



# Gypsum, mirabilite, and thenardite efflorescences of tuff stone in the underground environment

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## Abstract

This study deals with stone deterioration in underground cultural heritage and geoheritage, correlating the origin, compositional features, and space–time changes of salt weathering with the rock properties (petrography and geochemistry) and environmental setting (microclimate and chemistry of rainwater and groundwater). The material of study is Oya-ishi, one of the best-known building stones of Japan; it is a porous and soft acid tuff with a long tradition of use in historical and modern architecture. A number of underground sites of cultural or commercial significance was investigated in central Japan, where Oya stone appears extensively affected by efflorescence growth. The efflorescences are composed of mixed sulfates, including gypsum, mirabilite, and thenardite, whose development depends on the stone–environment interaction. The underground environment is extremely humid and water is the main driving force of salt weathering, having a twofold function. First, it conveys the alteration of the rock components, in particular pyrite, glass (pumice, *fiamme*, and shards), zeolites (clinoptilolite), clay minerals (smectites), and feldspars, which release  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$  ions. Second, water controls the salt stability and cycles of crystallization/deliquescence and hydration/dehydration, depending on the site depth and seasonal microclimate fluctuations; in this regard, knowing the specific thermodynamic behavior of the phases involved can help predicting where and when salt weathering and the resulting stone damage are most severe.

**Keywords** Salt weathering · Oya stone · Cultural heritage · Geoheritage decay · Microclimate monitoring · Cave

## Introduction

Japanese traditional architecture is mostly made of wood, hence the secondary importance of stone as building material in history. That has also echoes on the modern stone industry, which struggles to grow and relies almost completely on imports, especially from China, the European Mediterranean region, and South/Southeast Asia. Yet, large

stone amounts can be observed in the construction of Japanese cities or in cultural heritage (JETRO 2011; Inui 2014). Although granites are the most widespread nowadays, one of the best-known local building stones is a pyroclastic rock called Oya-ishi.

Oya stone is a Miocene acid tuff extracted near the city of Utsunomiya (Tochigi prefecture, Kanto region, central Japan). It is exploited mostly underground but, among the over two hundred existing quarries, only few are still active (Kohyama and Hayashi 1972; Seiki et al. 2007). It is widely used in vernacular architecture, for building houses, warehouses, barns, walls, foundations, small shrines, and carving gravestones, lanterns, and other sculptures (Yasumori 2021). The first traces of usage date back to almost 1500 years ago, but the extensive exploitation began in the Edo period (1603–1868). In the twentieth century, Oya stone also entered the market of large construction works, such as schools, churches, hotels, and factories (Oguchi and Yuasa 2010). The most renowned heritage site where Oya stone plays the lead role is the Oya-ji temple (810 AD), excavated into tuff cliffs and surrounded by caves decorated

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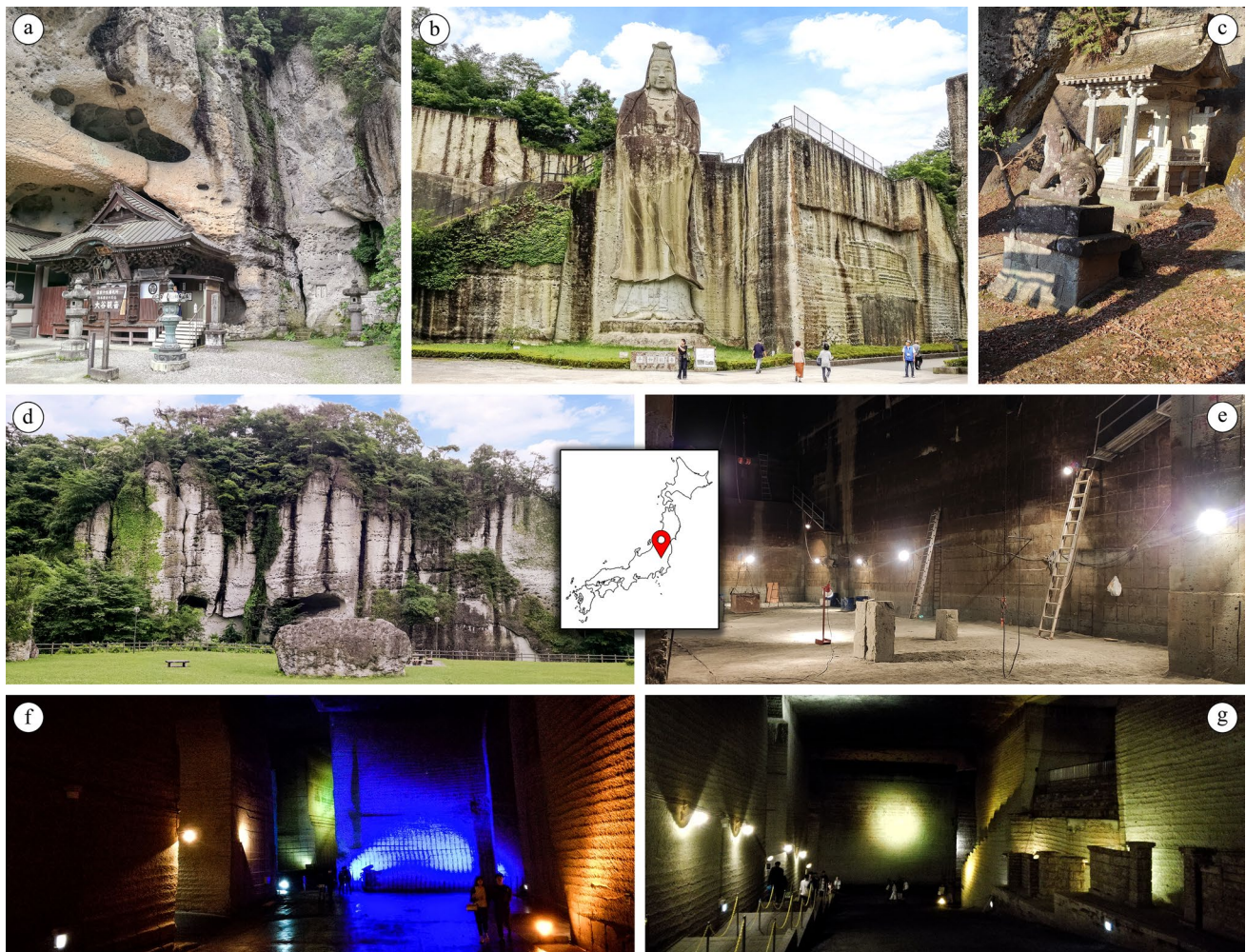
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**Fig. 1** Oya stone in the cultural heritage and geoheritage of Oya-machi in Japan: **a** the cliff of Oya-ji temple and Oya Stone Buddhas; **b** the sculpture of Heiwa Kannon; **c** a small Shinto shrine; **d** the cliffs of Oya Keikan Park; **e** Ishi-no-Sato active quarry; **f–g** Oya History Museum

with Buddhist rock art; near the temple rises the colossal 27-m-tall stone statue of Heiwa Kannon, carved from 1948 to 1954, dedicated to the dead of the World War II (Fig. 1).

Oya stone is a very porous and soft material, as indicated in several studies on its physical–mechanical properties. Its bulk density is around  $1.4 \text{ g/cm}^3$  and open porosity reaches 40–45%. The micropore system has a pore size mostly smaller than  $0.1\text{--}0.5 \mu\text{m}$ , which increases in the coarse-grained tuff varieties (Aoki et al. 2005; Oguchi and Yuasa 2010; Yu and Oguchi 2010; Sato and Hattanji 2018). The compressive strength is usually about 10–15 MPa, but is affected by a strong decrease (even of 70%) when the stone is wet; this performance drop is noticeable in other mechanical properties too, such as tensile strength—usually about 1–2.5 MPa (Aoki et al. 2005; Yu and Oguchi 2010; Aydan et al. 2011; Sato and Hattanji 2018). This represents a hazard especially in underground environments (the quarries can reach over 100 m in depth, Kohyama and Hayashi 1972), for

the buildings raised above them, and the local population; many sinkholes and rockfalls were reported in the area, this risk being exacerbated during the frequent earthquakes that plague Japan (Ando and Oka 1967; Aoki et al. 2005; Seiki et al. 2007; Aydan and Tano 2012). The general influence of moisture content on tuff failure is confirmed at various times in the literature (e.g., Kaşmer et al. 2013; Pola et al. 2014; Germinario and Török 2019).

Another branch of research on Oya stone regards the widespread issue of salt weathering. Field observations reported the recurrent formation of efflorescences, mostly composed of thenardite and gypsum (Imogawa et al. 2000; Oguchi and Yuasa 2010; Seiki et al. 2017). Laboratory tests highlighted that salt weathering acts quite rapidly on Oya stone, leading to severe disintegration after few weathering cycles of salt attack with sodium sulfate; this appears related chiefly to the specific pore-size distribution (Yu and Oguchi 2010; Sato and Hattanji 2018).

Although the properties of Oya stone are subject of several studies, none has explored deeply the driving forces of its deterioration. This research investigates the stone–environment interaction by correlating the origin, compositional features, and space–time changes of salt weathering of Oya stone with its petrographic–geochemical properties and the environmental setting, namely microclimate and water chemistry. The focus is on the subterranean environment. The findings integrate the scientific background about the vulnerability of underground cultural heritage and geoheritage (e.g., Germinario et al. 2020; Germinario and Oguchi 2021), often overlooked to the advantage of sites, buildings, and landscapes on the surface, which often demand different study approaches.

## Methods

### Sites and sampling

Field observations, a microclimate monitoring, and samplings of efflorescences, rocks, groundwater, and rainwater were done in Oya-machi, a suburban district of Utsunomiya, in four underground and semi-underground quarries of Oya stone, located in a radius of 1.5 km (Supplementary Fig. 1) (Fig. 1).

- Oya History Museum: a former extraction site, active from 1919 to 1986. During the World War II, it served as a hidden military warehouse and munition factory. It is now a museum showcasing the history of tuff quarrying in the region, but it is often used also as venue of music concerts, art exhibitions, theater performances, filmmaking, photo shoots, and even weddings. It has an impressive size, with an area of 20,000 m<sup>2</sup> and a depth of 30 m (Oya Museum of Art 2021).
- Oya Park: a former quarry area including the Oya-ji temple, the Heiwa Kannon monument, the panoramic cliffs of Keikan Park, and a number of old extraction sites, now restructured, redeveloped, and open to visitors.
- Daidoji: an abandoned underground/semi-underground quarry, quite shallow and with numerous large openings to the surface.
- Ishi-no-Sato: an active underground quarry, 50 m deep.

The fresh rock samples were provided by Ishi-no-Sato and two varieties were selected based on the different grain sizes. The efflorescences were sampled in Oya History Museum (at two different depths), in Daidoji, and outdoors in Oya Park, collecting with a spatula micro-samples from the quarry walls, both during the summer of 2019 and during the winter of 2019/20 (eight samplings in total). The rainwater was also sampled during the same seasons, collected outdoors using passive devices for 3–4 months nonstop (two samplings).

Finally, the groundwater samples were collected at the end of the same two seasons, from the quarry pools of Oya History Museum, Daidoji, and Ishi-no-Sato (six samplings).

### Techniques

The microclimate monitoring was performed over one year (August 2019–July 2020), recording air temperature and relative humidity (RH) in each site, at different depths and distance from the entrances when needed, including outdoors (nearby the Oya History Museum). The data loggers used are the Hygrochron by KN Laboratories, have an accuracy of  $\pm 0.8$  °C and  $\pm 5\%$  RH and a resolution of 0.5 °C and 0.6% RH; they were operated with a sampling rate of one measurement per hour.

The water samples were prepared by filtration at 0.45  $\mu$ m and then analyzed for their major-ion chemical composition by ion chromatography (IC), using a chromatograph Shimadzu Prominence HIC-NS, a non-suppressor system with a conductivity detector working in the range 0.01–51,200  $\mu$ S/cm and with detection limits down to about 0.05 mg/l; the pH was also assessed by the Pack Test, a visual colorimetric method by Kyoritsu Chemical-Check Lab. Corp.

The rock samples were prepared as thin sections and observed at the polarized-light microscope and, after carbon coating, at the scanning electron microscope (SEM) for their petrographic characterization; the SEM used is a Hitachi S-3400 N, equipped with a W cathode operated at 15 kV, detectors of secondary and back-scattered electrons (SE and BSE), and a system for energy-dispersive X-ray spectroscopy (EDS) Bruker Quantax 400 and semi-quantitative microchemical analysis. The bulk geochemical composition was analyzed on pressed powder pellets by X-ray fluorescence (XRF), using a wavelength-dispersive spectrometer Panalytical Axios with detection limits of 0.01% for major elements and about 10 ppm for traces, applying the fundamental-parameter method; loss on ignition (LOI) was also determined.

The efflorescence samples were powdered and analyzed for their mineralogical composition by X-ray diffraction (XRD), with a diffractometer Rigaku Ultima III equipped with a Cu anode operated at 40 kV and 40 mA, measuring in the range 3–65°2 $\theta$  with scan steps of 0.02°2 $\theta$  and scan speed of 4°2 $\theta$ /min. The efflorescences were also observed at the SEM, with no prior surface preparation (unpolished samples).

## Results

### Environmental survey

#### Microclimate

The climate of the Kanto region in central Japan is characterized by hot, humid summers and cold, dry winters, with a

rainy season between early June and mid-July (JMA 2021a). In summer and early fall, typhoons may also occur, bringing extremely violent rainfalls (JMA 2021b).

The climate series of temperature and RH recorded outdoors in Oya-machi is consistent with these remarks (Fig. 2). The one-year monitoring shows that summer and fall are the most humid seasons, hitting the highest mean RH of 92% in July, whereas winter and spring have the lowest and most variable values, reading the lowest mean of 73% in March. Mean temperature goes from 27 °C in August to 4 °C in January, with frequent sub-zero temperatures recorded in winter time, down to almost − 5 °C.

The underground microclimate is generally colder and much more humid, although showing remarkable differences between the shallow levels—that is, the areas nearby the outdoors and closer to the quarry entrances and surface—and the deep levels investigated (Fig. 2).

The shallow levels include Daidoji quarry and part of Oya History Museum, where the mean RH of winter months does not go below 82% (the former) or 90% (the latter), but with minima below 70% from fall to spring throughout; in summer, mean RH ranges from 96 to 98%, with maxima hitting 100%.

The deep levels include Ishi-no-Sato quarry and Oya History Museum again. These deep levels represent semi-closed systems with scarce influence of external airflows; they are characterized by stable microclimate parameters and narrow seasonal fluctuations, as demonstrated by the small standard deviations and ranges of the measures. Temperature varies around 0–5 °C in winter and 10 °C in summer. RH is also quite constant and remains extremely high: in winter, mean RH never goes below 94%, with minima almost never below 85%; in summer, it approaches or reaches steadily 100%.

### Water chemistry

Water has a significant role in the underground environment investigated, not only for the high RH. Water stagnates at the quarry bottoms, infiltrates and percolates through the rock vaults, and rises from the subsoil.

Compared to rainwater, the groundwater is enriched especially in Na and S, and has a higher pH, as detailed in Table 1. In particular, the average concentrations of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  are 57 and 83 ppm, respectively, that is, about 70 and 35 times larger than in rainwater, with maxima even exceeding 100 ppm. Considerably higher concentrations are reported for  $\text{NO}_3^-$  too. On the other hand, only one site (Oya History Museum) records a distinct enrichment in  $\text{Ca}^{2+}$ , which does never exceed 4 ppm though. The higher mineralization of groundwater reflects its

higher pH (about 7) compared to the typical slight acidity of rainwater.

The concentration patterns are not season specific nor site specific, apart from Daidoji quarry, which records values constantly lower than in the other locations (except for  $\text{NO}_x$ ), even of one order of magnitude. This is probably linked to the sampling that, only there, was done on water dripping from the vaults and accumulating in a container, instead of on large bodies of still groundwater.

## Stone characterization

### Petrography and geochemistry

Oya stone is a pumice tuff with a dacitic (nearly rhyolitic) composition and a eutaxitic (oriented) and pseudo-porphyrific texture. The vitric, crystal, and lithic fragments show a hiatal distribution, mainly comprising the coarse-ash and lapilli size classes, and a (sub) angular shape (Fig. 3; Table 2).

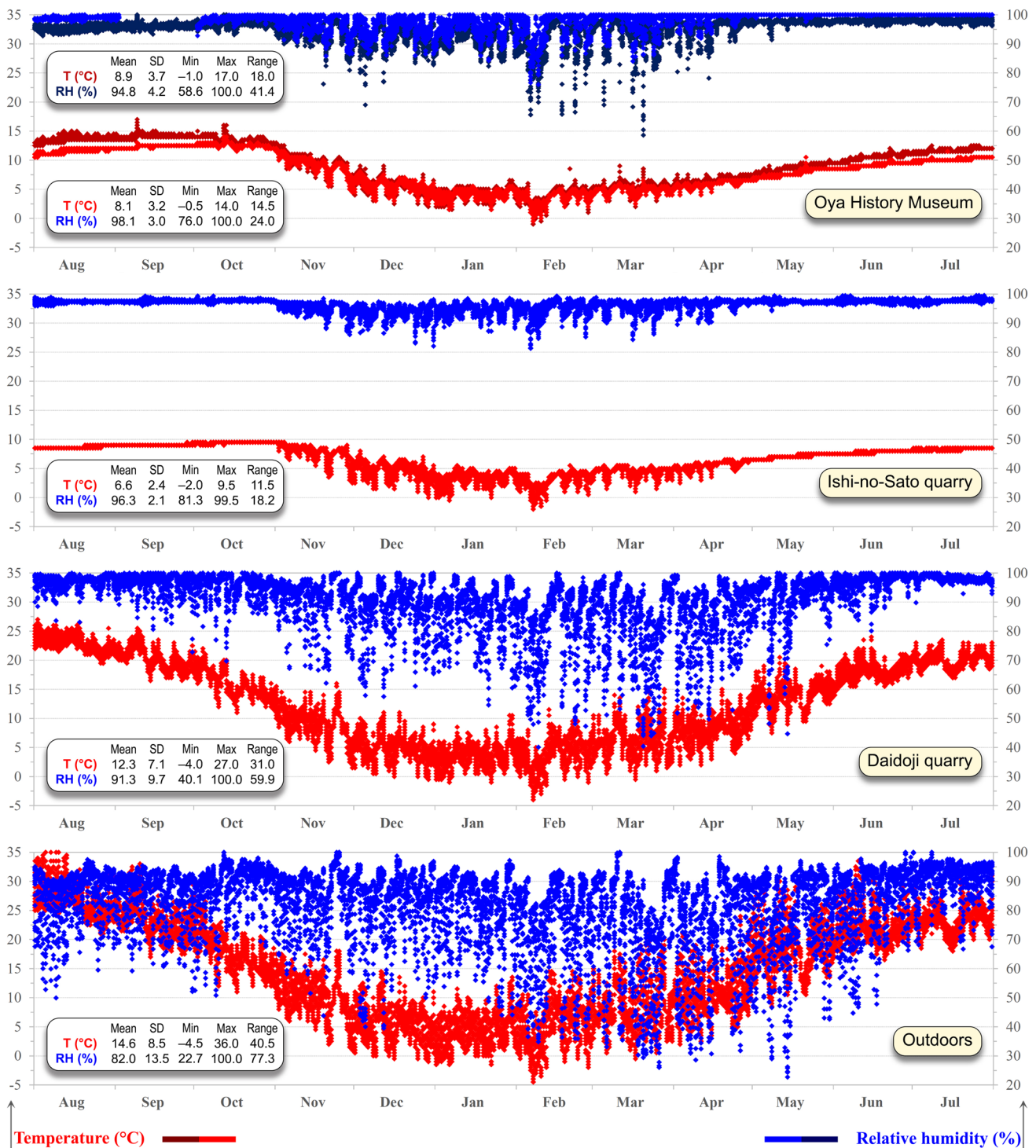
The glass fraction has an alkali-feldspar composition and is composed of pumice clasts, *fiamme*, and a matrix of fine-grained glass shards.

The primary phases include plagioclase, quartz, and minor biotite and amphibole as rock-forming minerals, along with Fe/Ti oxides and apatite as accessory minerals. The secondary phases include zeolites, clay minerals, pyrite, Fe oxyhydroxides, Fe/Ti oxides, baryte, and tridymite; traces of secondary sulfates can be detected too (see below). The minerals of the zeolite group are clinoptilolites rich in K and Na (Fig. 4a). They are often associated with the clay minerals (Fig. 4b), which are smectites mainly composed of montmorillonite (with a 5–15% iron content), with also saponite, beidellite, and chlorite, according to previous studies (Kohyama and Hayashi 1972; Yu and Oguchi 2010); their oxidation state controls the stone color (Kohyama and Hayashi 1972; Iguchi and Nakashima 2014; Seiki et al. 2017), which can be grayish, brownish/creamy, or greenish (Supplementary Fig. 2). The clay minerals may form brown clumps, varying from fine clusters to aggregates large several centimeters or even tens of centimeters. Finally, pyrite is disseminated in aggregates with a characteristic framboidal texture, but is observable only in the non-oxidized rock core (Fig. 4c).

Oya stone is commercialized in a number of varieties differing for the grain size, especially of the brown clumps. Other differences in texture and composition are negligible, as also indicated in Fig. 3 and Table 2 by the comparison of the finest and coarsest varieties sampled.

### Salt weathering

The efflorescences forming on Oya stone are composed of sulfates, i.e., mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), thenardite



**Fig. 2** Monitoring of air temperature and RH in the underground study sites and outdoors in Oya-machi (the first plot has brighter markers for the deepest spot of the site, and darker markers for a shallower spot closer to the entrance and the surface)

( $\text{Na}_2\text{SO}_4$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), in different proportions (Fig. 5 and Fig. 6).

Generally, mirabilite is the most abundant component and is always associated with thenardite, with gypsum either in low concentrations or absent (e.g., as in the shallow levels

of Oya History Museum and Daidoji quarry). Thenardite was detected without mirabilite only once outdoors (in Oya Park). This type of efflorescences are soft, fuzzy, scarcely adherent to the substrate, and can grow several centimeters outwards.

**Table 1** Average chemical composition by IC (in mg/l) and pH of groundwater and rainwater, with ranges in parentheses (“*bdl*” below detection limit)

	Groundwater	Rainwater
Na <sup>+</sup>	57.4 (14.2–120.9)	0.8
Mg <sup>2+</sup>	0.4 (0.3–0.6)	0.3
K <sup>+</sup>	1.8 (0.5–2.9)	<i>bdl</i>
Ca <sup>2+</sup>	1.9 (0.8–3.6)	1.9
NO <sub>3</sub> <sup>-</sup>	1.8 (1.2–2.7)	0.1
SO <sub>4</sub> <sup>2-</sup>	82.7 (8.0–186.7)	2.4
Cl <sup>-</sup>	5.1 (2.6–6.9)	1.5
pH	7.2 (7.0–8.0)	5.5

Gypsum is the only soluble salt present in the most humid environment investigated (i.e., the deepest levels of Oya History Museum, where the other sulfates were not detected). The gypsum-rich efflorescences are fine-grained, crystalline, more closely bound to the substrate, and scarcely developed in thickness and extent.

Overall, the qualitative composition of the efflorescences in each underground environment studied (ruling out the outdoor sampling) turned out to be quite constant all through the year of investigation. Significant changes across the seasons concerned only the extent of the efflorescences, reducing during and after the summer season, possibly even disappearing completely; on the other hand, the winter season was associated with a peak in the efflorescence growth. Moreover, the efflorescence composition does not change on the different varieties of Oya tuff.

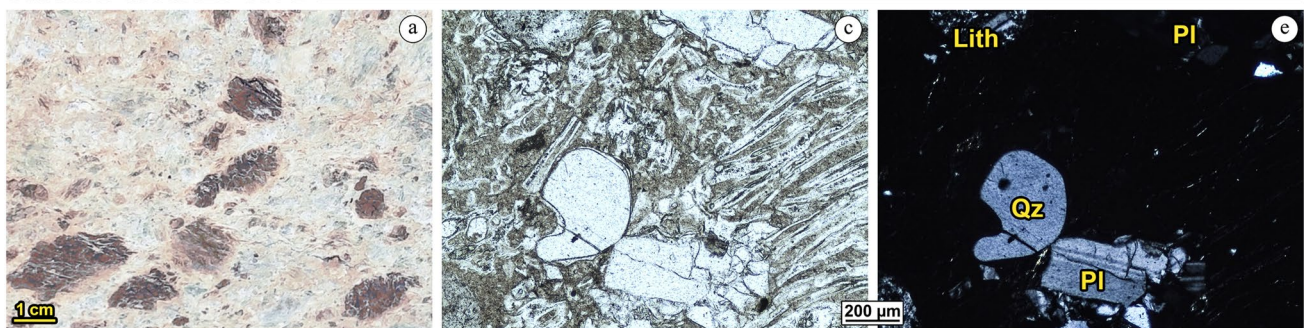
The only salt-free location was the active quarry, because of the ongoing exploitation of the quarry walls.

## Discussion

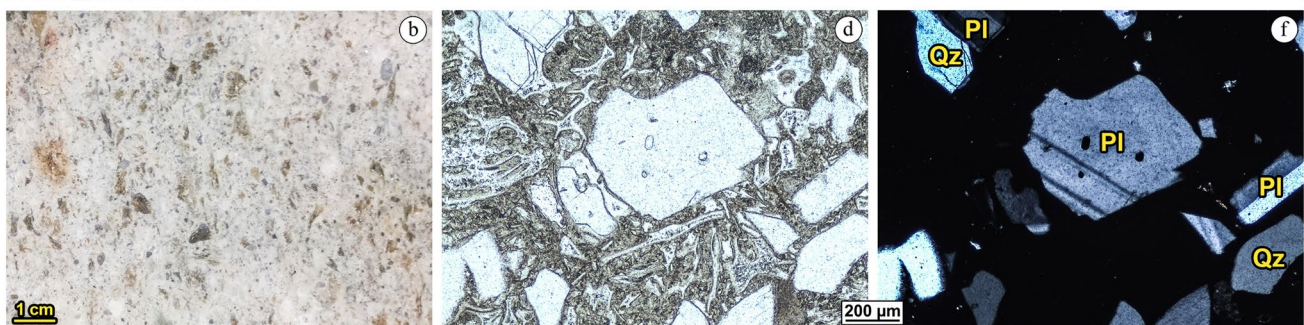
### Salt–environment interaction

The development of salt weathering can be discussed in terms of the environmental factors affecting the stability of the mineral phases involved. Gypsum, mirabilite, and

#### COARSE-GRAINED TYPE



#### FINE-GRAINED TYPE



**Fig. 3** Two varieties of Oya stone with different grain size of the brown clay clumps: photographs (a–b) and thin-section photomicrographs at the optical microscope in plane- (c–d) and cross-polarized light (e–f) (*Lith* lithic fragment, *Pl* plagioclase, *Qz* quartz)

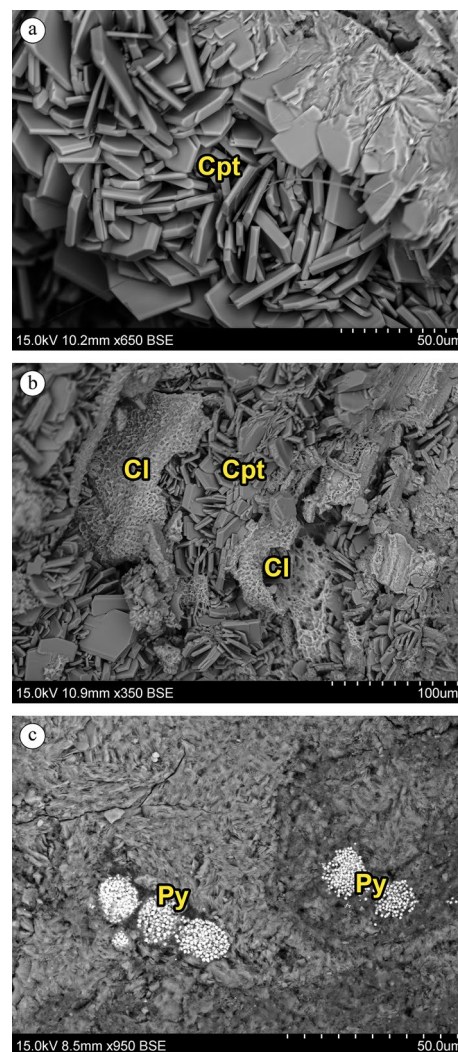
**Table 2** Bulk chemical composition of Oya tuff determined by XRF (major-element oxides and LOI are in weight %, trace elements in ppm; “*bdl*” below detection limit)

	Coarse-grained type	Fine-grained type
Na <sub>2</sub> O	2.13	2.31
MgO	0.69	0.72
Al <sub>2</sub> O <sub>3</sub>	11.07	11.08
SiO <sub>2</sub>	69.48	70.85
K <sub>2</sub> O	3.62	2.91
CaO	1.28	1.55
TiO <sub>2</sub>	0.14	0.11
Fe <sub>2</sub> O <sub>3</sub>	1.75	1.60
LOI	9.56	8.56
P	96	86
S	293	315
Cl	97	115
Mn	531	433
Zn	86	105
Ga	19	35
Rb	118	108
Sr	164	157
Y	34	28
Zr	156	156
Ba	310	293
Ce	<i>bdl</i>	188
Pb	32	<i>bdl</i>

thenardite all have their own thermodynamic behavior, so the microclimate and its variability play an extremely important part in controlling salt crystallization and dissolution.<sup>1</sup>

Gypsum has the lowest solubility and hygroscopicity, and its deliquescence occurs at a very high RH (over 99.9%, according to Charola et al. 2007), hence its stability in a variety of environmental settings, even extremely humid. In fact, gypsum is present in every season and in most of the efflorescences in the underground sites investigated (although in variable amounts). That also includes

<sup>1</sup> Some factors might cause deviations from the theoretical considerations reported here. Firstly, salt mixtures in aqueous solutions have different thermodynamic properties compared to the single pure phases, whose solubility may vary depending on the overall water composition (Price and Brimblecombe 1994; Steiger 2005). However, Price (2000) discussed the ternary system Na-Ca-SO<sub>4</sub>, showing that the only noticeable change in solubility among the phases of interest involves gypsum: depending on the Na<sub>2</sub>SO<sub>4</sub> concentration (and unless this is extremely low), gypsum solubility either slightly increases or its change is practically negligible. Secondly, although proper measures of sample storage were adopted, slight changes of sample temperature or moisture might occur in the period between the sampling and the actual mineralogical analyses, possibly triggering phase transitions that alter the balance between mirabilite and thenardite (in the case of a quantitative study).



**Fig. 4** Oya stone observed at the SEM-BSE: **a** coffin-shaped crystals of clinoptilolite (Cpt) of the zeolite group; **b** clinoptilolite associated with sponge-textured clay minerals (Cl); **c** framboidal pyrite (Py)

the deep levels of Oya History Museum, the most humid site, where the other sulfates cannot form and even the gypsum efflorescences are limited; in fact, dissolution easily occurs because of the more frequent and prolonged contact with liquid water, due to the enhanced hygroscopic condensation (especially in summer, when RH is nearly constant 100%) and the rainwater dripping from the quarry ceiling.

Mirabilite and thenardite are more affected by RH and temperature changes, so that seasonal climate and microclimate fluctuations have a stronger impact on the efflorescence formation or disappearance. Figure 7 shows the theoretical stability fields of the two phases. Mirabilite is stable at mid-high RH, especially at low temperatures, whereas the stability field of thenardite involves drier conditions and is larger at higher temperatures (Steiger and Asmussen

## MIRABILITE-THENARDITE



## GYPSUM



**Fig. 5** Sulfate efflorescences with their macroscopic features (a–d) and microscopic texture observed at the SEM-BSE (e–f)

2008; Linnow et al. 2014). Considering the underground sites where the two sulfates form, i.e., the shallow levels of Oya History Museum and Daidoji quarry, the efflorescence evolution may occur according to the following outline. In summer and early fall, there are continuous reactions of deliquescence and recrystallization of mirabilite; in fact, the typical combined variations of air temperature and RH are very close to the theoretical equilibrium of mirabilite, which is at 96.9% RH and 15 °C, or at 95.6% RH and 20 °C. As a result, the efflorescences are composed mainly of mirabilite but their development is at its minimum. As winter approaches, RH decreases, deliquescence events diminish, and mirabilite becomes more stable. In addition, phase transitions may occur in the days or hours recording low RH minima; in fact, at 5 °C, mirabilite dehydrates to thenardite at 64.3% RH. As a result, the efflorescence development is at its maximum in winter and early spring and thenardite concentration increases (although still lower than mirabilite concentration). Closing the yearly microclimate cycle, with another RH increase during the change of season, part of thenardite can persist in a metastable equilibrium (i.e., at RH above the phase transition curve), part of it dissolves (or hydrates) instead, leading to mirabilite crystallization; that is possible because of the much slower growth kinetics of mirabilite, compared to thenardite. If RH further increases, thenardite virtually disappears. Finally, with regard to the outdoor environment, since the microclimate

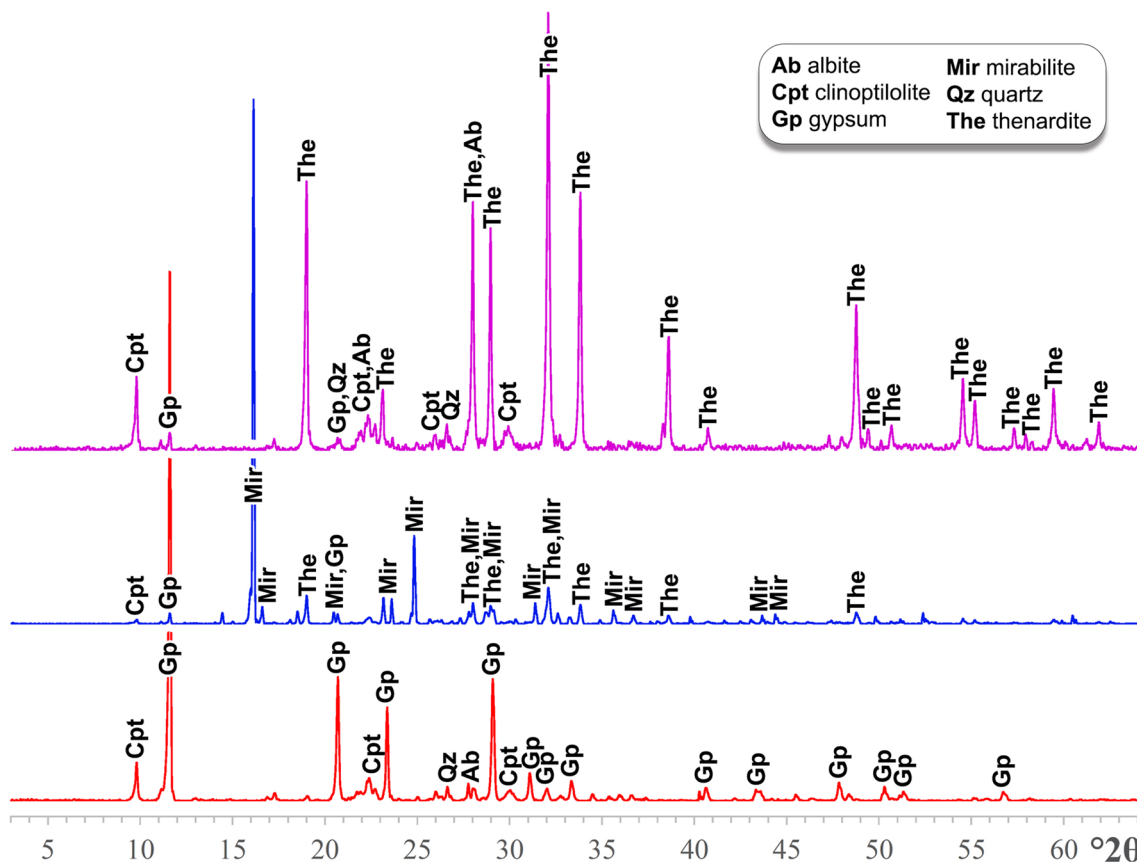
is quite different (drier) than underground, the formation of thenardite may be favored, with also more frequent phase transitions.

### Salt source

Salt weathering can also be viewed in the context of the lithological factors promoting salt formation. The origin of gypsum, mirabilite, and thenardite can be interlinked with specific mineralogical and geochemical properties of Oya stone and its interaction with rainwater and groundwater. The analyses of the stone substrate and the waters point out that  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , and secondarily  $\text{Ca}^{2+}$ , represent the main chemical markers of the processes of water-driven weathering; in other words, those elements are preferentially leached from the rock and mobilized through its pores, eventually recombining in the efflorescences.

The  $\text{SO}_4^{2-}$  anions derive principally from pyrite alteration. This process can occur in any pH conditions after pyrite is exposed to air, although oxidation is more rapid when water is in the system and involves framboidal minerals. The typical products of pyrite oxidation are Fe oxyhydroxides (Taylor 1988; Deer 2013). No pyrite is detected in the surface or near-surface layers of Oya stone, that is, within few mm or cm from where the efflorescences grow; in the same areas, an enrichment in Fe oxyhydroxides and the formation of other oxidation byproducts (e.g., baryte)

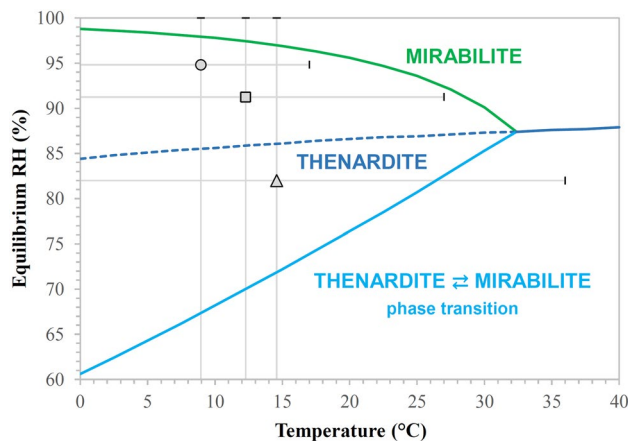




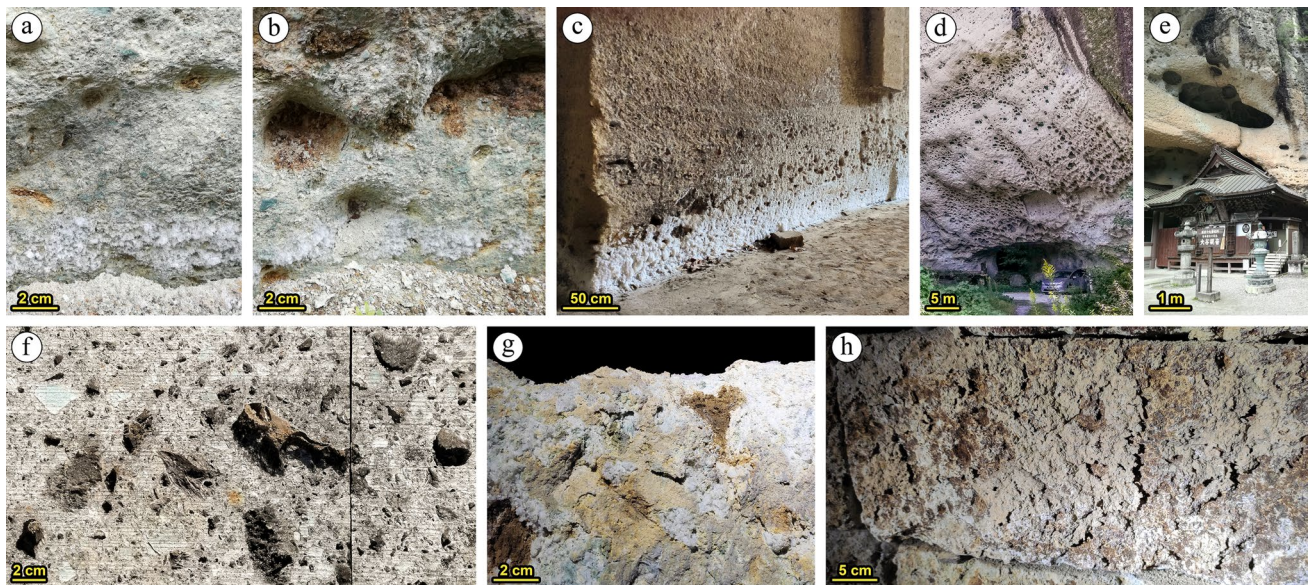
**Fig. 6** XRD patterns showing the mineralogical composition of efflorescences sampled in deep underground levels (Oya History Museum, in red), in shallower underground levels (Oya History Museum, in blue), and outdoors (Oya Park, in purple)

occur. These considerations are in agreement with previous studies reporting similar alteration processes in the underground environment (Germinario et al. 2020; Germinario and Oguchi 2021).

The  $\text{Na}^+$  and  $\text{Ca}^{2+}$  cations possibly derive from the alteration of the silicate rock components, in particular glass, zeolites, clay minerals, and plagioclase. Volcanic glass is thermodynamically unstable and its decomposition is more rapid if compared to most of the associated mineral phases (Fisher and Schmincke 1984). Considering the alkali-feldspar composition and high concentration of glass in Oya stone, that represents a primary source of  $\text{Na}^+$ . The occurrence of clay minerals and zeolites, typical alteration products of volcanic silicic glass (including smectites and clinoptilolite), further corroborates the importance of that process (Fisher and Schmincke 1984; Colella et al. 2001; Germinario and Török 2020). Zeolites in Oya stone also play a fundamental role as sources of  $\text{Na}^+$ , in view of the high Na concentration of clinoptilolite, the well-known cation-exchange properties, and the enhanced mobility of that element because of the weak



**Fig. 7** Equilibrium RH for deliquescence and phase transition of mirabilite and thenardite at different temperatures, with the dashed curve representing a metastable equilibrium (after Steiger and Asmussen 2008); the bars and markers indicate, respectively, the ranges and means of RH and air temperature recorded in the shallow levels of Oya History Museum (circle), in Daidoji quarry (square), and outdoors (triangle)



**Fig. 8** The main deterioration patterns of Oya stone: **a–e** growing levels of alveolization and **a–c** white efflorescences associated with rock disintegration at the bottom of quarry walls; **f** differential erosion

with the selective removal of large clay clumps; **g** surface disintegration, differential erosion, and peeling; **h** peeling

electrostatic bonds (Deer et al. 2013). Finally, the contribution of clay minerals—also having cation-exchange properties—and plagioclase needs to be taken into account. These phases may represent additional (minor) sources of  $\text{Na}^+$  but they also can release  $\text{Ca}^{2+}$  (Steiger 2003; Deer et al. 2013).

Apart from stone weathering, a possible extrinsic source of salts is the vegetation cover of the quarries in Oya-machi, with the underground water being enriched in organic acids and their decomposition products as precipitations wet the soil and foliage (Shestopalov 2009).

### Effects of salt weathering

The efflorescences do not affect just the appearance of Oya stone. Since they are often associated with subflorescences, they grow also in the inner pores, having a damaging effect on stone integrity during the cycles of salt crystallization/dissolution and hydration/dehydration, promoted by the microclimate variability. Those cycles produce mechanical stresses in the rock pores exceeding the tensile strength of the material, causing deterioration, particularly pronounced because of the high porosity and low strength of Oya tuff. Considering the formation of mirabilite, for example, its precipitation from thenardite hydration implies a volume expansion of 314% (Price 2000). Moreover, mirabilite is more damaging than thenardite during the crystallization phase: even though it generates lower pressures, its higher molar volume helps filling the pore spaces, producing larger contact areas with the pore walls, and facilitating stress propagation (Steiger and Asmussen 2008).

Some examples of the effects of salt weathering on Oya stone are reported in Fig. 8; the most common deterioration patterns include alveolization, differential erosion, disintegration, peeling, and scaling. The alveolization can be massive and form caverns large tens of centimeters or even meters. As for the differential erosion, it is also frequently caused by the selective loss of the clay clumps.

Stone damage might be contained by adopting measures of microclimate control, i.e., attempting to keep temperature and RH fluctuations within the stability ranges of the salts (Price and Brimblecombe 1994), particularly of gypsum and mirabilite, the most compatible with the humid underground environment. However, this control is very complicated in semi-natural settings as in Oya-machi. Preventive conservation may greatly benefit from indirect measures, such as the regulation of visitor flows, lighting regimes, rainwater drainage, and land use. Where direct measures are needed, these might involve the consolidation and structural reinforcement. The structural collapse hazard needs also to be continuously monitored, especially after extreme events like earthquakes and typhoons (Germinario et al. 2020).

### Conclusions

Salt weathering is one of the most distinct decay processes of Oya tuff, and may jeopardize the preservation of several sites of the cultural heritage and geoheritage of Japan where that stone material plays the lead role. The most widespread deterioration pattern involves the formation of

efflorescences, composed of gypsum, mirabilite, and thenardite in diverse proportions. The understanding of why and how those efflorescences form and develop is bound to the study of the relevant environmental setting and rock substrate properties.

The underground sites investigated are extremely humid, because of the high RH and the constant presence of liquid water, from percolating rain, vapor condensation, and capillary rise. Water has a twofold function as driving force of the salt weathering. On one hand, it interacts with Oya stone and conveys the alteration of its components, in particular pyrite, glass, zeolites, clay minerals, and feldspars, whose leaching provides the chemical elements for the sulfate formation. On the other hand, water controls the salt stability and cycles of crystallization/deliquescence and hydration/dehydration, depending on the site depth and the seasonal microclimate fluctuations between the humid summer/early fall and the dry winter/early spring; in this regard, knowing the specific thermodynamic behavior of gypsum, mirabilite, and thenardite can help predicting where and when salt weathering is most severe.

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**Data availability** The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Code availability** Not applicable.

## Declarations

**Conflict of interest** The authors have no conflict of interest to declare.

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