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# A laboratory experiment on salt weathering by humidity change: salt damage induced by deliquescence and hydration

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## Abstract

A laboratory experiment on salt weathering was carried out under changing humidity conditions. Three types of rock (tuff and dense and porous sandstone) with sodium chloride, sodium sulfate, or magnesium sulfate were subjected to humidity oscillations from 20%RH to 98%RH during 6 h periods at 20 °C. Prior to the weathering experiment, the rock specimens were oven-dried, and the water supply was restricted to only that from the air during the experiment. Salt on the rock specimens was deliquesced/hydrated at almost 100%RH during the high-humidity period and crystallized/dehydrated during the low-humidity period. Sodium chloride, which has high deliquescence ability, caused the most intensive weathering. Porous sandstone with sodium chloride was completely broken down after 100 cycles of humidity changes. The other two types of rock with sodium chloride showed flaking or swelling on their surfaces. For dense sandstone with sodium chloride, the Equotip rebound value decreased as the humidity cycles increased. Sodium chloride has a high susceptibility of deliquescence at humidities of more than 80%RH. Weathering by sodium chloride would occur extensively on the surfaces of stone heritages and geoheritages in humid coastal spray zones. Magnesium sulfate induced a weight loss in porous sandstone, flaking from the surface of tuff, and cracks on the surface of dense sandstone. Sodium sulfate had almost no effect in the humidity-change experiment, although salt efflorescence was obvious. The results for magnesium sulfate, salt deliquescence, hydration, and crystallization in the humidity-change experiment were easily repeated. Magnesium sulfate might have more influence than sodium sulfate when air humidity fluctuates in a short period.

**Keywords:** Rock breakdown, Weight loss, Equotip hardness value, Longitudinal wave velocity, Sodium chloride, Sodium sulfate, Magnesium sulfate

## Introduction

Salt weathering is one of the major processes of stone decay that causes serious damage to brick walls (Goudie 1977; Kuchitsu et al. 2000), structural foundations (Mottershead 1994; Takahashi et al. 1994), and historical buildings (Gauri 1990; Kamh 2005; Thomachot-Schneider et al. 2011). In natural environments, salt weathering occurs in coastal areas (Matsukura and Matsuoka 1991, 1996; Mottershead 1982), deserts (Cook 1981; Goudie and Cook 1984; Viles and Goudie 2013), and the Antarctic inland (Fahey 1985; Marchant and Head 2007; Miotke 1982; Selby and Wilson 1971). Field observations undertaken globally

in a range of environments have suggested the importance of microclimatic conditions in stone decay, including temperature (Høerlé 2006), insolation (Gunzburger and Merrien-Soukatchoff 2011; McFadden et al. 2005), moisture (Mol 2014), and humidity (Viles 2005).

Many laboratory experiments have simulated salt weathering under the conditions of “cyclic total immersion” or “continuous partial immersion”. In cyclic total immersion experiments, rock specimens are repeatedly subjected to total immersion in a saturated salt solution followed by drying (Goudie et al. 1970; Robinson and Williams 1982; Williams and Robinson 1998). In continuous partial immersion experiments, specimens partly immersed in saturated solutions are subjected to environmental conditions (Goudie 1986; Oguchi and Yuasa 2010; Robinson and Williams 2000). However, these conditions, in which

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abundant salt water is supplied to the rock specimens, are not likely to occur in the field, with the exception of intertidal zones and places with nearby groundwater. In addition, the drying temperature affects the formation of salt crystals (Aly et al. 2015). The disjuncture between field environments and laboratory experiments has often been pointed out (McGreevy and Smith 1982; Smith et al. 2005).

Air humidity is a water source affecting stone heritages. Arnold and Zehnder (1989) pointed out the importance of monitoring air humidity and temperature for their preservation, as these environmental conditions control salt crystallization and hydration. Goudie and Viles (1997) assumed that air humidity is an important factor in salt crystallization from solution, change of phase (hydration/dehydration), and crystallization pressure. Seasonal salt deliquescence and precipitation have been shown to occur on stone heritages in the presence of air humidity changes (Goudie 1977; Matsukura et al. 2004). In dry areas such as Antarctica and Mars, air humidity is also a major source of water, and salt weathering may be induced by cyclic changes in it (Campbell and Claridge 1987; Gough et al. 2016, 2017; Heinz et al. 2016; Wellman and Wilson 1965). The influence of humidity on hydration/dehydration has been thoroughly examined (Benavente et al. 2004; Rodriguez-Navarro and Doehne 1999; Steiger and Asmussen 2008).

Salt deliquescence occurs when the vapor pressure of a saturated salt solution on salt crystals is less than the vapor pressure of water in the air. Fahey (1985) and Goudie (1993) subjected rock specimens to six different climatic conditions. Both studies suggested that rock breakdown is most intensive under high humidity conditions close to 100%RH. These experimental studies suggested that only salt deliquescence and subsequent salt crystallization could cause the breakdown of rock. However, they partly immersed the rock specimens in water or a salt solution. They also subjected the specimens to humidity changes along with temperature fluctuations.

This study entailed a laboratory experiment on salt damage to rock specimens occurring when humidity fluctuates at a constant temperature. The water source was restricted to only that from air humidity.

## Methods/Experimental

### Rock properties

Three types of rock (Oya tuff, Aoshima sandstone, and Ubara sandstone) were used. Oya tuff is dacitic or rhyolitic marine pumice tuff of the Miocene age; it was quarried in Utsunomiya, central Japan. In Japan, a variety of buildings and stone statues are made from Oya tuff, which is often damaged by salt weathering (Oguchi and Yuasa 2010). Aoshima sandstone is a very fine-grained, well-cemented sandstone of the Pliocene age; it was collected in the

Nichinan Coast, Miyazaki Prefecture, southwest Japan. Ubara sandstone is a fine-grained, weakly cemented, porous sandstone of the Miocene age. The sample was collected on the southeast coast of Chiba Prefecture, central Japan. Tafoni and honeycomb weathering features are well developed on type B shore platforms (Takahashi et al. 1994; Tsujimoto 1987) in these coastal areas and are often associated with salt weathering (Bradley, Hutton, and Twidale 1978; Mustoe 1982; Mottershead 1994; Mottershead and Pye 1994; Strini et al. 2008; Young 1987).

Table 1 shows the physical properties of these rocks. Rock surface hardness was evaluated with the rebound value (L-value) of a type D Equotip hardness tester (Proceq). We used the single impact method, which is one of two methodologies for hardness tests with Equotip (Aoki and Matsukura 2007); this method measures the mean L-values of single impacts at ten different points. The longitudinal wave velocity (P-wave velocity) was measured with an ultrasonic tester (Pundit Plus, CNS Farnell).

### Humidity-change weathering experiment

Eight cubic specimens with a side of 5 cm were prepared from the Oya tuff and Aoshima sandstone. Only four cylindrical specimens with a diameter and a height of 3.5 cm were prepared from the Ubara sandstone because of the difficulties in shaping the material into cubes. The initial values of the weight, L-value, and P-wave velocity were measured after oven drying these specimens at 110 °C for 48 h.

Saturated solutions of sodium chloride (NaCl), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), or magnesium sulfate (MgSO<sub>4</sub>) were prepared at 20 °C. The rock specimens were immersed with one of the three salt solutions or distilled water for 72 h. After immersion, the specimens were oven dried again at 110 °C for 48 h to provide them with salt prior to the humidity-change experiment.

Each specimen was placed on a sieve with 2 mm openings and was subjected to a total of 200 cycles of humidity changes in an ambient chamber, in which the humidity was oscillated from 20 to 98%RH every 6 h (Figs. 1 and 2). The temperature of the air in the chamber was kept at 20 ± 2 °C during the experiment. Air temperature and relative humidity in the chamber were recorded every 5 min with a data logger (TR-72wf, T&D) with accuracies of ± 5% for RH and ± 0.5% for temperature. The sensor required 7 min to reach a 90% response. Weight, L-value, and P-wave velocity of the specimens were measured every 20 cycles. For Oya tuff and Aoshima sandstone, four specimens were used for measuring the weight; the other four specimens were used for measuring the L-value and P-wave velocity. The L-value and P-wave velocity were not measured in the Ubara sandstone because the specimens were small. All fragments remaining on the sieve were weighed. In addition, the weights of the specimens

**Table 1** Properties of the rocks used in experiments

	Bulk density, $\rho_{\text{bulk}}$ (g/cm <sup>3</sup> )	True density, $\rho_{\text{true}}$ (g/cm <sup>3</sup> )	Effective porosity $n_e$ (%)	Tensile strength, $S_t$ (MPa)*	Equotip rebound value, $L$	Longitudinal wave velocity, $V_p$ (km/s)
Ubara sandstone	1.56	2.67	41.8	1.67	392	0.84
Oya tuff	1.39	2.39	42.3	1.37	452	2.30
Aoshima sandstone	2.40	2.66	5.3	5.75	593	3.32

\*The tensile strengths were taken from Tsujimoto (1987) for Ubara sandstone and Yamada et al. (2005) for Oya tuff and Aoshima sandstone, respectively

were measured every hour only for the first humidity-change cycle in order to estimate the amount of water that absorbed from the air on the specimens in the high-humidity period.

### Continuous wetting/drying weathering experiment

Another weathering experiment involving repeated wetting/drying with a salt solution was carried out in order to compare its results with those of the humidity-change experiment. Eight cubic specimens each of Oya tuff and Aoshima sandstone were prepared in the same way as in the humidity-change experiment. Four cubes were used for measuring the weight; the other four cubes were used for measuring the L-value and P-wave velocity. After measuring

the initial weight or initial L-value and P-wave velocity, the specimens were subjected to a total of 20 cycles of wetting and drying, each of which was composed of the following treatment steps: the specimens were (1) immersed in one of the three salt solutions or distilled water for 24 h at 20 °C, (2) oven dried at 110 °C for 48 h, and (3) immersed in distilled water for 24 h to remove the salt that had crystallized in the specimens. After cooling, they were (4) oven dried again at 110 °C for 48 h and (5) weighed or their L-value and P-wave velocity measured. As in the humidity-change experiment, all fragments remaining on the sieve were weighed.

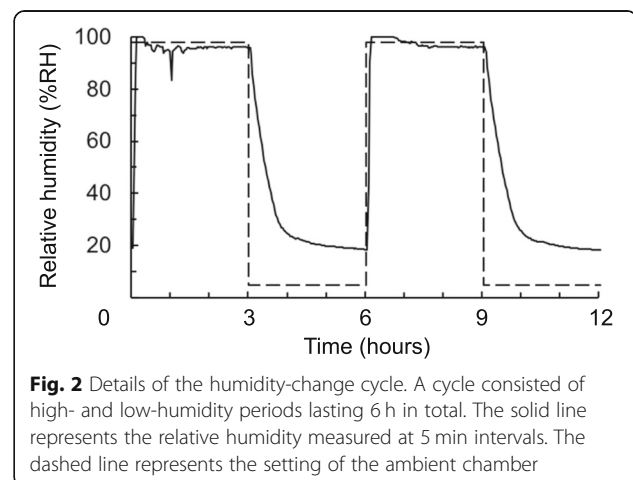
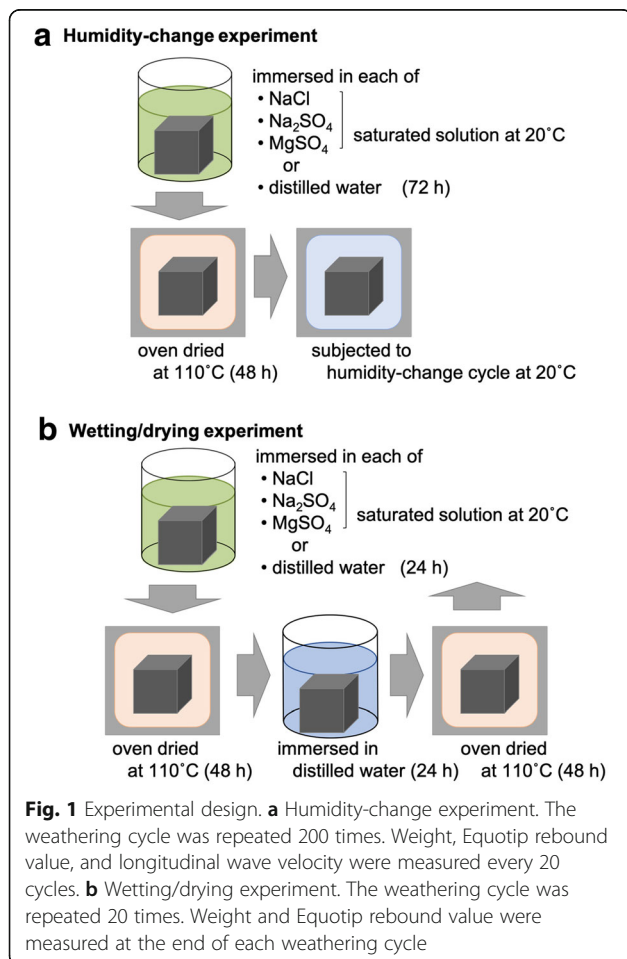
## Results and discussion

### Amount of salt in the humidity-change experiment

Table 2 shows the amount of salt contained in the rock specimens for each combination of rock and salt. The porous Oya tuff and Ubara sandstone contained more salt than the Aoshima sandstone did. The amounts of Na<sub>2</sub>SO<sub>4</sub> were smaller than those of the other two salts, which reflected the lower solubility of Na<sub>2</sub>SO<sub>4</sub> (19.0 wt%) than that of NaCl (26.4 wt%) and of MgSO<sub>4</sub> (25.2 wt%) at 20 °C.

### Salt pathway in the humidity-change cycle

The weights of the rock specimens increased in the high-humidity period and decreased in the low-humidity period. Figure 3 shows that there were significant increases



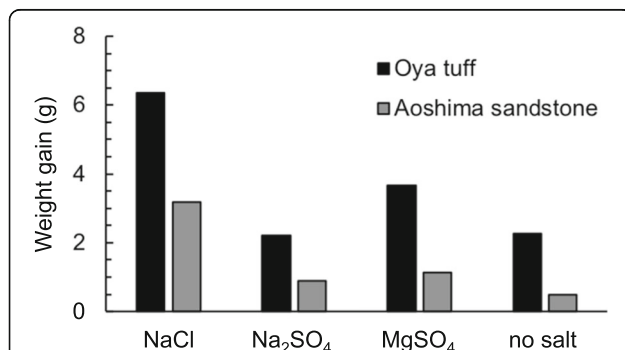
**Table 2** Salt content of rock specimens used in the humidity-change experiment

	Sodium chloride	Sodium sulfate	Magnesium sulfate
Ubara sandstone	5.3	2.9	6.1
Oya tuff	7.7	4.2	8.6
Aoshima sandstone	0.5	0.2	1.0

The values represent gram weights of salt in a 100 g salt-free rock specimen

in the weights of the specimens with NaCl during the high-humidity period. The specimens with  $MgSO_4$  also showed larger increases than the specimens with  $Na_2SO_4$  or no salt. The weight increases of the specimens with  $Na_2SO_4$  were comparable to the values of the specimens with no salt. The weight oscillation means that the rock specimens absorbed water from the air in the high-humidity period, and they dried out in the low-humidity period. At the beginning of the high-humidity period, all three salts appeared to form a solution by dissolving into the water absorbed from the air, indicating that salt deliquescence occurred. The practical deliquescence relative humidity (DRH) at 20 °C is 75.6%RH for NaCl (halite), 83.3–95.1%RH for  $Na_2SO_4$  (mirabilite), and 92.7%RH for  $MgSO_4$  (epsomite) (Apelblat and Korin 1998, 2002; Apelblat and Manzurola 2003). The relative humidity in the ambient chamber rapidly increased and reached almost 100%RH within a few minutes. The high salt content of the rock specimen and low DRH of the NaCl were the causes of the largest weight gain in the high-humidity period.

Hydration also occurred in the high-humidity period. Flatt (2002) and Steiger and Asmussen (2008) described the phase change of  $Na_2SO_4$ . Under the experimental conditions (20 °C),  $Na_2SO_4$  exists in two stable phases:



**Fig. 3** Weight gains in the first high-humidity period. The value represents the amount of water absorbed into specimens during the high-humidity conditions. The specimens with NaCl showed the largest absorption. The specimens with  $MgSO_4$  showed greater gains in weight than the specimens with  $Na_2SO_4$  or without salt (distilled water)

anhydrate (thenardite) and decahydrate (mirabilite). At the beginning of the experiment, thenardite should crystallize on the rock surface because it directly crystallizes from a saturated solution above 32.4 °C. At the beginning of the high-humidity period, salt deliquescence should cause a saturated solution to form. Because the saturated solution is supersaturated to mirabilite, mirabilite crystallizes from a salt solution (Flatt 2002). In fact, mirabilite crystallized in our experiment 30 min after the first high-humidity period started. In the low-humidity period, mirabilite should crystallize from the solution at 95.6%RH and dehydrate to thenardite below 76.4%RH (Steiger and Asmussen 2008). The crystallization of thenardite is dominant below the equilibrium humidity of 86.6%RH, although both mirabilite and thenardite crystallize directly from solution (Steiger and Asmussen 2008).

The sequence of deliquescence and hydration of thenardite should occur at the beginning of every high-humidity period. However, the deliquescence and phase changes of  $Na_2SO_4$  were most distinct in the first high-humidity period. These changes became unclear as the number of humidity cycles increased, and the rock surface became covered with the efflorescence of  $Na_2SO_4$ . Kwaad (1970) suggested that the hydration rate of  $Na_2SO_4$  is much slower than that of  $MgSO_4$ . Dehydration of mirabilite might hardly have occurred under our experimental conditions, in which the air humidity oscillated over a short interval. Deliquescence of  $Na_2SO_4$  might have been hindered by the high DRH of mirabilite (95.6% at 20 °C), and efflorescence of  $Na_2SO_4$  remained on the rock surface.

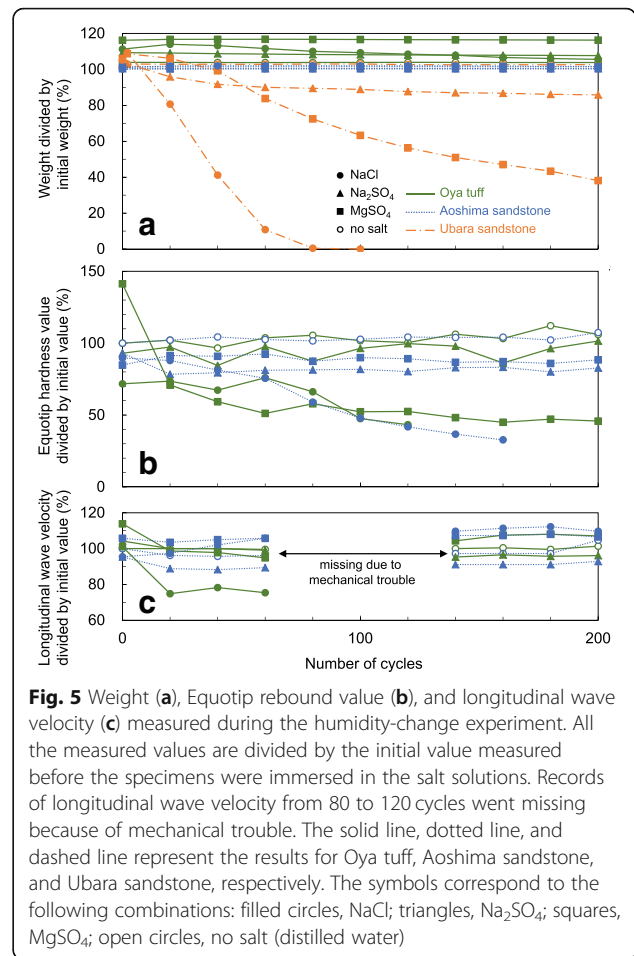
$MgSO_4$  has three stable hydrated forms: monohydrate (kieserite), hexahydrate, and heptahydrate (epsomite) (Chou and Seal 2003; Vaniman et al. 2004). The hexahydrate is metastable. Though a large number of metastable forms of  $MgSO_4$  have been identified besides hexahydrate, the behavior of these metastable forms is still unclear (Chipera and Vaniman 2007). At the beginning of the experiment, kieserite should have crystallized on the rock surface. Steiger et al. (2008) suggested that hydration of kieserite and formation of hexahydrate occur rapidly when the relative humidity exceeds the DRH of kieserite (60%RH at 25 °C), although the reaction proceeds above the equilibrium humidity of kieserite and hexahydrate (42%RH at 25 °C). The rapid reaction occurs as a two-step process of deliquescence and subsequent crystallization. They also reported that epsomite did not form above the equilibrium humidity of hexahydrate and epsomite (51%RH at 25 °C). However, they did not confirm which hydrated crystals form at relative humidities above the DRH of hexahydrate (81%RH at 25 °C). Epsomite would form when the relative humidity exceeds the DRH of hexahydrate. Although we could not distinguish the hydration pathways in our experiment, deliquescence of kieserite and direct crystallization

of epsomite would have occurred within a few minutes of exposure to humidity reaching almost 100%RH in the ambient chamber. The epsomite and hexahydrate would have crystallized in the low-humidity period. The kieserite might have occasionally crystallized under the humidity conditions of our experiment (Balboni et al. 2011). Dehydration of epsomite and formation of hexahydrate would also have occurred, whereas the kieserite formation might have been limited by the low equilibrium humidity of hexahydrate and kieserite.

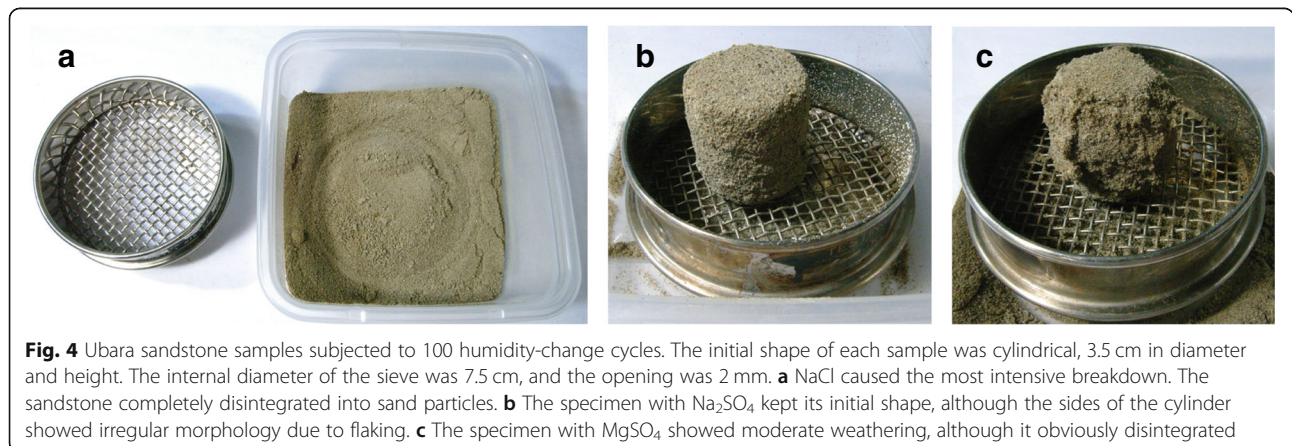
**Weight and L-value changes in the humidity-change experiment**

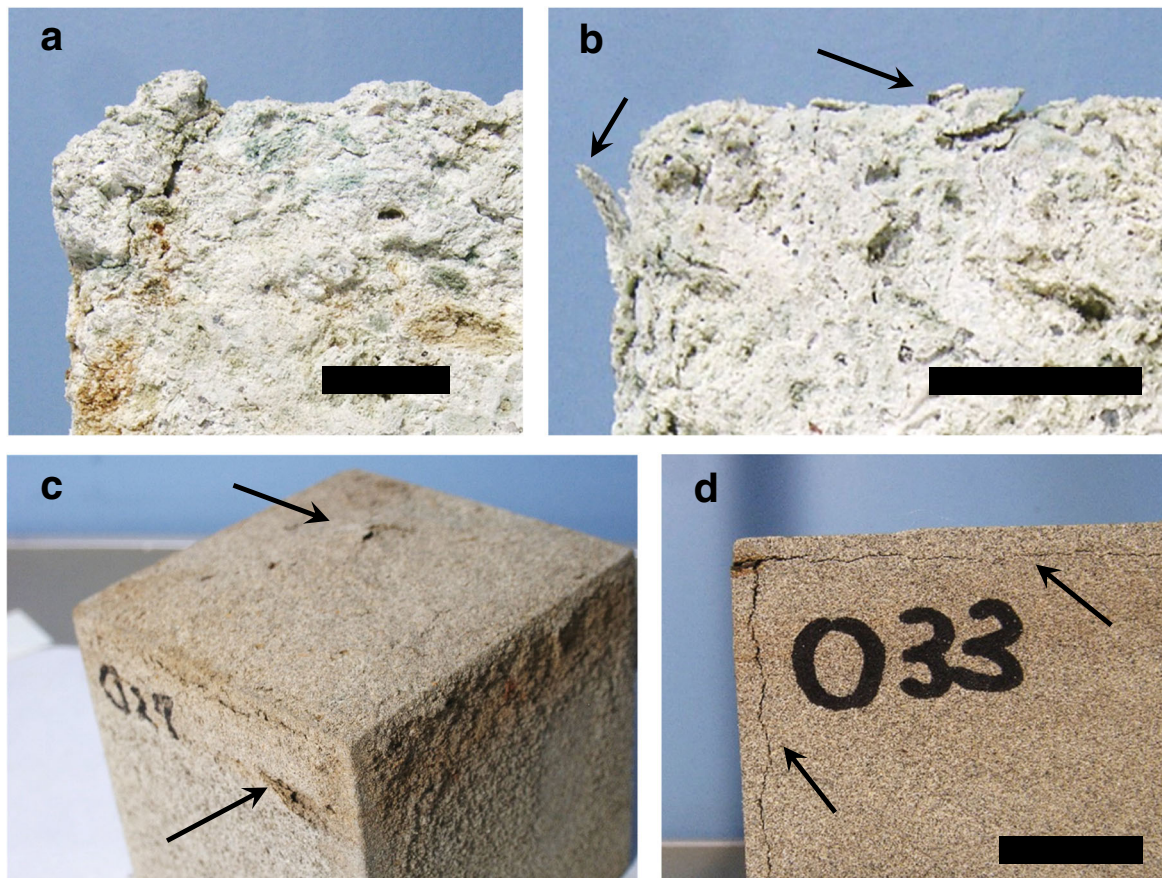
Among the three kinds of salt, NaCl caused the most damage to all types of rock in the humidity-change experiment. Ubara sandstone with NaCl was completely broken down after 100 cycles (Figs. 4a and 5a). The cycle 0 data in Fig. 5 refers to the ratio of the weight immediately before the first cycle to the initial salt-free weight; the specimens became heavier from salt precipitation. Oya tuff and Aoshima sandstone did not show any obvious weight losses (Fig. 5a), although a few granular fragments were deposited under the sieve in the cases of the specimens with salt. The samples of Oya tuff with NaCl showed flaking on their surfaces (Figs. 6a), while Aoshima sandstone with NaCl showed swelling on the surface (Fig. 6c). The L-values of the Oya tuff and Aoshima sandstone specimens with NaCl decreased as the number of cycles increased (Fig. 5b). The L-value of these specimens could not be measured after their surfaces became rough. The final L-value was 43.3% of the initial hardness after 120 cycles for Oya tuff and 32.7% after 160 cycles for Aoshima sandstone.

MgSO<sub>4</sub> caused the second most amount of damage to the specimens. The weight of Ubara sandstone with MgSO<sub>4</sub> decreased to 38.1% of the initial weight after 200 cycles. The samples of Oya tuff with MgSO<sub>4</sub> showed flaking on their surfaces (Fig. 6b) and a reduction in their L-value,



although the decrease over the first 20 cycles (from 140.3 to 70.9%) was greater than the change in the subsequent 180 cycles (from 70.9% to 45.8%). The decrease in the first 20 cycles was likely induced by salt deliquescence and hydration. The hydration of kieserite and crystallization of the hydrated crystals led to minor rock breakdown and minor changes to the surface micromorphology. These





**Fig. 6** Oya tuff and Aoshima sandstone with NaCl or MgSO<sub>4</sub> subjected to 200 humidity-change cycles. The scale bars are 1 cm long. Oya tuff with NaCl (a) and MgSO<sub>4</sub> (b) showed irregular morphology on their surface. Millimeter-scale fragments flaked from the surface of the Oya tuff with MgSO<sub>4</sub>. Aoshima sandstone with NaCl (c) showed swelling on the surface. Cracks parallel to the rock surface were observed on the edge of the Aoshima sandstone with MgSO<sub>4</sub> (d)

changes caused the L-value to decrease. Aoshima sandstone with MgSO<sub>4</sub> had cracks parallel to the rock surface (Fig. 6d). Cracks occurred on the six faces of the cube.

Na<sub>2</sub>SO<sub>4</sub> was relatively inactive as a weathering agent in the humidity-change experiment, with the exception of the weight loss of Ubara sandstone (14.2%) after 200 cycles. The L-value of the Oya tuff with Na<sub>2</sub>SO<sub>4</sub> fluctuated within a range from 84.5 to 101.5%. The L-value of Aoshima sandstone showed indistinct changes, except in the first 20 cycles. The L-value for Aoshima sandstone with Na<sub>2</sub>SO<sub>4</sub> had a similar trend to that with MgSO<sub>4</sub>. Tabular fragments flaked from the surface of the Oya tuff with Na<sub>2</sub>SO<sub>4</sub> when the specimen was immersed in distilled water after the weathering experiment.

The P-wave velocities of all the specimens were constant or increased slightly during the experiment (Fig. 5c). Only Oya tuff with NaCl recorded a significant decrease from the start to the first 20 cycles.

None of the rock specimens showed any obvious cracks, flaking, or swelling at the beginning of the humidity-change experiment. Therefore, we concluded

that the damage caused by the initial immersion in a salt solution and oven drying was relatively weak in comparison with the damage induced by the subsequent humidity changes. The results of the wetting/drying experiment described later supported this conclusion.

The degree of damage induced by each salt was in proportion to the weight gain during the high-humidity period. The lower DRH of NaCl resulted in greater water absorption from the air, and the greater absorption, in turn, induced greater weight losses and L-value reductions. The degree of damage would also have been affected by the fact that NaCl does not hydrate substantially. The hydration of two sulfates involves volume expansion of salt crystals. The hydrated crystals might have filled pores in the rock and hindered infiltration of water (Steiger and Asmussen 2008). The specimens with NaCl could absorb greater amounts of water because NaCl only dissolved and made a solution with deliquescence.

The specimens with Na<sub>2</sub>SO<sub>4</sub> were less damaged than the specimens with MgSO<sub>4</sub>, despite that the DRH of Na<sub>2</sub>SO<sub>4</sub> was lower than or comparable to the DRH of

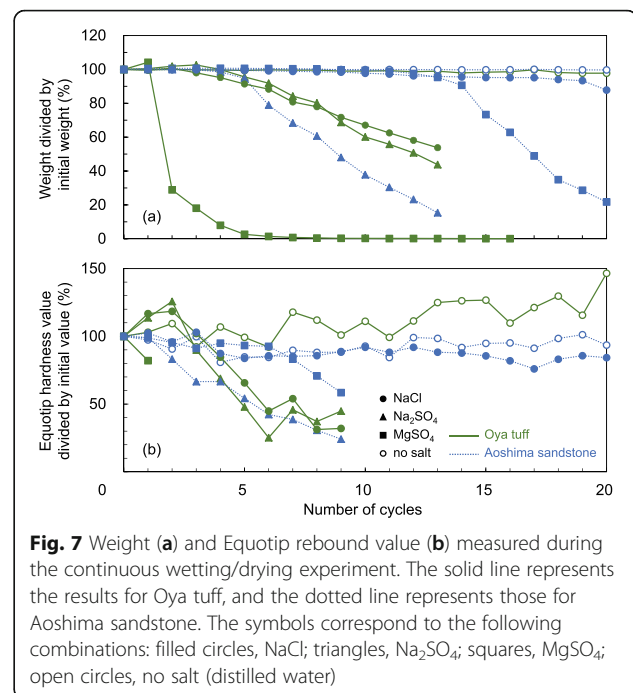
MgSO<sub>4</sub>. Ruiz-Agudo et al. (2007) carried out a laboratory experiment on the solutions of Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>. They reported that Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> were both extremely damaging. Balboni et al. (2011) explained that the different behaviors of the two sulfates are due to the different viscosities of their solutions. They assumed that the high viscosity of MgSO<sub>4</sub> retards the solution transport and crystal nucleation. High viscosity also causes pores to clog, which retards hydration and deliquescence. In our experiment, as previously mentioned, the slow hydration/dehydration rates of Na<sub>2</sub>SO<sub>4</sub> and the high DRH of mirabilite would have restricted their activity. Na<sub>2</sub>SO<sub>4</sub> is generally regarded as one of the most aggressive salts in both the field and the laboratory (Goudie and Viles 1995, 1997; Smith and McGreevy 1983; Thomachot-Schneider et al. 2011). However, the relative importance of MgSO<sub>4</sub> to Na<sub>2</sub>SO<sub>4</sub> might increase in environments in which available water is limited and the humidity is extremely high.

The difference in the water supply method affected how the sulfates induced breakdown of the rocks. Ruiz-Agudo et al. (2007) reported that Na<sub>2</sub>SO<sub>4</sub> caused localized damage and detachment, whereas MgSO<sub>4</sub> induced cracks and fractures. Their experiment, in which the lower part of the specimen was immersed in a salt solution, induced salt crystallization inside the rock interior. In contrast, in our experiment, both sulfates concentrated in the surface layer because of the limited water supply from the surface of the rock. Cracking parallel to the rock surface, which occurred in the Aoshima sandstone with MgSO<sub>4</sub> and in the Oya tuff with Na<sub>2</sub>SO<sub>4</sub>, suggests that salt weathering occurred only within several millimeters of the surface. The interiors were not weathered much because the P-wave velocities of the specimens did not decrease. López-Arce et al. (2011) suggested that porous dolostone is sensitive to diurnal cycles of air humidity at depths up to 3 cm. In our experiment conducted in a short time interval, the depth at which air humidity could have had an effect would have been less than a centimeter from the rock surface.

The specimens with NaCl did not show any cracks. Because NaCl tends to crystallize on the surface, this crystallization pattern is referred to as efflorescence. In contrast, Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> tended to crystallize within rock pores, referred to as subflorescence. Salt subflorescence induces greater crystallization pressure than salt efflorescence does (Doehne 2002; Moteershead 2013; Rodriguez-Navarro and Doehne 1999). The difference in the crystallization patterns may be reflected in the absence or presence of cracks on the surface.

#### Comparison with continuous wetting/drying experiment

The results of the wetting/drying experiment contrasted with those of the humidity-change experiment (Fig. 7). Oya tuff immersed in MgSO<sub>4</sub> disintegrated rapidly, and



**Fig. 7** Weight (a) and Equotip rebound value (b) measured during the continuous wetting/drying experiment. The solid line represents the results for Oya tuff, and the dotted line represents those for Aoshima sandstone. The symbols correspond to the following combinations: filled circles, NaCl; triangles, Na<sub>2</sub>SO<sub>4</sub>; squares, MgSO<sub>4</sub>; open circles, no salt (distilled water)

no fragments remained on the sieve after 16 cycles. The L-value of this specimen could not be measured after 2 cycles. Among the Aoshima sandstone specimens, MgSO<sub>4</sub> showed the second greatest weight loss and L-value reduction. Although the effect of NaCl was comparable to that of Na<sub>2</sub>SO<sub>4</sub> for Oya tuff, NaCl was obviously inactive for Aoshima sandstone. Na<sub>2</sub>SO<sub>4</sub> substantially damaged the Oya tuff and caused the most damage to the Aoshima sandstone.

The weights of some of the specimens could not be measured after the sieve openings became clogged with rock fragments. In addition, the L-values could not be measured after the surfaces of the specimens became rough.

For Aoshima sandstone specimens with Na<sub>2</sub>SO<sub>4</sub>, the final weight was 15.4% of the initial weight after 13 cycles, and the final L-value was 24.1% of the initial hardness after 9 cycles. Oya tuff specimen with Na<sub>2</sub>SO<sub>4</sub> disintegrated rapidly; the final weight was 43.8% of the initial weight after 13 cycles. The L-value of another Oya tuff specimen rapidly decreased; the final value was 44.8% of the initial hardness after 9 cycles. Aoshima sandstone immersed in NaCl did not show any distinct changes in either weight or L-value.

The less hydrated forms of each salt, i.e., halite, thenardite, and kieserite, would crystallize by oven drying at 110 °C. Breakdown and disintegration mainly occurred when the specimens were immersed in distilled water. Hydration of thenardite and kieserite would have occurred during the immersion. We used distilled water in the wetting sequence, whereas the previous experiments often used salt solutions

in various concentrations. Thenardite and kieserite in rock specimens dissolve in distilled water, and their solution would have reached saturation as the water penetrated the rock. There was no sign of rock breakdown during the subsequent oven drying and immersion in salt solution, although crystallization and hydration would have been possible if salt remained in the specimens.

As we described above, the dominant weathering processes in the wetting/drying experiment would be salt crystallization of halite and hydration of thenardite or kieserite. These processes are almost the same as those expected in the humidity-change experiment, i.e., deliquescence/recrystallization of halite and hydration of thenardite and hexahydrate of  $\text{MgSO}_4$ . The difference in damage between the two experiments thus did not result from the salt pathways, despite that the crystallization/hydration pressures vary with temperature and humidity (Flatt 2002). The difference between these two experiments was mainly due to the difference in the water supply methods.

#### Comparison of rock properties

Pore size distribution, micropore volume, and specific surface area generally affect susceptibility to physical weathering (Benavente et al. 2004; Matsukura and Matsuoka 1996; Matsuoka 1990; Ordóñez et al. 1997; Yu and Oguchi 2010; Arnold and Zehnder 1989). The specific surface area probably affects the salt weathering susceptibility by humidity changes because a larger specific surface area causes greater absorption.

Ubara sandstone with higher porosity and lower tensile strength (Table 1) showed the greatest weight losses (Fig. 4). Although Oya tuff has comparable properties to Ubara sandstone, Oya tuff has large pores resulting from the alternation of pumice, while Ubara sandstone is composed of uniform fine sand. These facts imply that the micropore volume and the specific surface area of Ubara sandstone are greater than those of Oya tuff. The differences in micropore volume might have affected the weathering rates in the humidity-change experiment.

#### Conclusions

This study highlights that salt weathering obviously occurs under conditions in which the water supply is limited to air humidity. The humidity oscillation induced a cycle of repeated salt deliquescence, hydration, and crystallization. The degrees of damage were strongly correlated with the volume of water absorbed in the rock specimens.

$\text{NaCl}$  caused the most damage to the specimens. Porous and weak sandstones with  $\text{NaCl}$  were completely broken down after 100 cycles of humidity change. The other two types of rock also showed concentrated damage on their surfaces. The lower DRH of  $\text{NaCl}$  resulted in more water being absorbed from the air, which in turn induced greater

weight losses and L-value reductions. The absence of hydrated forms would also have facilitated water absorption from the air.

The salt pathways of  $\text{Na}_2\text{SO}_4$  would be deliquescence of thenardite and subsequent recrystallization of mirabilite. For  $\text{MgSO}_4$ , deliquescence of hexahydrate and recrystallization of epsomite would also occur.  $\text{MgSO}_4$  induced damage in all of the rock specimens, whereas  $\text{Na}_2\text{SO}_4$  had almost no effect in our experiment.  $\text{Na}_2\text{SO}_4$  may be ineffective as an agent of salt weathering in high-humidity conditions. The volume expansion with hydration of  $\text{Na}_2\text{SO}_4$  might hinder infiltration of water into the rock. The high DRH of mirabilite would also prevent salt deliquescence.

Aoshima sandstone with  $\text{MgSO}_4$  developed cracks parallel to its surface that reflected the different crystallization patterns (efflorescence or subflorescence).  $\text{MgSO}_4$  tends to form subflorescence, unlike  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$ . The tendency was observed under the condition in which a limited volume of water from air humidity was supplied to the rock surface.

Tafoni, which is often associated with salt weathering, occasionally appears hundreds of meters away from coastlines. In supratidal zones, salts are provided by sea spray on their surface. In such conditions,  $\text{NaCl}$  is supplied to and precipitates on the rock surface in stormy weather; subsequent humidity fluctuations would induce salt weathering.

Sulfates are often found on building materials, and sodium sulfate is thought to be one of the most aggressive salts. However, the restricted activity of  $\text{Na}_2\text{SO}_4$  in our experiment suggests that deliquesce and hydration of  $\text{Na}_2\text{SO}_4$  are hindered by the clogging of rock pores with the hydrated salts.  $\text{MgSO}_4$  did not show such behavior, although deliquesce and hydration of  $\text{MgSO}_4$  would have occurred.  $\text{MgSO}_4$  would be more effective than  $\text{Na}_2\text{SO}_4$  under conditions in which the water supply is limited to air humidity.

#### Abbreviations

DRH: Deliquescence relative humidity; L-value: Equotip rebound value;  $\text{MgSO}_4$ : Magnesium sulfate;  $\text{Na}_2\text{SO}_4$ : Sodium sulfate;  $\text{NaCl}$ : Sodium chloride; P-wave velocity: Longitudinal wave velocity

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#### Availability of data and materials

Requests for data should be sent to the contact author.

#### Authors' contributions

Both authors designed the experiments, wrote the manuscript, and read and approved the final manuscript.



### Competing interests

Both authors declare that they have no competing interests.

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