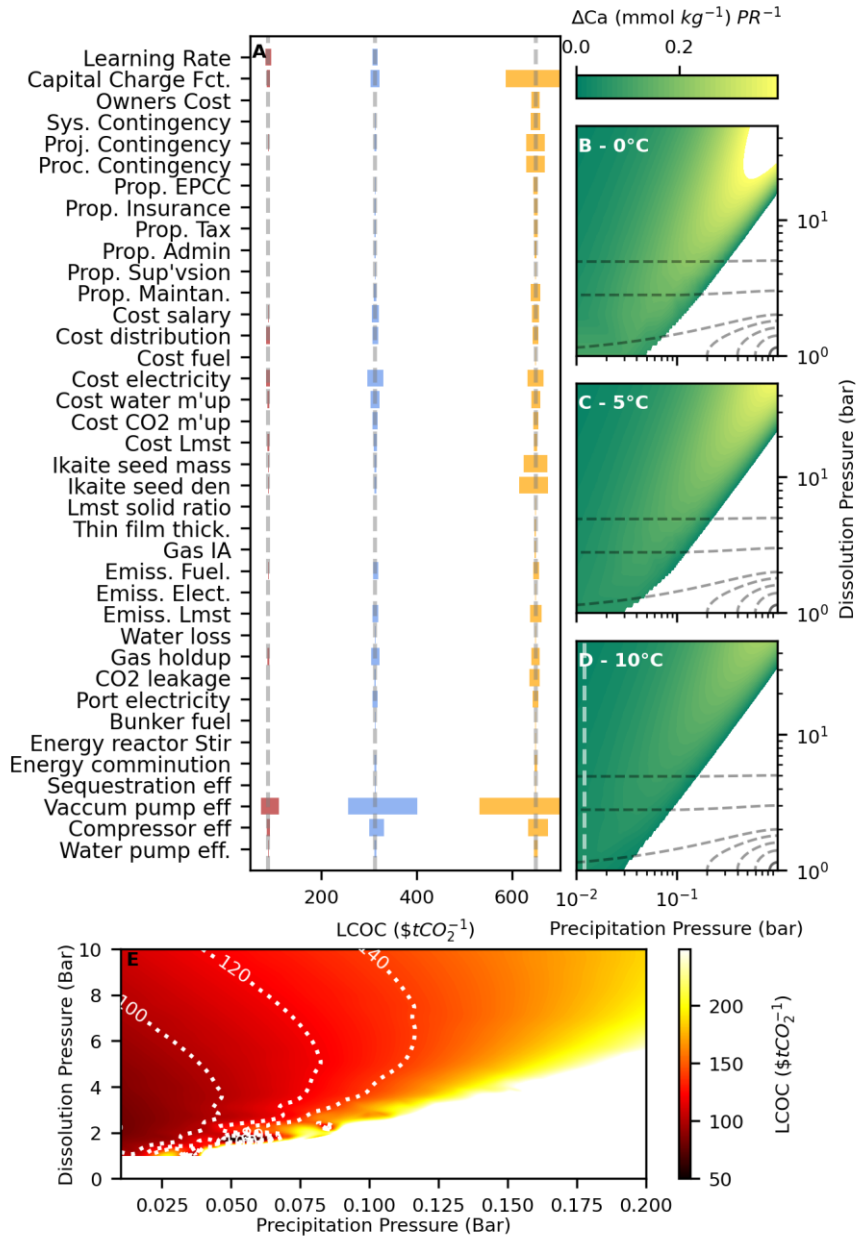
1 Given that ikaite is rare and ephemeral in natural environments, we discuss the potential of a
 2 multi-step system for its mass production (Figure 2). The process uses high pressure pure
 3 CO₂ in contact with water to dissolve calcite bearing limestone (which is abundant and
 4 naturally occurring), the product solution of this reaction is passed to additional reactors in
 5 which the CO₂ is degassed. This would cause the solution to become supersaturated with
 6 respect to ikaite. If calcite precipitation was inhibited under cold temperatures, then solid ikaite
 7 would be formed and removed from the reactor for addition to the ocean.



8
 9 Figure 2: A simplified process flow diagram of a multi-step system for producing ikaite. Mass
 10 flow quantities (italicized with units in kt year⁻¹) and power requirements (kW, and MWh yr⁻¹)
 11 for an industrial scale base-case scenario are shown.

12 Given its important environmental function, the dissolution behaviour of calcite is well
 13 described, and has been the focus of sustained research for decades. As such, it is possible
 14 to sufficiently constrain the operation of the high-pressure dissolution reactor. Work has also
 15 examined the precipitation behaviour of ikaite, and postulate a similar rate to calcite
 16 precipitation from calcite seeded solutions¹¹. Therefore, estimates can be made on the
 17 potential size of the reactors and their capital cost.

18 The energy requirements of the pressure swing system depend on the pressure ratio between
 19 the dissolution reactor and the precipitation reactor. Maximising the quantity of ikaite
 20 precipitated for the smallest ratio of pressure change is desirable as it would reduce the
 21 relative amount of water recirculation, and lower pumping/compression costs. The relative
 22 solubility of calcite and ikaite⁶ can be used to evaluate the change in calcium concentration of
 23 a solution for a given CO₂ gas-phase pressure ratio, and results suggest that at dissolution
 24 (~2 bar) and precipitation total pressures (~0.02 bar) larger calcium concentrations (~0.02 mol
 25 kg⁻¹) are possible for a given pressure ratio (Figure 3B, C, and D).



1

2 Figure 3: Panel A shows the sensitivity of the model outcomes to $\pm 20\%$ changes in input
 3 assumptions for the base-case system (2 bar dissolution pressure, 0.02 bar precipitation
 4 pressure, 3°C operating temperature) for a 1st-of-a-kind industrial scale system (yellow bars),
 5 nth-of-a-kind industrial scale system (blue bars) and a million tonne scale nth-of-a-kind system
 6 (red bars). In the pressure swing system, solutions exiting the dissolution (high CO₂ pressure)
 7 reactor will be in equilibrium with calcite and a relatively rich calcium concentration. Solutions
 8 exiting the precipitation (low CO₂ pressure) reactor will be in equilibrium with ikaite with a
 9 relatively lean calcium concentration. The colour change in panels B, C, D shows this change
 10 in calcium concentration for a given ratio of pressure (PR) between dissolution and
 11 precipitation for temperatures 0, 5, and 10°C respectively (see Figure S3 for the base case
 12 concentration changes). The dark dotted lines represent concentric circles around 1 bar
 13 intended to show relative pressure changes from ambient conditions. The white dotted line is
 14 the vapour pressures of H₂O at 10°C and thus delineate a likely minimum for the precipitation
 15 reactor pressure (for 0 and 5°C the vapour pressure is <10 mbar). Panel E shows the change
 16 in the levelized cost of net carbon removal for a first of nth-of-a-kind mega-tonne scale system

1 operating at 3°C. Variations due to temperature are presented in Figure S8 in the
2 supplementary information.

3

4 **Technoeconomic considerations for large-scale ikaite production**

5 To assess the potential costs of the approach, we developed a bespoke technoeconomic
6 model in which the dissolution, gas transfer and precipitation processes were simulated using
7 the geochemical modelling software PHREEQC (v3.4) in conjunction with the supplied
8 phreeqc.dat thermodynamic database. The process model was nested in a mass and energy
9 balance model coded using Python (Anaconda v3.9), and it evaluates '1st-of-a-kind' (FOAK)
10 pilot (10³ t ikaite per year) and industrial scale (10⁵ t ikaite per year) processes. Learning rates
11 are applied to consider the cost of industrial and mega-tonne (~10⁶ t ikaite per year) 'nth-of-a-
12 kind' (NOAK) processes. See Supplementary Text 3-6 and references therein for details on
13 the modelling.

14 For the base case system (temperature at 3°C), the dissolution of calcite at 2 bar (pure CO₂)
15 occurred over ~8 minutes (for the solution to reach 95% equilibrium), the rate of reaction was
16 controlled by CO₂ mass transfer into solution and hydration kinetics. Given the relatively rapid
17 reaction, the reactor volume is relatively low (12 m³ for the 1 kt yr⁻¹ FOAK pilot system, 1201
18 m³ for the industrial scale plant). The degassing of the solution (at 0.5 bar) takes longer (16
19 min) requiring a larger reactor. The precipitation of ikaite is similar (11 min) requiring a similar
20 sized reactor (20 m³ for the 1 kt yr⁻¹ FOAK pilot system, 2080 m³ for the industrial scale plant).
21 The capital cost of the dissolution and precipitation reactors will, partly, be increased by the
22 deviation of the absolute pressure from ambient conditions, and the time required for the
23 reaction to reach a desired extent.

24 The model predicts that the levelized cost of net carbon removal (LCOC) for this system to be
25 approximately \$3,800 tCO₂⁻¹ for a pilot-scale process, and \$650 tCO₂ for a FOAK industrial
26 scale process, and <\$310 tCO₂ for 'NOAK industrial scale processes. In these systems the
27 fixed running costs, which include labour, maintenance, supervision, administration and
28 company overheads, taxes, insurance, and ocean distribution, dominate the total cost of
29 carbon (20 – 50%). These together with the capital expenditure offer the largest potential for
30 cost reduction through economies of scale in component selection or possible cost reductions
31 through technology development. The model suggests that a NOAK million tonne scaled
32 system could drive down costs to <\$90 tCO₂⁻¹. This compares favourably with projected future
33 costs of direct air capture (\$90 – 200 tCO₂⁻¹¹²) or ocean liming (\$70 – 160 tCO₂⁻¹³) approaches
34 to remove carbon dioxide from the atmosphere. Energy requirements for the system amount
35 to 850 kWh of electricity, and 54 MJ of fuel per net tCO₂ for the pilot and industrial scale
36 systems. This compares to 140-554 kWh and 5 – 6 GJ for direct air capture, or 270 – 1,400
37 kWh and 3 – 6 GJ for other methods of OAE¹.

38 The LCOC is sensitive to changes input parameters (Figure 3A) particularly the ratio between
39 CO₂ uptake and total alkalinity ('sequestration efficiency' see Figure S7). A full list of base
40 case parameters is presented in Table S5 and represent reasonable present day (FOAK) or
41 possible future (NOAK) values. The system LCOC decreases for lower dissolution and lower
42 precipitation reaction pressures (Figure 3E), with the apparent favourable conditions being
43 <0.05 bar for the precipitator and >1 bar for the dissolution reactor. However, there is limited
44 applicability of the results beyond maximum compression pressures (35-70 bar for the
45 compressors, 100 bar for the water pumps, and 50 bar for the dissolution reactors), or below
46 minimum vacuum pressures (1 mbar for the vacuum system, or 6-12 mbar for the vaporization

1 pressure of water), given the constraints of the selected equipment. As such, 0.02 and 2 bar
2 are reasonable choices for the base case but may be further optimised.

3 **Challenges**

4 The environmental consequences of increasing ocean alkalinity remain uncertain. Some
5 suggest that targeted addition may ameliorate the effects of ocean acidification or to moderate
6 the CO₂ absorption capacity of the ocean¹. However, it is possible that the increase in alkalinity
7 may also stimulate carbonate precipitation if threshold carbonate saturation levels (>12
8 $\Omega_{\text{aragonite}}$) are exceeded or create conditions more favourable for carbonate producing
9 organisms¹³. The addition of pure ikaite avoids co-addition of bioactive elements (e.g., Si, Fe,
10 Ni) which possibly limits other OAE approaches¹³. Limestone used for industrial purposes can
11 typically be made up of ~97% calcium carbonate¹⁴, with the remaining primarily composed of
12 Mg (incorporated into the calcium carbonate phase), and silica (which is considerably less
13 soluble than carbonate and may be retained within the dissolution reactor).

14 Results suggest that ikaite is sufficiently stable (over days at <15°C) such that it could be
15 loaded onto dedicated ocean vessels and dispersed from the back of a ship. Work considering
16 addition of lime to the ocean³ suggests 3 – 4 days would be needed to unload a large 300 kt
17 vessel, while smaller vessels would shorten this time their use could potentially be more
18 expensive. There may be spare capacity within the existing shipping fleet to transport and
19 distribute billions of tonnes of OAE materials¹⁵, but given the temperature and time constraints
20 associated with ikaite production, a dedicated delivery system may be more appropriate. In
21 the base-case process described here the distribution method³ accounts for <6% of the energy
22 and around 40% of the fixed running costs. Ikaite crystals <300 μm will dissolve within the
23 ocean mixed layer and thus the alkalinity increase could contribute to CO₂ removal from the
24 atmosphere (see Figure S4).

25 If ocean addition of ikaite is limited to waters <15°C, this approach is applicable to the coasts
26 of Northern Europe, Alaska, Maine and N.W. United States, Canada, Chile, Argentina,
27 Southern Peru, Western South Africa, Southern Australia, New Zealand, N.W Russia and
28 Northern Japan (Figure S5). Large sedimentary carbonate deposits are present in most of
29 these regions, and nations collectively extract >1 Gt of limestone annually primarily for
30 aggregate or cement production (Figure S6). There may be on the order of ~100 Mt yr⁻¹ of
31 waste rock dust generation (5-20% of bulk rock production), which could be used as a raw
32 material for this processes (Table S1). Much of the existing extractive capacity was created
33 over the last 50 years, and global aggregate extraction will increase to meet a growing
34 population. As such, there may be sufficient material to facilitate scale to hundreds of MtCO₂
35 yr⁻¹ over the next 20-30 years, and subsequently >Gt yr⁻¹ thereafter. However, more work is
36 required to investigate the relationship between resource locations, the suitability of resources
37 for the process (e.g., raw material purity), appropriate siting of facilities in nation socio-
38 economic and regulatory context, logistics of transport between the facilities and optimum
39 addition sites.

40 Here we describe a system for removing CO₂ from the atmosphere by increasing ocean
41 alkalinity using ikaite, a hydrated carbonate mineral. Ikaite is meta-stable in solutions <15°C
42 and transforms into more stable unhydrated polymorphs (e.g., calcite) over days. The pressure
43 swing process proposed here synthesises ikaite by dissolving limestone in a reactor at
44 elevated CO₂ partial pressure (>1 bar). The resulting alkaline water is passed to a series of
45 reactors that vent and vacuum the CO₂ (0.5 and <0.05 bar respectively) causing the solution
46 to become supersaturated with ikaite, which precipitates as a solid. Experiments show that
47 adding the precipitated ikaite to seawater results in an increase in total alkalinity. The energy
48 requirements (850 kWh tCO₂⁻¹ of electricity and 54 MJ tCO₂⁻¹ of fuel) and the cost of this

1 approach ($\$650 \text{ tCO}_2^{-1}$ FOAK, $<\$90 \text{ tCO}_2^{-1}$ NOAK) are comparable to, if not lower than,
2 alternative approaches to permanently removing CO_2 from the atmosphere at scale. The
3 abundant raw materials suggest a scalable potential, possibly on the order of $>\text{Gt yr}^{-1}$. The
4 approach avoids the addition of bioactive elements (Si, Fe, Ni), which may lower the
5 environmental feasibility or social acceptability of other OAE approaches.

6

7 **Experimental Procedures**

8 All supporting data and model code is freely available at Heriot-Watt University's publication
9 portal (*DOI 10.17861/082667ec-1eba-45e4-989e-8d114f58e9d9*), or can be obtained on
10 request to the corresponding authors.

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17

18 **Author contributions**

19 The concept was initiated by PR, and developed by PR and JH. Laboratory experiments scope
20 and design: JH and SB. Sample collection and analysis: SB and BDM. Data analysis: PR, SB,
21 KP, BDM, and JH. Technoeconomic assessment model development: PR. Manuscript writing
22 and editing PR, SB, KP, BDM, and JH.

23

24 **Declaration of interests**

25 PR, SB and JH are the inventors of the Patent (GB2206475.2) Method of producing a solid
26 metal carbonate hydrate.

27

28 **References**

- 29 1. Renforth, P., and Henderson, G. (2017). Assessing ocean alkalinity for carbon
30 sequestration. *Reviews of Geophysics* 55, 636–674. 10.1002/2016RG000533.
- 31 2. Kheshgi, H.S. (1995). Sequestering atmospheric carbon dioxide by increasing ocean
32 alkalinity. *Energy* 20, 915–922. 10.1016/0360-5442(95)00035-F.
- 33 3. Renforth, P., Jenkins, B.G.G., and Kruger, T. (2013). Engineering challenges of ocean
34 liming. *Energy* 60, 442–452. 10.1016/j.energy.2013.08.006.
- 35 4. Caldeira, K., and Rau, G.H. (2000). Accelerating carbonate dissolution to sequester
36 carbon dioxide in the ocean: Geochemical implications. *Geophysical Research Letters*
37 27, 225–228. 10.1029/1999GL002364.
- 38 5. Xing, L., Pullin, H., Bullock, L., Renforth, P., Darton, R.C., and Yang, A. (2022). Potential
39 of enhanced weathering of calcite in packed bubble columns with seawater for carbon

- 1 dioxide removal. *Chemical Engineering Journal* 431, 134096.
2 10.1016/j.cej.2021.134096.
- 3 6. Bischoff, J.L., Fitzpatrick, J.A., and Rosenbauer, R.J. (1993). The solubility and
4 stabilization of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) from 0 to 25 C: Environmental and paleoclimatic
5 implications for thinolite tufa. *The Journal of Geology* 101, 21–33. 10.1086/648194
- 6 7. Schultz, B., Thibault, N., and Huggett, J. (2022). The minerals ikaite and its
7 pseudomorph glendonite: Historical perspective and legacies of Douglas Shearman and
8 Alec K. Smith. *Proceedings of the Geologists' Association*.
9 10.1016/j.pgeola.2022.02.003.
- 10 8. Hu, Y.-B., Dieckmann, G.S., Wolf-Gladrow, D.A., Nehrke, G., and S. Ndoye^{1, 2}, X.
11 Capet², P. Estrade¹, B. Sow³, D. Dagorne⁴, A. Lazar², A. Gaye¹, and P.B. (2014).
12 Laboratory study on coprecipitation of phosphate with ikaite in sea ice. *Journal of*
13 *Geophysical Research: Oceans* 119, 7007–7015. 10.1002/2014JC010079.
- 14 9. Moras, C.A., Bach, L.T., Cyronak, T., Joannes-Boyau, R., and Schulz, K.G. (2021).
15 Ocean Alkalinity Enhancement - Avoiding runaway CaCO_3 precipitation during quick
16 and hydrated lime dissolution. *Biogeosciences Discuss.* 2021, 1–31. 10.5194/bg-2021-
17 330.
- 18 10. Sekkal, W., and Zaoui, A. (2013). Nanoscale analysis of the morphology and surface
19 stability of calcium carbonate polymorphs. *Scientific reports* 3, 1587.
20 10.1038/srep01587.
- 21 11. Papadimitriou, S., Kennedy, H., Kennedy, P., and Thomas, D.N. (2014). Kinetics of
22 ikaite precipitation and dissolution in seawater-derived brines at sub-zero temperatures
23 to 265K. *Geochimica et Cosmochimica Acta* 140, 199–211. 10.1016/j.gca.2014.05.031.
- 24 12. Keith, D.W., Holmes, G., St. Angelo, D., and Heidel, K. (2018). A Process for Capturing
25 CO_2 from the Atmosphere. *Joule* 2, 1573–1594. 10.1016/j.joule.2018.05.006.
- 26 13. Bach, L.T., Gill, S.J., Rickaby, R.E.M., Gore, S., and Renforth, P. (2019). CO_2 Removal
27 With Enhanced Weathering and Ocean Alkalinity Enhancement: Potential Risks and Co-
28 benefits for Marine Pelagic Ecosystems. *Frontiers in Climate* 1, 7.
29 10.3389/fclim.2019.00007
- 30 14. Harrison, D.J. (1993). High-purity limestones in England and Wales. *QJEGH* 26, 293–
31 303. 10.1144/GSL.QJEGH.1993.026.004.05.
- 32 15. Caserini, S., Pagano, D., Campo, F., Abbà, A., De Marco, S., Righi, D., Renforth, P., and
33 Grosso, M. (2021). Potential of Maritime Transport for Ocean Liming and Atmospheric
34 CO_2 Removal. *Frontiers in Climate* 3, 1–18. 10.3389/fclim.2021.575900.

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