

EXAMPLES OF STONE DECAY DUE TO SALT EFFLORESCENCE

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Introduction

Identification and characterization of the nature of the efflorescences that are found on deteriorating building stone is an important preliminary to the diagnosing of the cause of the decay, as well as an aid in devising the strategy of preservative interventions. Previous studies¹⁻⁵ have called attention to a number of sources of salts, both intrinsic and extrinsic, that may be transported by imbibed water to the surface of the building stone. The present work reports several additional examples that are significant in that they demonstrate how rapid and extensive the damage can be from salts whose presence and hazard may be unsuspected by architects and maintenance personnel.

1. Limestone statuary attacked by sodium sulfate

Figure 1 shows two recent, life-size sculptures of finegrained Italian limestone that were mounted indoors in close proximity to potted plants and a water-curtain type of recirculating fountain. During the first ten years after installation of this statuary, there were no signs of any decay. During the tenth year, the surface of the stone was cleaned with solutions of sodium hypochlorite and detergent; shortly thereafter surface blistering began to be noticed, and within a period of about three months the kind of massive decay shown in Figure 2 developed.

Analysis of the stone showed it to be a quite pure calcitic limestone, with only trace amounts (less than 1%) of quartz and clays. The calcite crystals are well-developed and about 10 micrometers in dimensions in some parts of the stone (Fig. 3A), and very imperfectly formed and small, 0,2-1 μm (Fig. 3B), in other parts. The calcite grains are weakly indurated, and the stone is quite porous.

Examination of exfoliation flakes and scrapings of the surface efflorescence disclosed the presence of thenardite, Na_2SO_4 . The presence of crystals of this salt in the pores of the stone flakes is evident in the micrograph of Figure 4. Positive identification was based upon the x-ray diffraction pattern and wet chemical analysis. No other substance was found in the decayed parts.

All the materials employed by the conservator (i.e., the hypochlorite solution, detergent, whiting, silicone water-repellent liquid) were analyzed and no sulfates nor any significant amounts of any other deleterious substance were found. However, analysis of the soil in which the adjacent plants were growing revealed the presence of substantial amounts of sodium sulfate. These plants had been re-potted and the fresh soil was enriched with a commercial plant «food» (containing, among other ingredients, inorganic sulfate) at about the time the sculptures were cleaned.

Thus, it becomes clear that water spray from the recirculating fountain had leached sodium sulfate from the soil, and capillary action drew this salt solution into the stone. The fact that the stone decay is most severe at the base, diminishes with increasing height, and had increased progressively with time, further support this interpretation.



Fig. 1A - Male figure in Italian limestone, with water-curtain at rear and plantings near base.

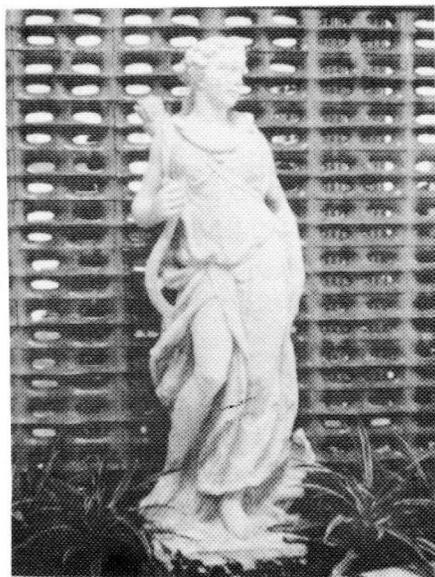


Fig. 1B - Female figure at other side of water-curtain.

This case illustrates how rapidly and severely a susceptible stone can be deteriorated by salt crystallization. Furthermore, it is significant that the salt deposit in this case is anhydrous Na_2SO_4 and not the decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ⁶. For example, at 25°C the solubility of this hydrate is 21.7 g/100 g of solution; whereas the solubility of the anhydrous form, thenardite, is more than 50% greater, viz., 34.0 g/100 g ⁷. When the ambient relative humidity is 70% or less, the crystals of decahydrate decompose to the anhydrous salt ^{8,9}. At temperatures above 32.34°C, the decahydrate is unstable and only thenardite deposits from solution.

Thus, the destructive effect of sodium sulfate crystallization in stone is generally due to the initial formation of mirabilite. When these crystals then decompose to thenardite, there is a volume decrease, which does not contribute additional damage to the stone. Subsequent rehydration to form mirabilite if the humidity becomes great enough cannot result in a larger volume of crystals than were present originally.

The destructive effect of sulfate efflorescences is often attributed to the volume expansion accompanying hydration of the anhydrous salt ¹⁰, but as the above data demonstrate, this is not a necessary condition for sulfate induced stone decay. As we have shown ^{11, 12}, the formation and growth of crystals of *any* solid phase in a zone of relatively dry stone at the surface suffices to produce the observed crumbling, blistering, and exfoliation.

The fact that the crystalline phase which separates from saturated sodium sulfate solutions at temperatures below 32.34°C is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ does not make it any more destructive to stone than any other crystalline deposit *formed in similar quantity*, such as, e.g., anhydrous salts like NaCl. It is the number of crystal seeds that form, and their rate of growth, which determine the magnitude of the disruptive forces that are generated, and not the specific volume of the solid. The nucleation frequency and growth rate depend upon solubility, lattice energy, and the presence of crystallization promoters or inhibitors ¹³ and not upon whether the crystals are hydrates.



Fig. 2A – Detail of the salt decay near base of statue of Figure 1A.



Fig. 2B – Detail of salt decay of statue of Figure 1B.

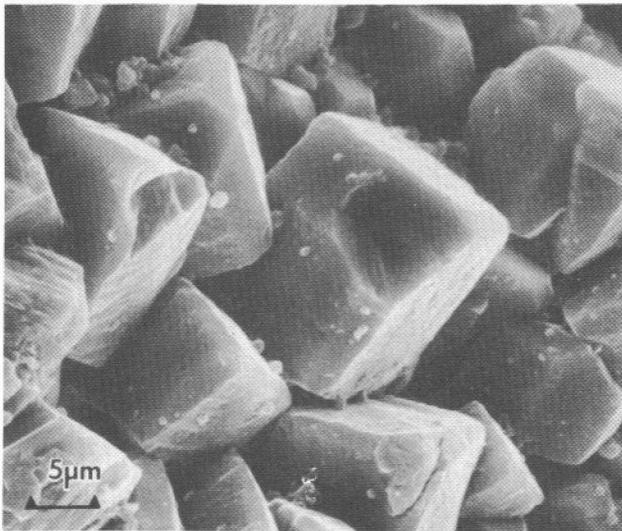


Fig. 3A – Coarse calcite crystals composing parts of the stone of the statuary of Fig. 1A and B.

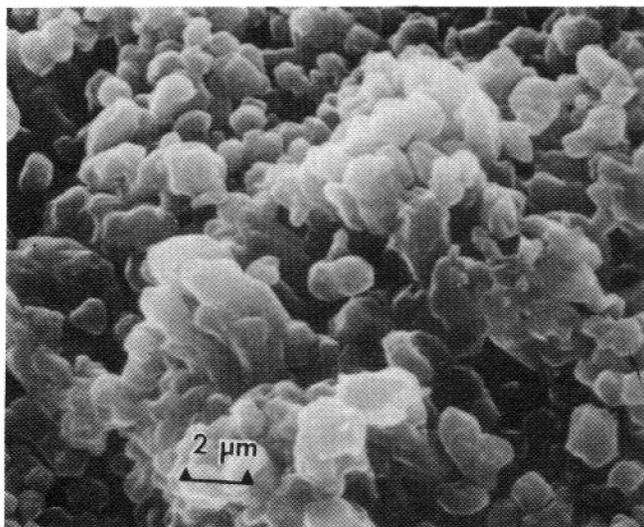


Fig. 3 B. – Finer calcite crystals composing bulk of the stone.

The only circumstances under which sodium sulfate efflorescences would be uniquely more destructive than other types of (e.g., non-hydratable) salt deposits would be when the initial crystallization consists of thenardite, which later hydrates *in situ* to the decahydrate. As shown above, this may indeed occur, but only under a very unusual combination of conditions.

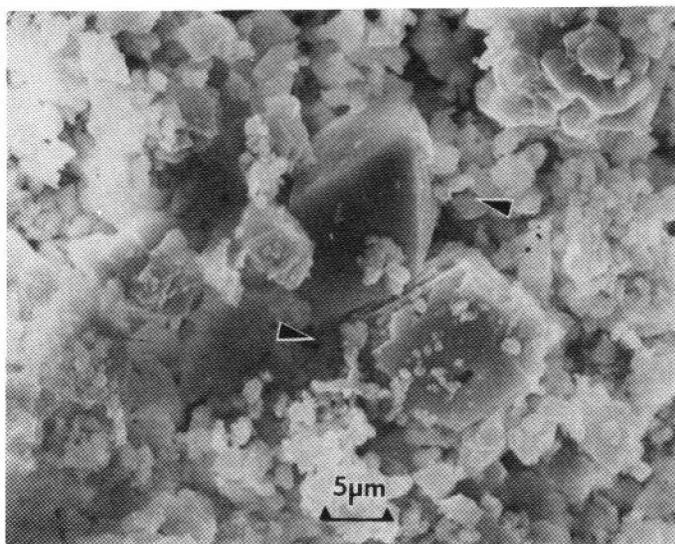


Fig. 4. – Crystals of thenardite (arrow) in pores of limestone statuary damaged by efflorescence.

2. Granite decay due to dicalcium phosphate

Figure 5 shows a view of a granite wall that is being severely damaged by blistering. This wall supports an indoor conservatory for potted plants. The granite is a good grade of dense, crystalline stone, composed of quartz, feldspars, and micas.

The tiled floor of the conservatory showed a deposit of a white substance that appeared to be the residue of water run-off from the flower pots. Since it appeared likely that crystallizable matter from the soil of the plantings was being carried down to the exterior wall and depositing there to produce the damage, analyses were carried out of scrapings from the surfaces of the tiles and of the flakes of the blistered granite. Both types of specimens gave strong positive tests for phosphate ion (molybdc acid procedure); the conservatory floor deposit also showed the presence of soluble sulfate, but the granite flakes gave a negative sulfate test (acidic barium chloride).

X-ray powder diffraction patterns showed the presence of brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and that this was the sole nonindigenous material detectable in the stone flakes or in aqueous extracts from these flakes. (It should be noted that components present to the extent of less than about 1-3% by weight generally do not contribute detectable lines to the x-ray pattern).

Thus, it is clear that the source of the granite decay is dicalcium phosphate that was leached out of the soil in the flower pots housed directly above the victimized stone.

To our knowledge, this is the first instance in which a calcium phosphate has been identified as the source of stone decay. That this is not a rare and isolated occurrence is shown by a second instance we have observed.

A wall was recently constructed indoors in the National Museum of Natural History, Washington, D.C., to serve as a backdrop for a water cascade. Shortly after the construction was completed, the water flow was started, and within one week a disfiguring series of white streaks was formed, emanating from the mortar seams.



Fig. 5A – Conservatory above granite wall at Cooper-Hewitt Museum, N.Y.C.

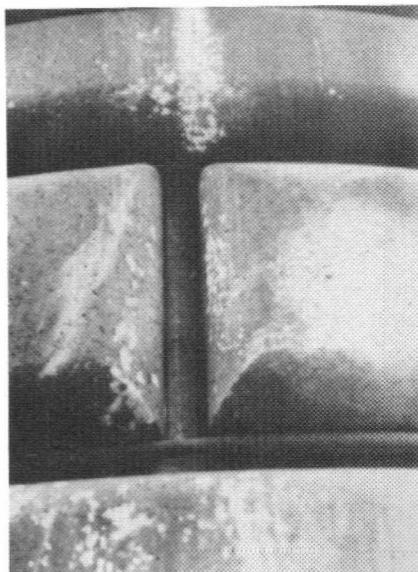


Fig. 5B – Detail of stone decay due to phosphate-containing leachings from flower pots in conservatory.

Table 1
X-Ray Powder Diffraction Data for Gypsum and Brushite

GYPSUM						BRUSHITE					
6-46		21-816 [*]		This Work		9-77		11-293		This Work	
d	I/I _m	d	I/I _m	d	I/I _m	d	I/I _m	d	I/I _m	d	I/I _m
7.56	100	7.61	45	7.63	85	7.57	100	7.62	100	7.54	50
---	---	4.74	4	---	---	4.93	2	---	---	---	---
4.27 ^a	50	4.28 ^a	90	4.29 ^a	70	4.24 ^a	100	4.27 ^a	2	4.26 ^a	80
3.79	20	3.80	8	3.80	14	3.80	8	3.80	3	3.80	1
---	---	---	---	---	---	3.75	1	---	---	---	---
---	---	---	---	---	---	3.63	2	---	---	---	---
3.16	4	3.17	4	---	---	---	---	---	---	---	---
3.06 ^b	55	3.07 ^b	30	3.06 ^b	100	3.05 ^b	75	3.06 ^b	8	3.05 ^b	100
---	---	---	---	---	---	2.93	50	2.93	1	2.93	40
2.87	25	2.87	100	2.86	36	2.86	10	2.86	1	---	---
2.79	6	2.79	20	2.79	7	2.80	2	2.80	1	---	---
2.68	28	2.68	50	2.68	20	2.67	4	2.67	1	---	---
---	---	---	---	---	---	2.65	4	---	---	---	---
---	---	---	---	---	---	2.62	50	2.63	1	2.62	28
2.59	4	2.59	2	2.59	1	2.60	30	---	---	2.60	10
---	---	---	---	---	---	2.55	4	---	---	---	---
2.53	1	---	---	---	---	2.53	2	2.53	6	---	---
---	---	---	---	---	---	2.52	4	---	---	---	---
2.50 ^b	6	2.49 ^b	20	2.49 ^b	14	---	---	2.47 ^b	1	---	---
2.45	4	2.45	6	2.46	1	---	---	---	---	---	---
---	---	---	---	---	---	2.43	14	---	---	---	---
2.40	4	2.41	2	2.40	1	2.42	16	---	---	2.42	4
---	---	---	---	---	---	2.27	4	2.27	1	---	---
---	---	---	---	---	---	2.25	2	---	---	---	---
2.22	6	2.22	6	2.23	7	---	---	---	---	---	---
---	---	---	---	---	---	2.17	20	2.17	1	2.17	4
2.14	2	2.14	2	---	---	2.15	16	2.15	1	2.15	4
---	---	---	---	---	---	2.12	2	---	---	---	---
---	---	---	---	---	---	2.10	6	2.10	1	---	---
2.08	10	2.09	14	2.08	14	2.08	10	2.09	1	2.09	1
2.07	8	2.07	20	2.05	1	---	---	---	---	---	---
---	---	---	---	---	---	2.02	4	2.03	1	---	---
---	---	---	---	---	---	2.00	10	2.01	1	2.00	1
1.99	4	1.99	2	1.99	1	1.98	6	1.98	1	---	---
1.95	2	1.95	6	1.95	1	1.94	2	1.94	1	---	---
1.90 ^b	16	1.90 ^b	4	1.90 ^b	14	---	---	---	---	---	---

* Oriented crystal; by transmission – hence relative intensities differ from the usual diffraction technique included here since efflorescences may consist of oriented crystals.

^a Coincidence with common stone constituents: alpha quartz.

^b Coincidence with common stone constituents: calcite.

This deposit was sampled and analyzed by wet chemistry and by x-ray diffraction. Calcite, calcium silicate hydrate, brushite, and alpha-quartz could be positively identified. The water cascade, having been started before the mortar had adequately cured, leached components from the cement-sand mixture in the mortar, and deposited them on the adjacent stone surfaces.

The presence of brushite in this deposit is unexpected, and may have been present in the cement, or may have arisen from contaminants or additives in the circulating water (e.g., softeners or conditioning agents).

With respect to the detection and identification of brushite in stone conservation problems, it should be noted that brushite and gypsum are very similar crystalline phases¹⁴. Because of the very common occurrence of the latter in weathered calcareous stones, cements, mortars, and plasters, the former can easily be mistaken for it, or masked by it, if the phosphate ion is not specifically tested for.

The HPO_4^{2-} ion is electronically and stereochemically very similar to the SO_4^{2-} ion, and the remaining constituents (Ca^{++} and $2\text{H}_2\text{O}$) are identical in both phases. Consequently, the x-ray diffraction patterns of brushite and gypsum are very similar, as can be seen by comparing the data for the two substances that are summarized in Table I. The ASTM data for standard and synthetic samples¹⁵ are given, together with the corresponding patterns as we find them in our studies of natural efflorescences.

Brushite has moderately intense diffraction lines at 2.93 and 2.62Å, and a weak line at 2.17Å, which are not overlapped by gypsum lines. Consequently, the presence of these lines, in addition to the others which are common to both substances, can be taken as conclusive proof of the presence of brushite. However, the intensities of these lines can be quite variable, and it is likely that they would be too weak to be observed in some cases, particularly in specimens that contain a small amount of brushite, or where it is poorly crystalline. The absence of these lines, therefore, cannot be considered as proof that brushite is absent.

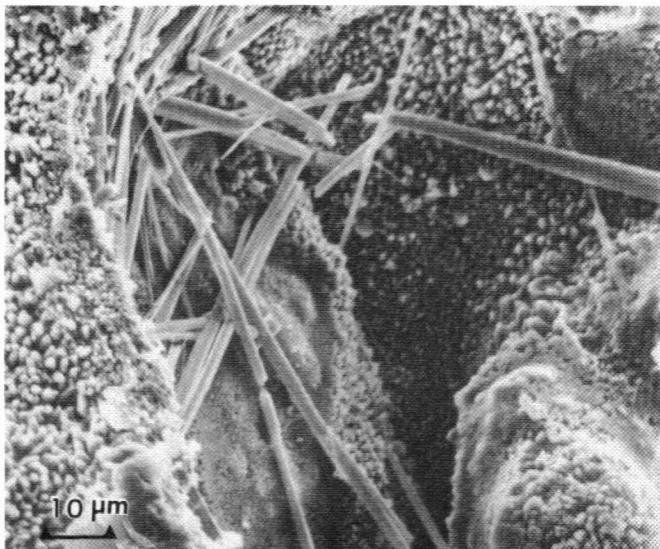


Fig. 6A – Micrograph of brushite efflorescence on granite. The needle-like habit is similar to that commonly noted for gypsum in efflorescences, particularly on siliceous substrates.

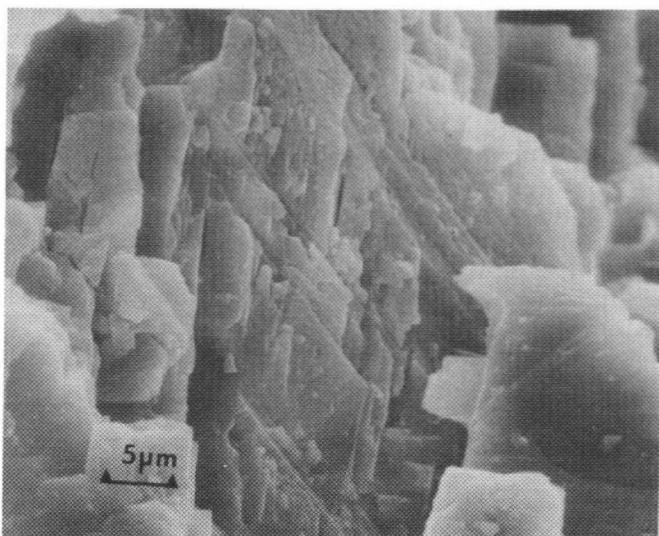


Fig. 6B – A second habit of brushite on granite is similar to the rhombic plates and prisms commonly seen in gypsum deposits on calcitic substrates.

Gypsum has moderately strong lines at 2.87, 2.79, and 2.68 Å, whereas the lines of brushite that overlap these are weak. Hence, lines at these d-values can be taken as showing probable gypsum; but the diffraction pattern alone cannot suffice to establish its presence unambiguously. Only if these data are coupled with chemical analyses or other physical data, such as infrared spectra¹⁶ that show sulfate present and phosphate absent can the presence of brushite be ruled out. It should be noted that the IR spectra are useful in this connection only if there is a substantial amount of specimen, and if the brushite content in it is large. If gypsum is present it tends to interfere with the detection of the brushite characteristic peaks. The phosphomolybdate test, by contrast, is effective even with micro-samples, and there is no interference by sulfate, carbonate, or other common stone constituents.

The microscopic appearance of brushite in efflorescences is also indistinguishable from that of gypsum, as shown in the SEM micrographs of Figure 6.

Wherever phosphate ions in solutions come into contact with a source of calcium ions, brushite is very likely to form¹⁷. Thus, brushite has been reported as arising from the action on limestone of ground water¹⁸, guano leachings¹⁹, and fertilizer run-off²⁰. It is also found as an encrustation on bones and teeth, and on calcareous stones in their vicinity^{21, 22}.

Thus, it is clear that the possible presence of dicalcium phosphate should be considered in stone decay problems, and care must be taken to avoid confusing it for gypsum, and *vice versa*. For this reason, it is recommended that the phosphomolybdate test be employed whenever gypsum is suspected.

3. Granite decay due to cement

Figure 7 shows an example of the deterioration of high quality, black, polished granite in an office building courtyard due, in one section, to the migration into the stone of leachings from bags of

portland cement which had been stored adjacent to the wall while repairs were being made elsewhere. The decay consists in a roughening and discoloration of the stone surface from the base upwards for a distance of about 0.5 meters. At the top of this zone the granite shows a line of white, feathery efflorescences and of exfoliation.

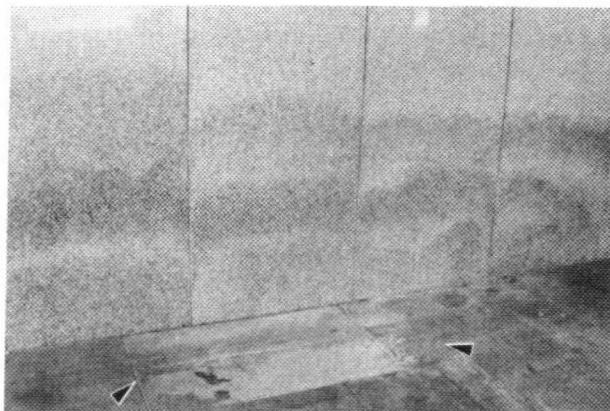


Fig. 7. – View of wall of granite panels disfigured by efflorescences due to cement bags (arrow shows cement residue on floor) and de-icing salts.

X-ray powder diffraction analysis of these efflorescences discloses the presence of trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$), apthitalite ($\text{K}_3\text{Na}(\text{SO}_4)_2$), sylvite (KCl), and halite (NaCl). Figure 8 shows the appearance of some of these scrapings.

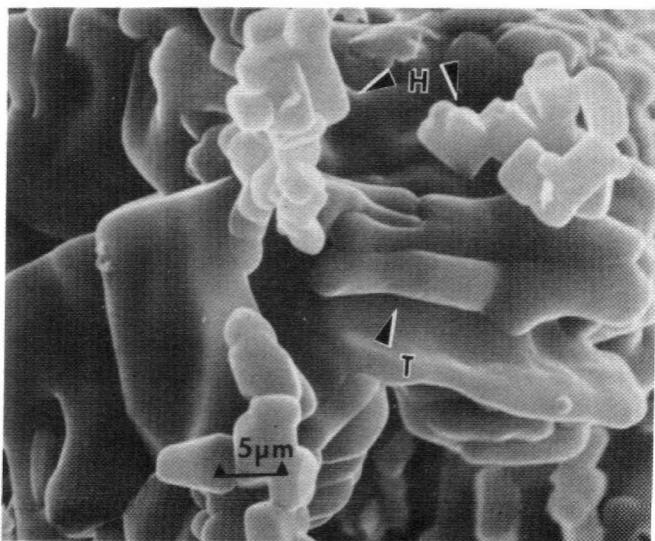


Fig. 8. – Micrograph of the efflorescence on granite wall near where bags of cement had been stored, showing alkali halide (H) and trona (T) crystals.

We have shown previously¹ that trona and aphthitalite efflorescences are characteristically the result of water percolating through cement. Aphthitalite may also come from other sources, but trona does not. The other components of the efflorescences, viz., the alkali halides, have as their origin the salt that was employed to melt snow and ice in the courtyard during winter weather. The efflorescences are found on all the wall panels; the efflorescence containing trona is only found on panels near where the cement bags had been stored.

The relatively high concentration of potassium in the alkali halides present in the efflorescences may reflect the composition of the de-icing compound, or may be the result of ion exchange between the sodium and/or calcium ions migrating through the granite, and the potassium of the feldspars composing the stone^{23, 24}.

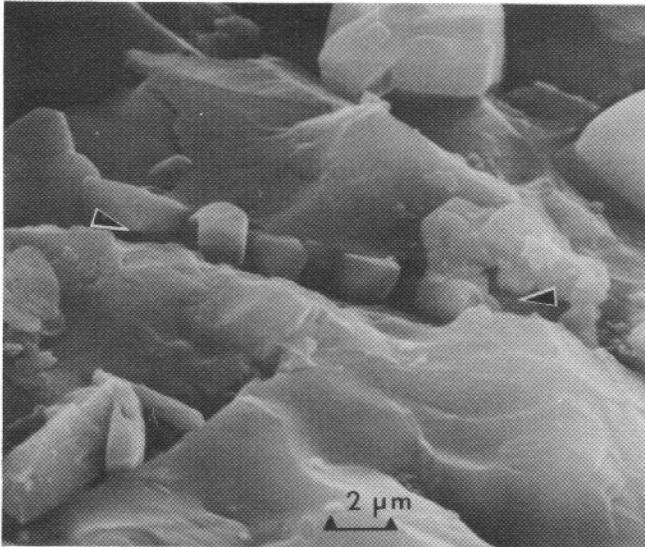


Fig. 9 – Micrograph of underside of a granite exfoliation flake, showing a row of cubic alkali halide crystals (arrow) in a crack in the stone.

This case shows how damaging any source of soluble, crystallizable material can be, even to mechanically strong and chemically stable stones, such as granite. Figure 9 shows a portion of an exfoliation flake of this granite, taken from an area where the alkali halides were the predominant salt in the efflorescence. A row of these cubic crystals is present in a crack; it is in fact the formation and growth of such crystals that creates and enlarges cracks, and produces the eventual decay.

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