

# Alkali ion ( $\text{Na}^+$ or $\text{K}^+$ ) incorporation into the crystal structure of $\text{CaCO}_3$

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Natural calcium carbonate (for instance, the minerals of limestone or exoskeletons of marine animals) may contain varying yet quite small amounts of alkali ions (*e.g.*,  $\text{Na}^+$  and  $\text{K}^+$ ) in accord with the chemical composition of natural waters from which the formation of  $\text{CaCO}_3$  originally took place. If such natural waters (such as seawater) also contain  $\text{Mg}^{2+}$  ions, then the  $\text{CaCO}_3$  formed will incorporate a portion of that  $\text{Mg}^{2+}$  to form what is called as “[magnesian-calcite](#).”

Uptake of alkali ions by  $\text{CaCO}_3$  did not receive so much of the attention it deserves especially in industrial circles. Would such an uptake of alkalis lead to defect formation in the crystal structure of crystalline  $\text{CaCO}_3$ ?

This technical note will present some of the important published work on the Na and/or K incorporation into the crystal structure of  $\text{CaCO}_3$ .

- *The hyperlinks throughout the text allow access to the references.*

Na<sup>+</sup> and K<sup>+</sup> are monovalent alkali ions.  
Ca<sup>2+</sup> (and Mg<sup>2+</sup>) are divalent alkaline earth ions.

Their ionic radii (in 6-coordination) are given below,  
in comparison to that of the divalent Ca<sup>2+</sup> ion.

Na<sup>+</sup>: 1.02 to 1.16 Å

K<sup>+</sup>: 1.38 Å

Ca<sup>2+</sup>: 1.08 to 1.14 Å (to compare; Mg<sup>2+</sup> = 0.72 Å)

One thus notices that the ionic radius of Na<sup>+</sup> is quite comparable to that of Ca<sup>2+</sup>, where K<sup>+</sup> is a much larger cation. The incorporation of larger cations into the CaCO<sub>3</sub> (*e.g.*, calcite) structure will be difficult (at least under atmospheric conditions), essentially due to geometrical and crystallographic constraints.

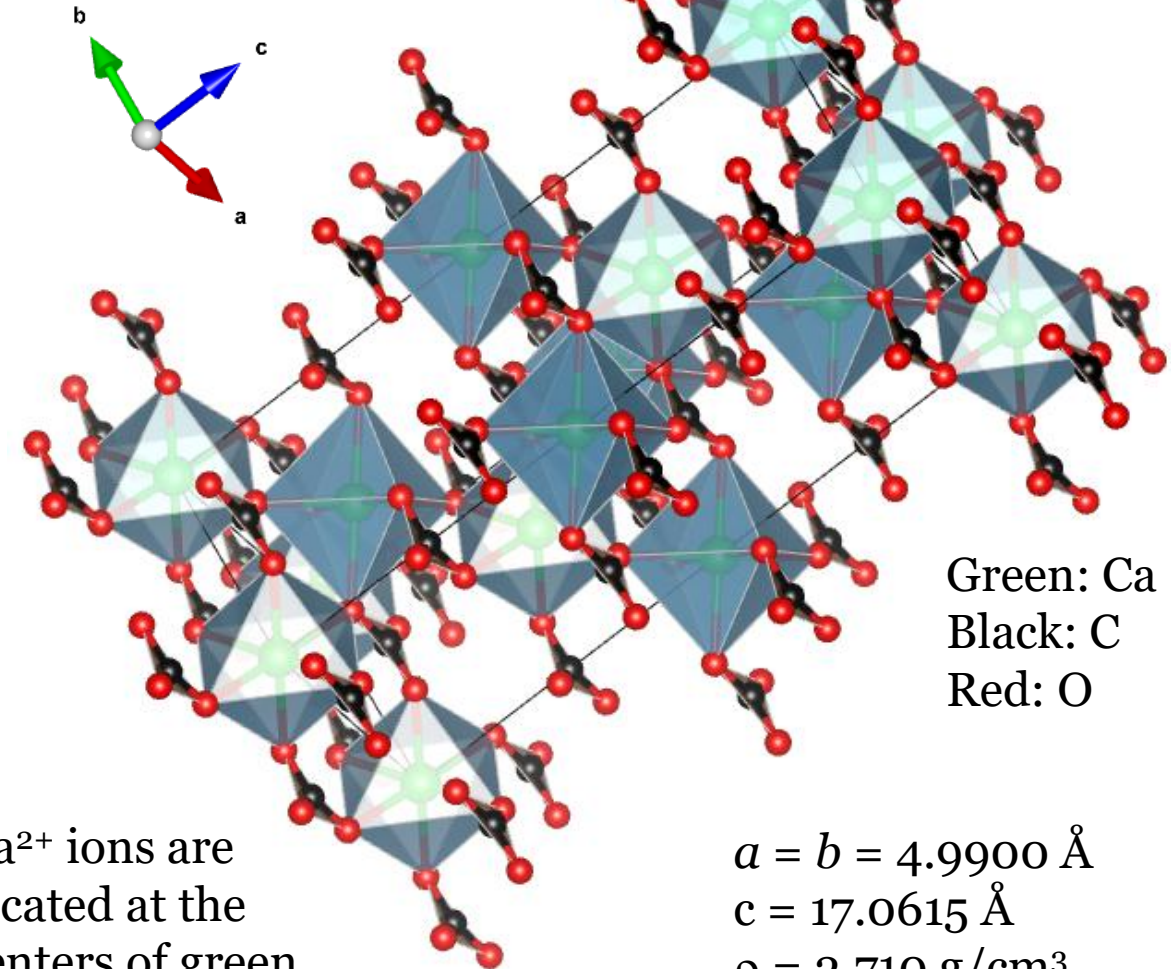
*other alkali ions (Group I of periodic table)*

Li<sup>+</sup>: 0.76 Å

Rb<sup>+</sup>: 1.52 Å

Cs<sup>+</sup>: 1.67 Å

## Rhombohedral crystal structure of calcite



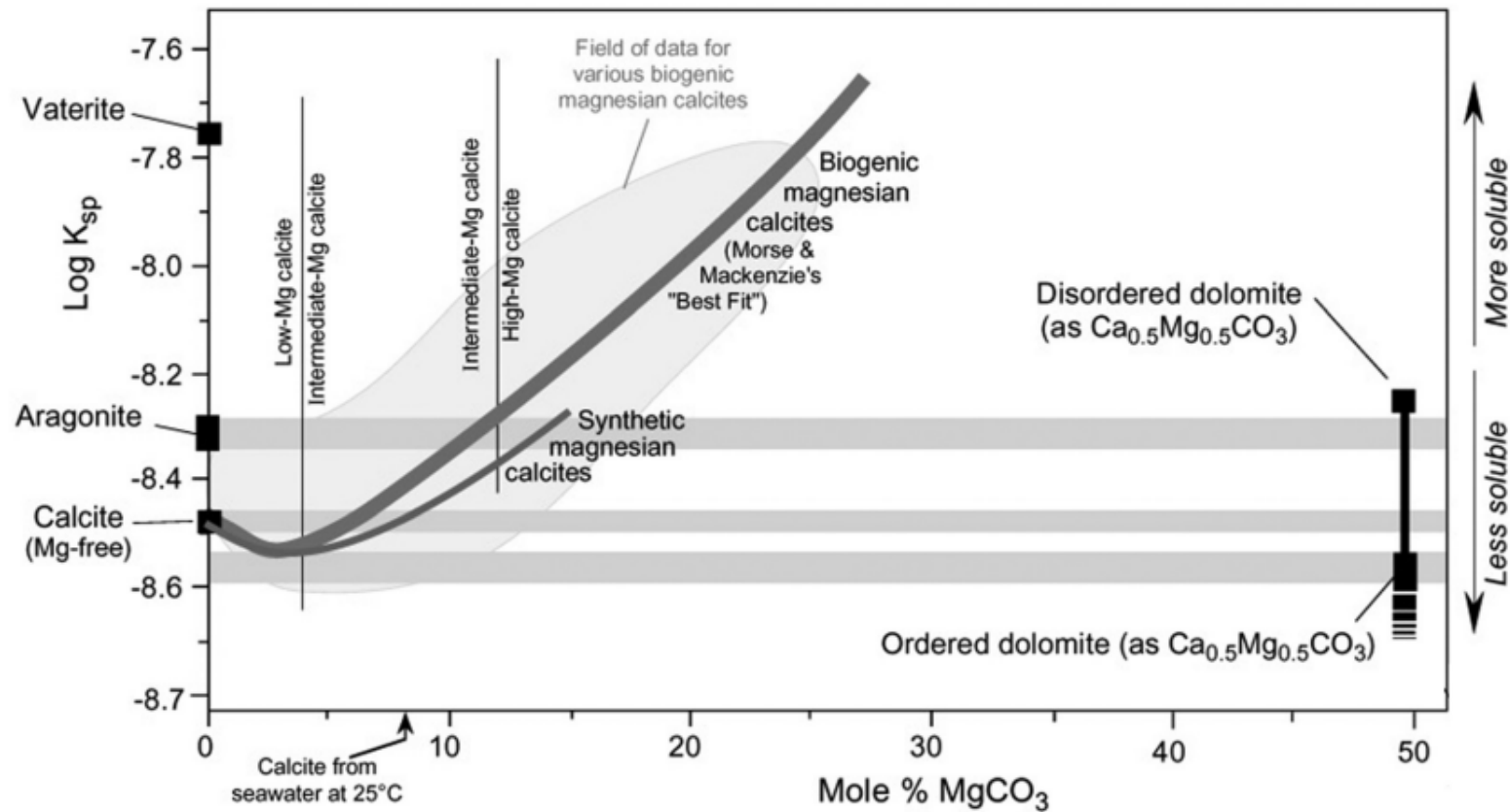
Ca<sup>2+</sup> ions are located at the centers of green octahedra. CO<sub>3</sub> triangles share their O<sup>2-</sup> with the CaO<sub>6</sub> octahedra.

$a = b = 4.9900 \text{ \AA}$   
 $c = 17.0615 \text{ \AA}$   
 $\rho = 2.710 \text{ g/cm}^3$   
 $V = 367.916 \text{ \AA}^3$   
R -3 c (H-M No. 167)

As mentioned in the previous page,  $\text{Mg}^{2+}$  is a cation smaller than  $\text{Ca}^{2+}$  and since both Mg and Ca are divalent cations, the substitution of Mg for Ca in the carbonate minerals does not lead to the generation of vacancies (to maintain electrical neutrality) in the final structure of Mg-doped Ca-carbonates.

This “ease” in substitution of Mg in the Ca (crystallographic) sites depicts itself in the occurrence of a wide range of “magnesian calcites” in nature. The authoritative diagram [1] on the right is useful in realizing the occurrence of Mg-substituted Ca-carbonates. The 50-50 equimolar replacement of Ca by Mg results in the formation of the mineral “[dolomite](#),  $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$ ” which has an aqueous solubility lower than that of calcite.

To learn more about the magnesian-calcite mineral of sea stars (*i.e.*, starfish of the echinoderm family), visit <https://www.cuneyttas.com/Magnesian%20calcite%20globules%20of%20a%20sea%20star.pdf>



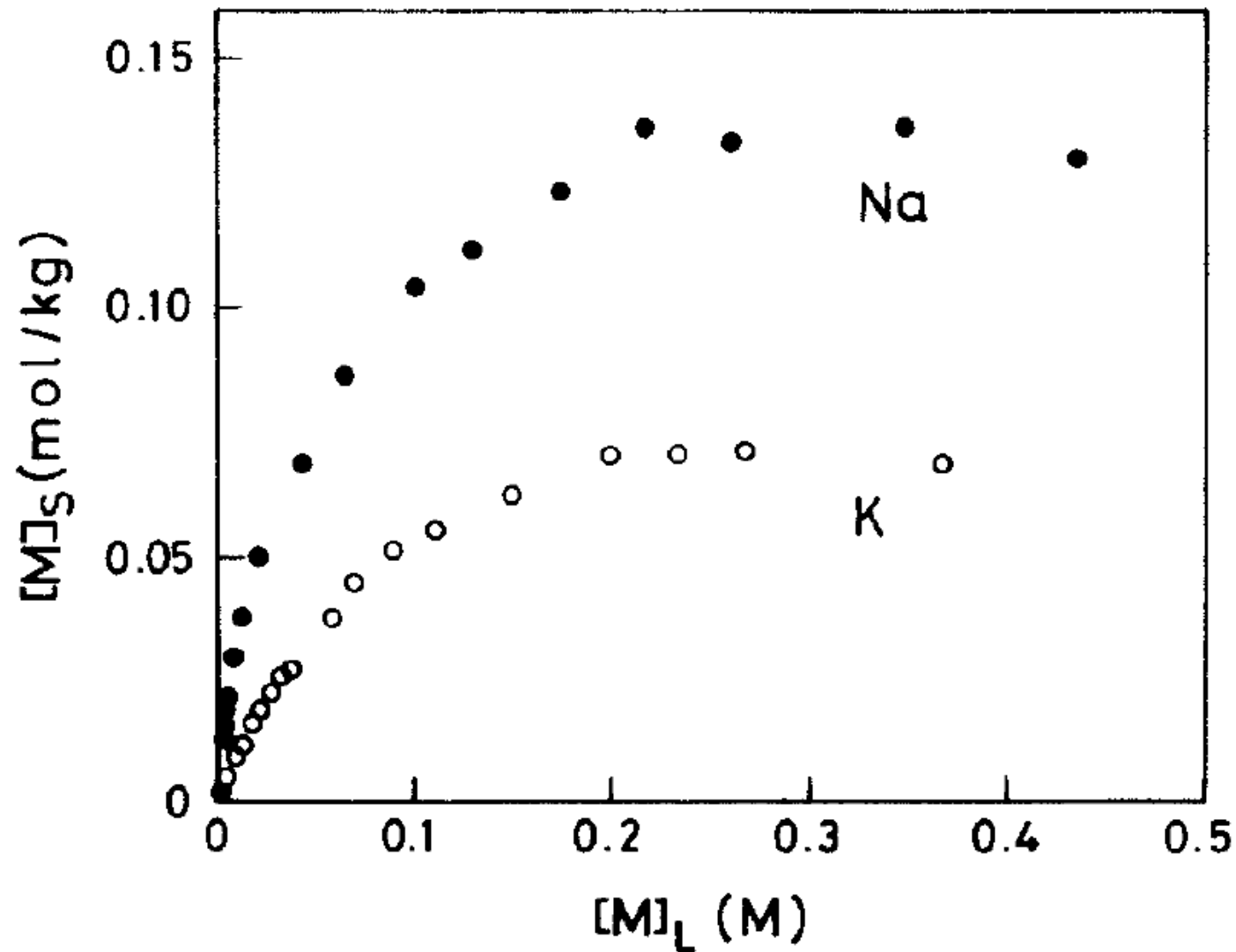
[1] Emeritus Prof. L. Bruce Railsback, Department of Geology, University of Georgia, <https://railsback.org/Fundamentals/820HMC-LMCSolubilities05LS.pdf>

Ishikawa and Ichikuni [2], in a simple yet quite important study, precipitated Na- and/or K-doped calcite as we summarized below.

They first added 0.142 g of  $\text{Ca}(\text{OH})_2$  in 455 to 474 mL of water (at 20°C). This was a clever approach since that 0.142 g was much lower than the solubility limit of  $\text{Ca}(\text{OH})_2$  in water, while studying the presence of water soluble NaCl or KCl over the concentration range of 0 to 0.44 M together with that small amount of  $\text{Ca}(\text{OH})_2$ . They separately prepared aqueous solutions (at 0°C) of saturated  $\text{CO}_2$  as the  $\text{CaCO}_3$  formation agent. At the time of initiating the precipitation (to form  $\text{CaCO}_3$ ), Ishikawa and Ichikuni added 26 to 45 mL (to obtain a total volume of 500 mL) of their saturated  $\text{CO}_2$  solution, followed by sealing the reaction vessel and stirring at 20°C for 40 h and filtering the precipitates out of their mother liquor using a 0.45  $\mu\text{m}$  membrane and washing the solids with distilled water. The obtained precipitates were finally dried at 100°C prior to further chemical analyses (such as EDTA titration for Ca in the solution and atomic absorption spectrophotometry, AAS, for Na and K in the solids). The reaction solutions of the Ishikawa and Ichikuni study [2] covered the pH range of 7.4 to 10.6.

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[2] M. Ishikawa and M. Ichikuni, “Uptake of sodium and potassium by calcite,” *Chemical Geology*, 42, 137-146 ([1984](#)).



This is Fig. 1 of the Ishikawa and Ichikuni study [2]. It supports what we wrote in p. 2 about the role of the ionic radii of Na<sup>+</sup> and K<sup>+</sup>. Incorporation of the smaller Na<sup>+</sup> into the CaCO<sub>3</sub> crystal structure was much easier with respect to K<sup>+</sup> which is larger than Ca<sup>2+</sup>.

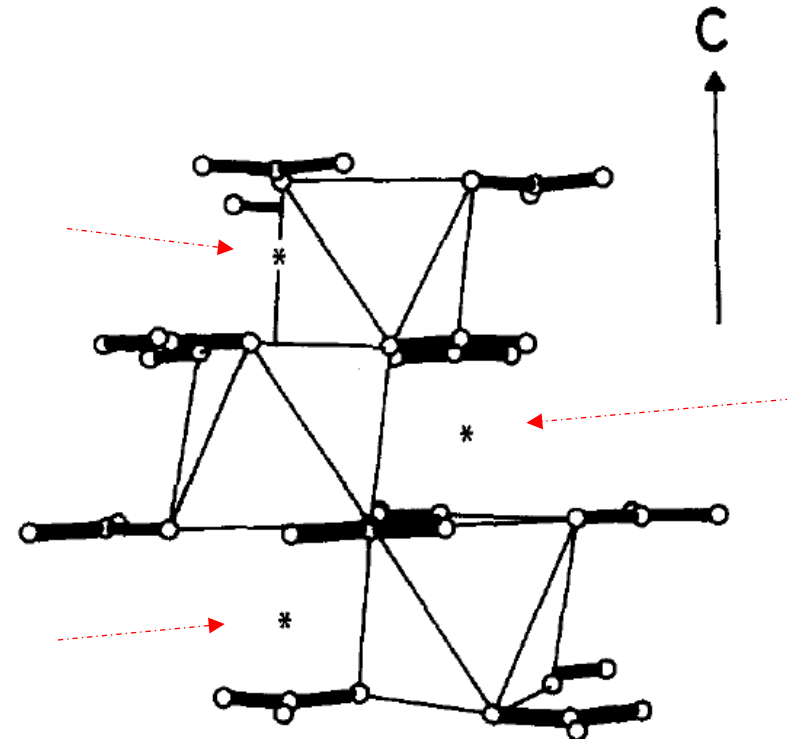
This study was also able to distinguish between the physically adsorbed Na and K on the surfaces of 1 μm size rhombohedral crystals of calcite and the Na and K incorporated into the structure of calcite.

**Fig. 1. Coprecipitated amounts of sodium and potassium plotted against their aqueous concentration (● = sodium; ○ = potassium).**

[2] M. Ishikawa and M. Ichikuni, "Uptake of sodium and potassium by calcite," *Chemical Geology*, 42, 137-146 (1984).

According to Ishikawa and Ichikuni [2], the monovalent  $\text{Na}^+$  and  $\text{K}^+$  did go into the interstitial sites (as shown in their Fig. 4 reproduced here; the stars inside the figure indicate the probable interstitial sites for Na and K) which are located between the  $\text{CO}_3^{2-}$  triangles and the  $\text{CaO}_6$  octahedra of the calcite structure. This leads to one positive excess charge, which needs to be compensated either by the incorporation of foreign anions for each  $\text{Na}^+$  or  $\text{K}^+$  or by the generation of  $\text{Ca}^{2+}$  site vacancies in the  $\text{CaO}_6$  octahedra.

Ishikawa and Ichikuni [2] measured the  $\text{Cl}^-$  concentrations in the solids and their results indicated that there was no  $\text{Cl}^-$  incorporation into the solids; this finding enhanced their claim of Ca vacancies being generated in the  $\text{CaO}_6$  octahedra upon the entry of  $\text{Na}^+$  and  $\text{K}^+$  into the interstitial sites.



*Red arrows are placed by A. C. Tas.*

**Fig. 4. Crystal structure of calcite (half hexagonal unit cell). Solid lines indicate coordinated octahedra around  $\text{Ca}^{2+}$  ions. The symbol \* represents the most probable interstitial sites which can incorporate  $\text{Na}^+$  and  $\text{K}^+$  ions.**

[2] M. Ishikawa and M. Ichikuni, "Uptake of sodium and potassium by calcite," *Chemical Geology*, 42, 137-146 (1984).

The last few decades have seen some industrial attempts, across multiple continents, that use NaCl or NaOH as the chemical agent to accelerate the decomposition of calcitic CaCO<sub>3</sub> either in solid state (NaCl) or in liquid media (NaOH). Some solid-state attempts (especially those performed under non-atmospheric process conditions) even regarded the use of NaCl as a “catalyst.”

The experimental study we highlighted in the previous pages contributed a lot to understanding the role of Na<sup>+</sup> ions in such attempts. Na<sup>+</sup> enters into the interstitial sites of the crystal structure of calcite and this could result in the “significant” effect of “creating Ca<sup>2+</sup> vacancies” in the CaO<sub>6</sub> octahedra (see the crystal structure drawing we provided in p. 2).

Why significant? If one ever wants to decompose calcite (of, for instance, limestone, which is quite an inexpensive Ca source the earth has) for a given process purpose, it is always better to attain a defective, non-stoichiometric calcite sample at one stage of the process. A calcite with Ca-vacancies in its CaO<sub>6</sub> octahedra will be thermodynamically easier to decompose in comparison to a calcite of perfect stoichiometry.

Why would one want to decompose naturally-formed calcite that will result in fresh CO<sub>2</sub> emissions, when and if one does not even have the economically-feasible ability to store that CO<sub>2</sub> for limited sequestration usage (*e.g.*, in successive and artificial CO<sub>2</sub> mineralization processes)? That is another great discussion one can perhaps write a book on it, if needed.

Busenberg and Plummer [3] synthesized  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ -containing  $\text{CaCO}_3$  and studied the chemical composition and physical chemical properties of the recovered precipitates. Their goal in that study was to clarify the conditions of  $\text{CaCO}_3$  formation in marine calcites and aragonites in the presence of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ . Natural or artificial (*a.k.a.*, synthetic) seawater contains significant amounts of these cations and anions [4]. Natural limestones also possess sodium and potassium as low level impurities.

We shall note here that Busenberg and Plummer were scientists of the U.S. Geological Survey at the time and they had published many other articles in the research field of carbonated minerals which were overflowing with extremely accurate and time-defying data/results/conclusions. <https://www.researchgate.net/scientific-contributions/L-Niel-Plummer-2163656689>

Significant amounts of  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , and  $\text{OH}^-$  are incorporated in marine biogenic calcites. Biogenic high Mg-calcites average about 1 mole percent  $\text{SO}_4^{2-}$ . Aragonites and most biogenic low Mg-calcites, on the other hand, contain significant amounts of  $\text{Na}^+$ , but very low concentrations of  $\text{SO}_4^{2-}$  [3].

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[3] E. Busenberg and L. N. Plummer, “Kinetic and thermodynamic factors controlling the distribution of  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  in calcites and selected aragonites,” *Geochimica et Cosmochimica Acta*, 49, 713-725 (1985).

[4] A. C. Tas, “Aragonite coating solutions (ACS) based on artificial seawater,” *Applied Surface Science*, 330, 262-269 (2015).

Table 3. Preparation, composition and solubility data for synthetic calcites

Run No.	CRYSTAL GROWTH <sup>1</sup>						COMPOSITION OF SOLIDS <sup>2</sup>						APPARENT SOLUBILITY			
	Na <sub>2</sub> SO <sub>4</sub> Molality	Ω Calcite	Ω Gypsum	pH	Rate mg·min <sup>-1</sup> ·g <sup>-1</sup>	D <sub>SO<sub>4</sub></sub> <sup>2-</sup> cal. x10 <sup>5</sup>	ppm		Stoichiometry x100				P <sub>CO<sub>2</sub></sub> atm.	Ca mmoles/kgH <sub>2</sub> O	log IAP <sup>3</sup> for the solids	log <sup>4</sup> IAP CaCO <sub>3</sub>
							SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	Ca <sup>2+</sup> (x)	Na <sup>+</sup> 2(1-x)	CO <sub>3</sub> <sup>2-</sup> (y)	SO <sub>4</sub> <sup>2-</sup> (1-y)				
21a	0.0 <sup>5</sup>	10	0.24	7.45	46.0	18.2	36000	3980	99.12	1.76	96.20	3.80	0.965	11.166	-8.266	-8.302
22a	0.0	10	0.0	7.45	—	—	0	710	99.85	0.31	100.00	0.00	0.966	9.19	-8.494	-8.483
23a	0.10	10	0.67	7.51	21.6	8.6	47100	6040	98.66	2.68	95.00	5.00	0.960	11.357	-8.241	-8.290
24a	0.050	10	0.42	7.47	27.0	12.1	41240	4810	98.94	2.13	95.63	4.37	0.961	11.359	-8.242	-8.286
25a	0.025	10	0.24	7.45	45.0	15.2	30350	3730	99.18	1.64	96.80	3.20	0.960	10.514	-8.336	-8.360
26a	0.0125	10	0.13	7.44	56.6	18.8	20640	2860	99.37	1.26	97.83	2.17	0.958	9.870	-8.410	-8.418
27a	0.00625	10	0.070	7.43	62.4	22.0	12680	1880	99.59	0.82	98.67	1.33	0.960	9.240	-8.466	-8.485
28a	0.003	10	0.034	7.42	72.2	17.0	4870	1180	99.74	0.51	99.49	0.51	0.958	9.052	-8.509	-8.500
29a	0.025	2.5	0.25	7.14	3.03	2.5	20710	1750	99.62	0.77	97.83	2.17	0.958	9.803	-8.407	-8.428
30a	0.025	5.0	0.25	7.30	14.1	7.0	28380	2510	99.45	1.10	97.01	2.99	0.961	10.150	-8.366	-8.398
31a	0.025	15	0.25	7.54	68.6	26.4	34330	3520	99.22	1.55	96.38	3.62	0.961	10.779	-8.301	-8.337
32a	0.025	30	0.25	7.70	137.	57.1	35610	4380	99.03	1.93	96.24	3.76	0.961	10.320	-8.351	-8.384
33a	0.00625	2.5	0.072	7.12	10.4	4.5	10770	774	99.83	0.34	98.87	1.13	0.953	9.333	-8.463	-8.471
34a	0.00625	5	0.071	7.27	16.8	10.4	12320	1170	99.74	0.51	98.71	1.29	0.953	9.552	-8.440	-8.446
35a	0.00625	15	0.068	7.52	86.1	37.4	14130	1670	99.63	0.73	98.52	1.48	0.961	9.561	-8.444	-8.450
36a	0.00625	30	0.065	7.68	195.	77.4	14020	3320	99.27	1.45	98.53	1.47	0.953	9.465	-8.468	-8.454
37a	0.003	2.5	0.036	7.12	14.8	5.2	6210	616	99.87	0.27	99.35	0.65	0.953	9.044	-8.500	-8.501
38a	0.0125	2.5	0.14	7.13	6.38	3.3	14960	660	99.86	0.29	98.43	1.57	0.953	9.536	-8.433	-8.451
39a	0.050	2.5	0.44	7.17	1.39	1.3	18670	194	99.96	0.09	98.40	1.96	0.953	9.533	-8.443	-8.456

<sup>1</sup> The molality of NaCl and CaCl<sub>2</sub> were 0.50 and 0.010, respectively. P<sub>CO<sub>2</sub></sub> was 0.0287 atm. Rate is in mg·min<sup>-1</sup>·g<sup>-1</sup> of seed calcite.

<sup>2</sup> The formula is represented as Ca<sub>(x)</sub>Na<sub>(2(1-x))</sub>CO<sub>3(y)</sub>SO<sub>4(1-y)</sub>.

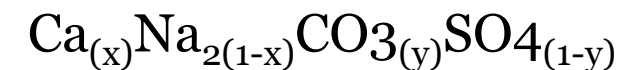
<sup>3</sup> Solubility in CO<sub>2</sub>-H<sub>2</sub>O solutions containing 0.1 mmol/l KH<sub>2</sub>PO<sub>4</sub>. Calculations of the apparent solubility product, log IAP, used the observed P<sub>CO<sub>2</sub></sub> and calcium concentration and is based on the aqueous model of PHREEQE (Parkhurst *et al.*, 1980) modified to include the carbonate solution model of Plummer and Busenberg (1982). The calculations took into account the presence of Na, SO<sub>4</sub>, K and PO<sub>4</sub> in solution. Log IAP = x log a Ca<sup>2+</sup> + 2(1-x)log a Na<sup>+</sup> + y log a CO<sub>3</sub><sup>2-</sup> + (1-y) log a SO<sub>4</sub><sup>2-</sup> where x and y are the stoichiometric coefficients of calcium and carbonate in the solid.

<sup>4</sup> Log activity product of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>.

<sup>5</sup> For Sample 21a, 0.025 molal K<sub>2</sub>SO<sub>4</sub> was used.

Table 3 of the Busenberg and Plummer article [3] is reproduced here. Their synthesis solutions did not contain any Mg<sup>2+</sup> (unlike seawater), but had Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>.

The formula they suggested in the footnote of this table is important:



This implied that the SO<sub>4</sub><sup>2-</sup> ions substitute CO<sub>3</sub><sup>2-</sup> in the crystal structure of CaCO<sub>3</sub>.

radius of CO<sub>3</sub><sup>2-</sup>: 1.78-1.80 Å  
radius of SO<sub>4</sub><sup>2-</sup>: 2.30-2.58 Å

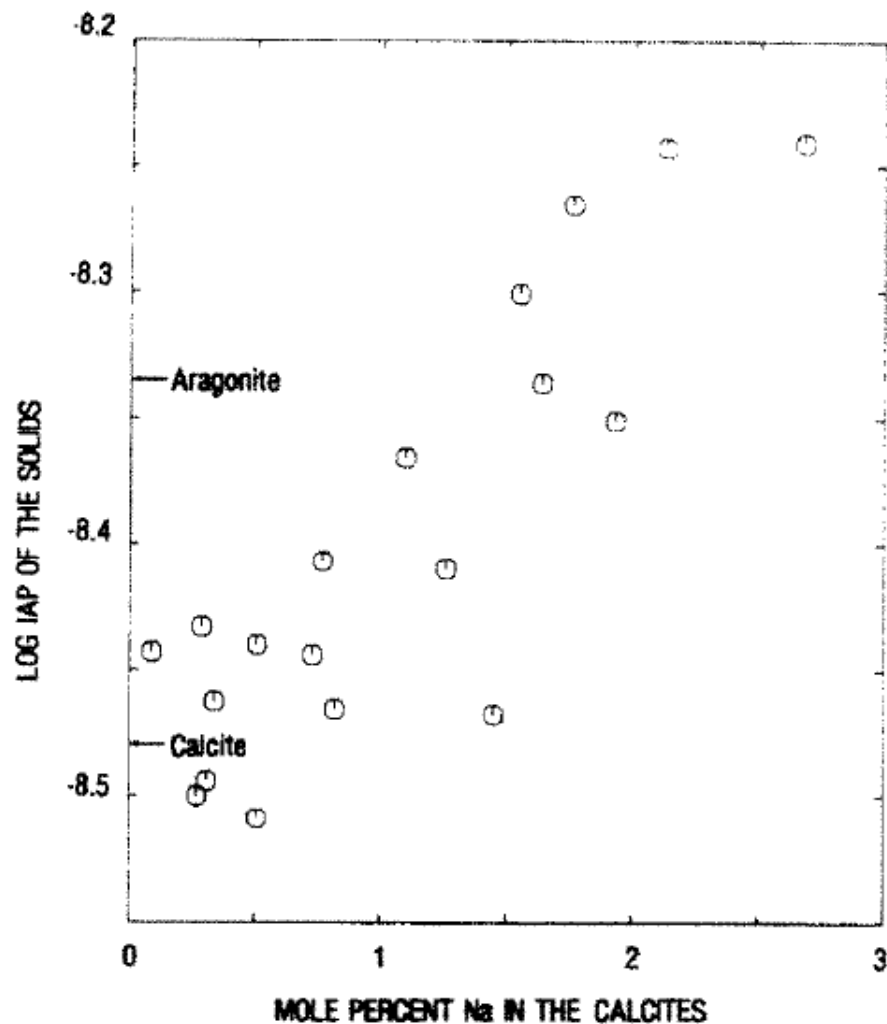


FIG. 11. Log activity product of the solid  $\text{Ca}_{(x)}\text{Na}_{2(1-x)}\text{CO}_{3(y)}\text{SO}_{4(1-y)}$  as a function of mole percent sodium in the solid.

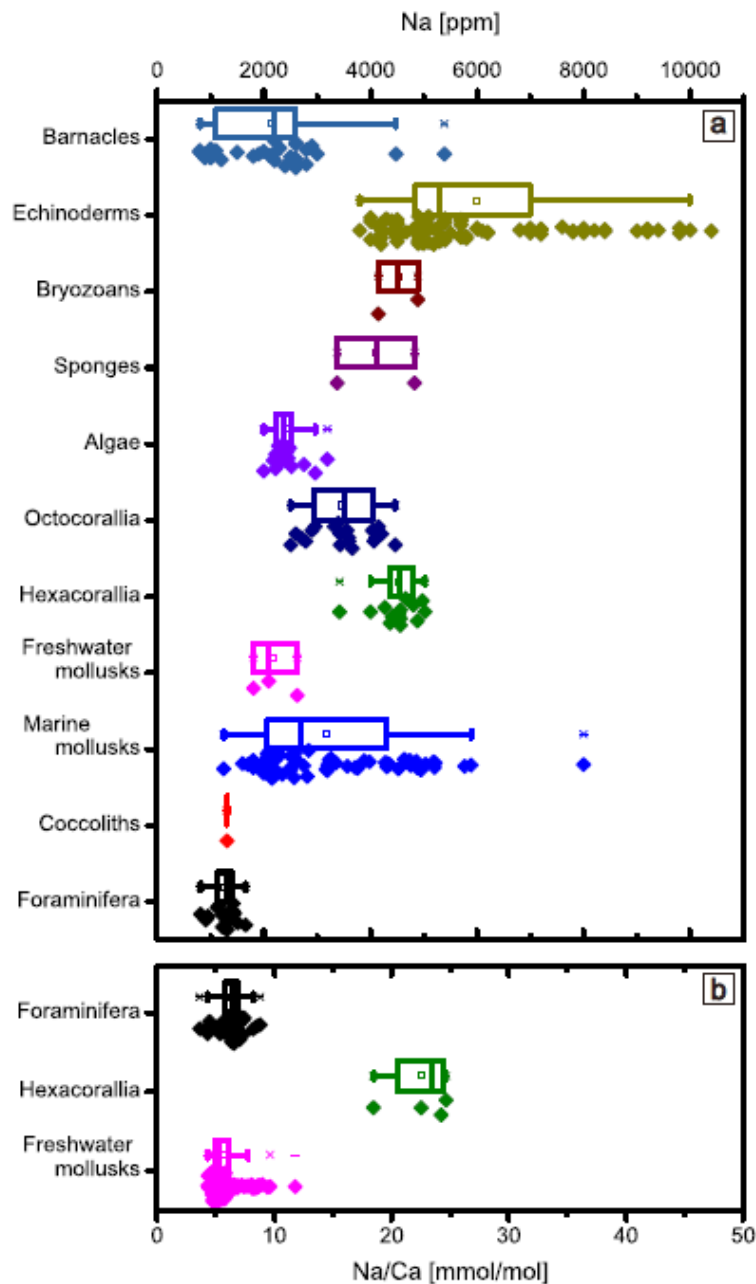
Fig. 11 of the Busenberg and Plummer article [3] is reproduced here and the data points of this plot were from Table 3 of the previous page.

The plotted data tells that the solubility of alkali doped defective calcites can be higher than that of pure and stoichiometric calcite. This is theoretically expected to be so, however, seeing its experimental proof in this study is good.

Busenberg and Plummer [3] stated (upon citing the study of Ishikawa and Ichikuni [2]) that  $\text{Na}^+$  ions occupy the interstitial sites and do not substitute for  $\text{Ca}^{2+}$  in the  $\text{CaO}_6$  octahedra of calcite.

[2] M. Ishikawa and M. Ichikuni, "Uptake of sodium and potassium by calcite," *Chemical Geology*, 42, 137-146 (1984).

[3] E. Busenberg and L. N. Plummer, "Kinetic and thermodynamic factors controlling the distribution of  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  in calcites and selected aragonites," *Geochimica et Cosmochimica Acta*, 49, 713-725 (1985).



This is Fig. 1 of the Yoshimura *et al.* [4] article and the data in this *box-and-whisker* plot were harvested from the previous literature.

The plot shows that the exoskeletons of echinoderms (a family of marine animals including sea stars (*a.k.a.*, starfish)) and marine mollusks (including clams, oysters, snails, octopus, squids, *etc.*) can have quite high concentrations of Na<sup>+</sup> incorporated into their magnesian calcite- or aragonite-based mineralized hard tissues. Octo- and hexa-corallia are also able to uptake Na<sup>+</sup> ions from the seawater.

Yoshimura *et al.* [4] used synchrotron X-ray spectroscopy (XAS), *K*-edge X-ray absorption near-edge structure (XANES), ICP-MS and micro X-ray fluorescence ( $\mu$ -XRF) to determine the structural position of Na<sup>+</sup> ions in biogenic calcium carbonates.

Yoshimura *et al.* [4] discussed, at length, and then concluded that Na<sup>+</sup> seemed to structurally-substitute for Ca<sup>2+</sup> ions (of CaO<sub>6</sub> octahedra) of biogenic calcium carbonates while the charge compensation achieved through the creation of CO<sub>3</sub><sup>2-</sup> vacancies.

One shall always be careful about the time allocated to a nucleation and growth process when comparing several R&D work with one another.

While the time of synthesis in lab-based benchtop nucleation and growth processes is typically limited to hours or at most to days, the time of nucleation and growth processes in biogenic species take place over months, if not years.

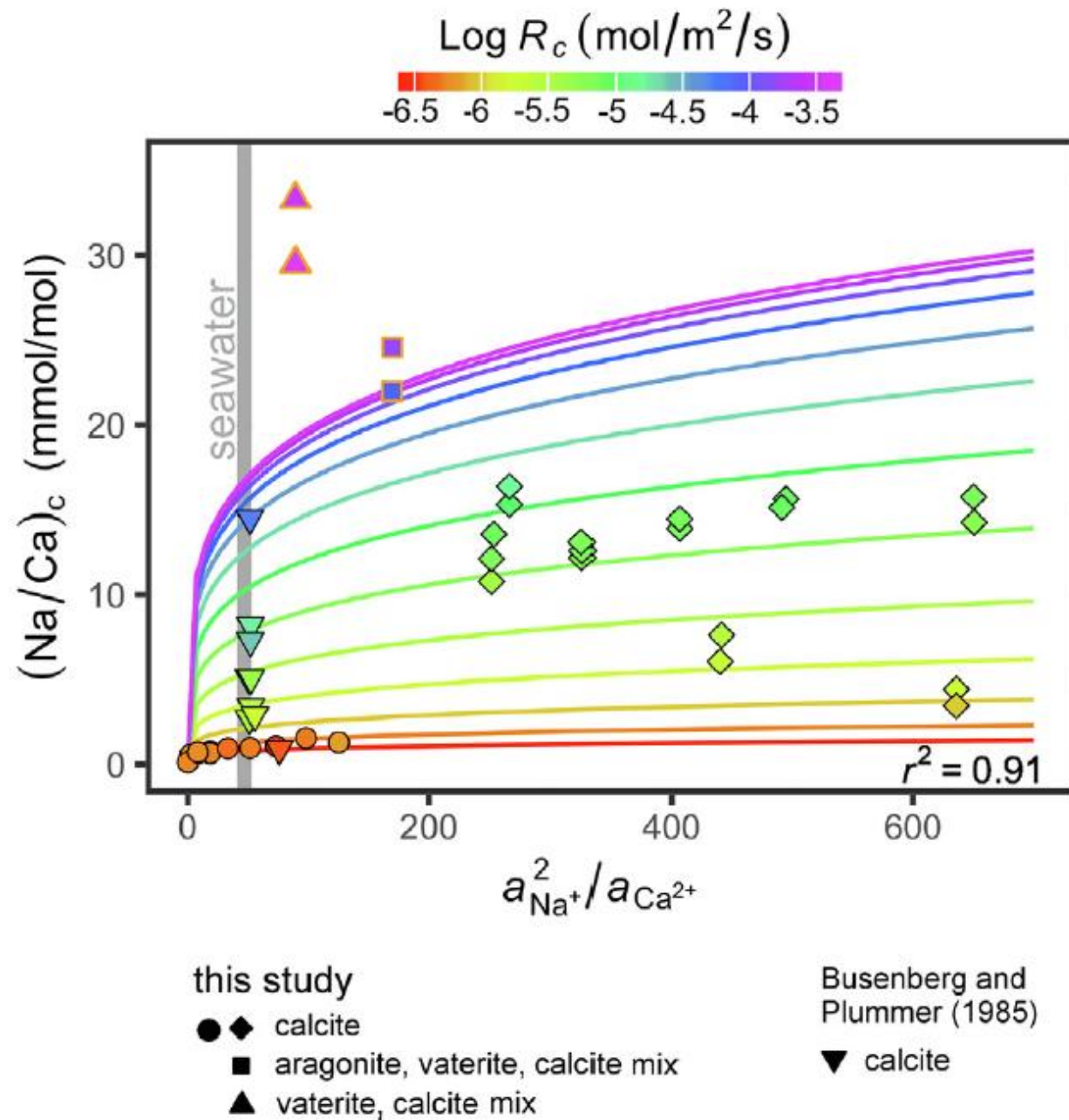
Ishikawa and Ichikuni [2] prepared synthetic Na-doped CaCO<sub>3</sub> over the maximum synthesis time of 40 hours. Yoshimura *et al.* [4], on the other hand, worked on ready-to-analyze tissues of biogenic marine species.

The important question to ask here may be “do Na<sup>+</sup> ions initially go into the interstitial sites of the calcium carbonate structure (with the generation of Ca<sup>2+</sup> vacancies) and then with the passage of maturation time would they start substituting for the Ca<sup>2+</sup> sites (with the end result of creating CO<sub>3</sub><sup>2-</sup> vacancies)?”

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[2] M. Ishikawa and M. Ichikuni, “Uptake of sodium and potassium by calcite,” *Chemical Geology*, 42, 137-146 ([1984](#)).

[4] T. Yoshimura *et al.*, “Altrivalent substitution of sodium for calcium in biogenic calcite and aragonite,” *Geochimica et Cosmochimica Acta*, 202, 21-38 ([2017](#)).



Another article: Devriendt *et al.* [5] conducted inorganic CaCO<sub>3</sub> precipitation experiments to assess the effect of solution composition and crystal growth rate on Na<sup>+</sup> uptake by carbonate crystals. This study was not focused on the determination of which crystal site Na<sup>+</sup> will go through.

Calcite crystals were precipitated at rates varying from 106.5 to 104.5 mol/m<sup>2</sup>/s, while growth rates faster than 104.5 mol/m<sup>2</sup>/s resulted in the coprecipitation of aragonite and vaterite. For a given crystal growth rate, calcite's Na/Ca ratio increased by 0.22% per % increase in solution (Na<sup>+</sup>)<sup>2</sup>/Ca<sup>2+</sup> activity ratio. However, calcite Na/Ca increased up to fivefold per order of magnitude increase in crystal growth rate. The authors characterized the precipitates with XRD, as well.

This is Fig. 6 of the Devriendt *et al.* [5] study, where  $\log R_c$  is the observed crystal growth rate during their CaCO<sub>3</sub> precipitation experiments. The plot shows the dependence of the extent of Na uptake (by CaCO<sub>3</sub>) on the crystal growth rate; at low growth rates (red traces) Na uptake is limited, however, it drastically increases at higher crystal growth rates (purple traces). Busenberg and Plummer [3] also underlined the effect of crystal growth rate on alkali ion uptake in their 1985 article.

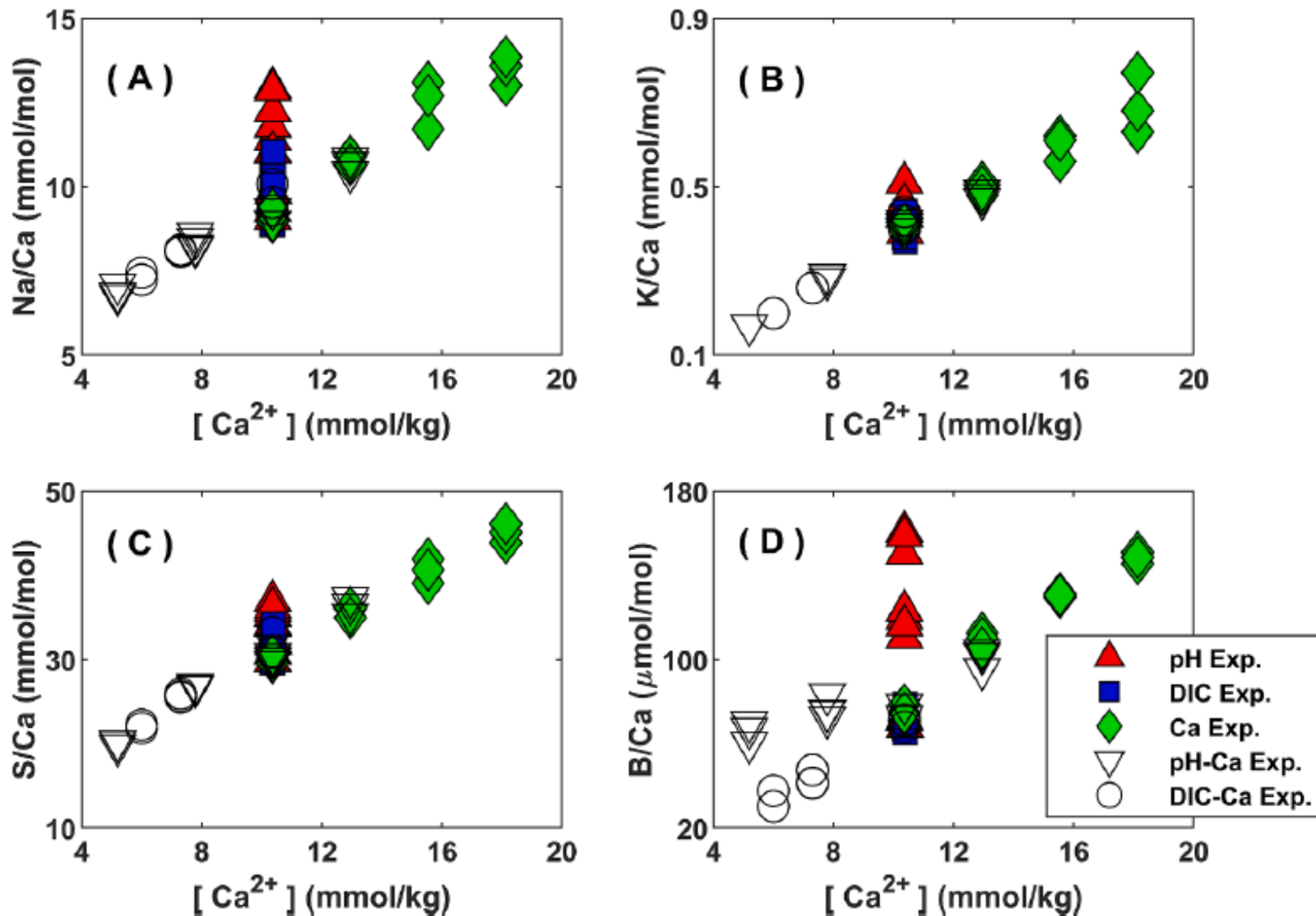


Fig. 3. Composite  $E/Ca$  data from all experimental series plotted as a function of  $[Ca^{2+}]$  of the Mg-free ASW.

This is Fig. 3 of the Uchikawa *et al.* [6] article and it showed that Na, K, S and B were incorporated into calcite during their inorganic precipitation runs.

In the precipitation experiments of Uchikawa *et al.* [6] the source chemicals for B and S were  $H_3BO_3$  (boric acid) and  $Na_2SO_4$ , respectively.

An increase in the  $Ca^{2+}$  concentration of precipitation solutions (*i.e.*, mother liquors) did increase the non-native ion uptake by calcite. That increase in  $Ca^{2+}$  actually means “increasing the crystal growth rate (in accord with references [3] and [5]).”

Stoichiometric, or near stoichiometric, calcium hydroxyapatite (HA:  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) [7] as well as apatitic calcium phosphate (Ap-CaP) [8] are well-known to absorb (*i.e.*, heavy metal (*e.g.*, Pb, Cd, Co, Cu, Zn, *etc.*) sequestration) non-native ions typically from their aqueous surroundings by one or more of the following chemical mechanisms, such as, ion exchange, initial surface adsorption but leading to ionic substitution in the bulk, surface complexation or even electrostatic interactions.

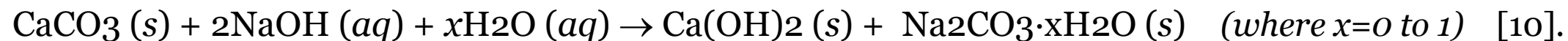
The ability of uptake of non-native ions by  $\text{CaCO}_3$  was not able to reach the popularity of the apatite family until the present note, which reviewed the previous literature. 😊

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[7] A. Garley, S. E. Hoff, N. Saikia, S. Jamadagni, A. Baig, and H. Heinz, “Adsorption and substitution of metal ions on hydroxyapatite as a function of crystal facet and electrolyte pH,” *The Journal of Physical Chemistry C*, 123 (27), 16982-16993 (2019).

[8] A. C. Tas, “How to synthesize apatitic calcium phosphate, Ap-CaP?” February 20, 2026  
<https://www.cuneyttas.com/How-to-synthesize-apatitic-calcium-phosphate-Ap-CaP-or-ACP.pdf>

A single group of researchers [9-13] took the aqueous degradation (eventually decomposition) of  $\text{CaCO}_3$  (s) in solutions containing high concentrations of dissolved NaOH as a route to produce  $\text{Ca(OH)}_2$  (s) and aqueous carbonate ions or crystalline Na-carbonate according to the below simplified, overall reaction:



Upon dissolution of NaOH in water, it immediately turns into  $\text{Na}^+$  (aq) and  $\text{OH}^-$  (aq), therefore, the “initiation” of the above reaction (with  $\text{CaCO}_3$ (s)) follows what was discussed in p. 11 of the current note. That “initiation” starts with the incorporation of  $\text{Na}^+$  into  $\text{CaCO}_3$  which then forms vacancies in the  $\text{CO}_3$  sites, once those vacancies start forming,  $\text{CaCO}_3$  begins losing its chemical stability.

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[9] T. Hanein *et al.*, “Decarbonisation of calcium carbonate at atmospheric pressures and pressures, with simultaneous  $\text{CO}_2$  capture, through production of sodium carbonate,” *Energy & Environmental Science*, 14, 6595-6604 ([2021](#)).

[10] M. Simoni, “Towards more sustainable cement production: A no-combustion approach for the decarbonization of  $\text{CaCO}_3$ ,” [Ph.D. Dissertation](#), The University of Sheffield, United Kingdom, May 13, 2022.

[11] M. Simoni *et al.*, “Decarbonisation of calcium carbonate in sodium hydroxide solutions under ambient conditions: effect of residence time and mixing rates,” *Physical Chemistry Chemical Physics*, 24, 16125–16138 ([2022](#)).

[12] M. Simoni *et al.*, “Effect of impurities on the decarbonization of calcium carbonate using aqueous sodium hydroxide,” *ACS Sustainable Chemistry & Engineering*, 10, 11913-11925 ([2022](#)).

[13] M. Simoni *et al.*, “Synthesis of  $\text{Ca(OH)}_2$  and  $\text{Na}_2\text{CO}_3$  through anion exchange between  $\text{CaCO}_3$  and NaOH: Effect of reaction temperature,” *RSC Advances*, 12, 32070-32081 ([2022](#)).

Some of the aggregates (in both fine and coarse aggregate forms) used in concrete-making/concreting are simply calcitic limestone, sometimes dolomitic limestone.

Na<sup>+</sup> ions, if and when they have a certain significant concentration in concrete, may start reacting with those carbonate aggregates, especially when they are dolomitic limestone. This phenomenon is named and known as “**alkali carbonate reaction,**” **ACR.**

The ACR reaction was first discovered [14, 15] in the late 1950s by Edward G. Swenson of the National Research Council of Canada as the cause of damage (cracking) observed in sidewalks, curbs, floors and foundation walls in Kingston, Ontario.

The ACR reaction is an alkali-dolomite reaction (popularized as “dedolomitization”), which is described by the following equation

$$\text{CaMg}(\text{CO}_3)_2 (s) + 2 \text{M}^+ (aq) + 2\text{OH}^- (aq) \rightarrow \text{Mg}(\text{OH})_2 (s) + \text{CaCO}_3 (s) + \text{CO}_3^{2-} (aq) + 2 \text{M}^+ (aq),$$
where M stands for one or more of the monovalent alkali cations Na<sup>+</sup>, K<sup>+</sup> or Li<sup>+</sup> [16].

While dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) has a density of 2.84 g/cm<sup>3</sup>, the formation of brucite (Mg(OH)<sub>2</sub>) with a density of 2.39 g/cm<sup>3</sup> would also contribute to the mechanical damage to concrete caused by ACR.

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[14] ACR <https://www.fhwa.dot.gov/pavement/concrete/asr/slides/session02.pdf> pp. 54-63

[15] E. G. Swenson, “A reactive aggregate undetected by ASTM test,” *ASTM Bulletin*, 226, 48-51 (1957).

[16] W. Li *et al.*, “Alkali carbonate reaction (ACR): Investigations on mechanism of dedolomitization of dolomite in dolostones,” *Construction and Building Materials*, 351, 128942 ([2022](#)).

## Abridged biography

May '93	Ph.D. in Materials Sci. and Eng., Major: ceramic engineering ( <i>Iowa State University, Iowa, USA</i> )
Jun '93 - Nov '97	Assistant Professor ( <i>METU, Ankara, Turkey</i> )
Nov '97 - Jan '02	Associate Professor ( <i>METU</i> )
Feb '99 - Feb '01	Visiting Professor ( <i>Max-Planck-Institut für Metallforschung, Stuttgart, Germany</i> ) – now defunct
Sep '01 - May'03	Senior Staff Scientist ( <i>Merck Biomaterials GmbH, Darmstadt, Germany</i> ) – now defunct
May '03 - Apr '06	Research Associate Professor ( <i>Clemson University, South Carolina, USA</i> )
May '06 - Nov '06	Professor ( <i>Mersin University, Mersin, Turkey</i> )
Nov '06 - Sep '10	Professor ( <i>Yeditepe University, Istanbul, Turkey</i> )
Aug '07 - Jul '08	Visiting Prof. ( <i>New York University, New York, USA</i> )
Sep '10 - Oct '11	Visiting Prof. ( <i>University of Oklahoma, Oklahoma, USA</i> )
Apr '12 - Jun '15	Research Scholar ( <i>University of Illinois at Urbana-Champaign, Illinois, USA</i> )
Jul '15 - Dec '22	Senior Principal Scientist ( <i>Solidia Technologies, New Jersey, USA</i> ) – now defunct
Jan '23 - Dec '23	Principal Scientist ( <i>Queens Carbon, New Jersey, USA</i> )
Start date: Mar '24	Principal Materials Scientist ( <i>Carbon Limit, Florida, USA</i> )

## Metrics

Peer-reviewed Journal publications:	71
Google Scholar metrics:	>7300 citations    h-index: 43    i <sub>10</sub> -index: 79
Symposium/Conference talks:	129
Book chapters:	34
ICDD X-ray diffraction patterns:	18
Phase diagrams:	2
Patents ( <i>granted</i> ):	31
Graduate (M.Sc. & Ph.D.) theses supervised:	10
Undergraduate theses supervised:	28

Academician: from 5/1993 to 9/2001 and from 6/2003 to 6/2015, total of 20 years

Industrial scientist (*CO<sub>2</sub> mineralization*): since 7/2015, >10 years