



Preservation of York Minster historic limestone by hydrophobic surface coatings

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Magnesian limestone is a key construction component of many historic buildings that is under constant attack from environmental pollutants notably by oxides of sulfur via acid rain, particulate matter sulfate and gaseous SO₂ emissions. Hydrophobic surface coatings offer a potential route to protect existing stonework in cultural heritage sites, however, many available coatings act by blocking the stone microstructure, preventing it from ‘breathing’ and promoting mould growth and salt efflorescence. Here we report on a conformal surface modification method using self-assembled monolayers of naturally sourced free fatty acids combined with sub-monolayer fluorinated alkyl silanes to generate hydrophobic (HP) and super hydrophobic (SHP) coatings on calcite. We demonstrate the efficacy of these HP and SHP surface coatings for increasing limestone resistance to sulfation, and thus retarding gypsum formation under SO₂/H₂O and model acid rain environments. SHP treatment of 19th century stone from York Minster suppresses sulfuric acid permeation.

Common with many historic structures of its era, the exterior stonework of York Minster, the largest Gothic cathedral in northern Europe which has occupied the same site in England since 600 A.D., has suffered extensive weathering by atmospheric pollutants. Limestone (CaCO₃), magnesian limestone (Ca_xMg_y(CO₃)₂), and its related pure mineral form dolomite (wherein x=1, y=1), were widely used by medieval builders in the construction of historic monuments such as York Minster. However, periodic renovation and attempted restoration efforts, using the best available materials of the time, have in some instances accelerated masonry decay through inappropriately sourced, gypsum-contaminated, replacement materials, which release soluble sulfate species. In recent decades, conservationists working on such architectures across Europe and North America have become increasingly concerned by mortar and stonework damage arising from environmental pollutants¹. Despite regulation of anthropogenic environmental SO₂ emissions, atmospheric SO₂ and sulfate release from natural sources such as volcanic eruptions remain ever-present, and their subsequent interaction with limestone masonry continues to damage cultural heritage via dry and wet deposition pathways (Fig. 1a)². Such sulfate-induced limestone decay is widely believed to proceed via formation of sparingly soluble Ca²⁺ salts from the reaction of limestone with SO₂ or acid rain, of which the hemi-hydrate (CaSO₄·0.5H₂O) and gypsum (CaSO₄·2H₂O) are most commonly formed dependent on relative humidity³. Dry deposition occurs when sulfation proceeds in sheltered areas, resulting in salt crystallisation and the genesis of ‘gypsum crusts’ (notably over porous and sculpted surfaces), which can in turn fracture the underlying stone^{4,5}. Wet deposition likewise involves initial surface sulfation, but subsequent dissolution of weathered stonework under rainwater, causing more gradual weathering of external limestone facia⁶. Gypsum solubilization and permeation through limestone matrices is held responsible for sub-surface sulfate accumulation during the Industrial Revolution, resulting in higher current decay rates than expected on the basis of modern air pollution levels, the so-called ‘memory effect’⁷, impacting on the selection of replacement limestone used in repairs⁸.

In light of the above, surface coatings to protect limestone against the aggressive chemical environments encountered in urban areas, without irreversibly altering the appearance of historic buildings, are urgently sought^{9,10}. Since water both initiates limestone sulfation and drives wet deposition, several protective hydrophobic treatments have been investigated¹, including acrylic polymers, phosphoric and polymaleic acid¹¹, water-based fluoroalkylsiloxane, polydimethyl siloxanes¹² and methyl triethoxy silanes¹³. However, suitable coatings must

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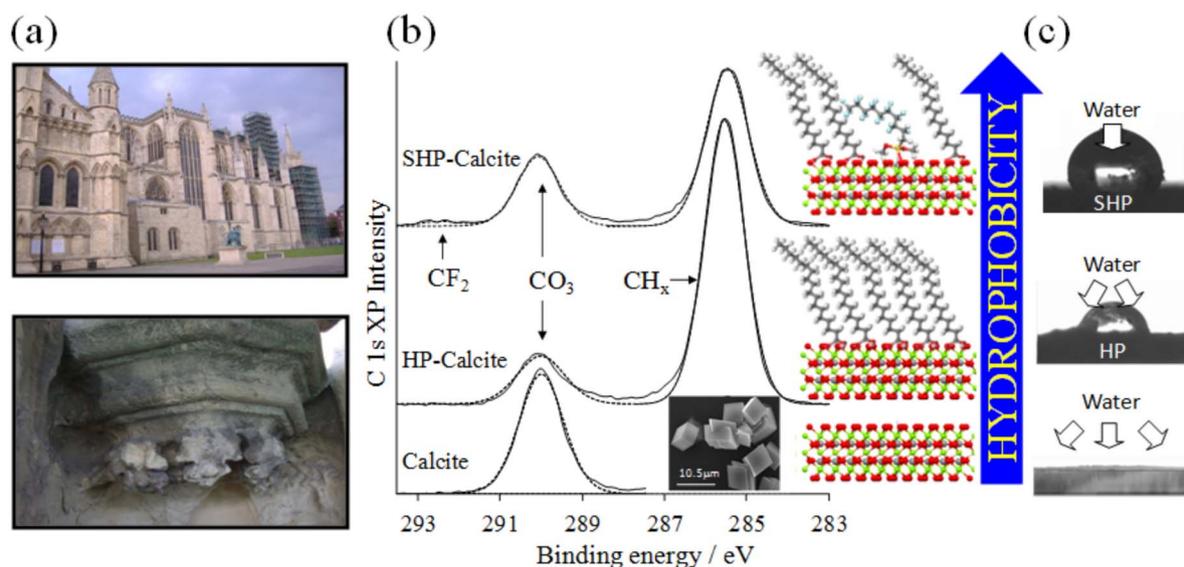


Figure 1 | (a) York Minster, showing scaffolding on East Front (far right) where damage to the famous Great East Window is the focus of a major ongoing development campaign to repair weathered and chemically degraded, discoloured stonework (lower photograph). (b) C 1s XPS spectra for Calcite and coated HP-Calcite and SHP-Calcite; inset shows SEM of the parent calcite whose surface morphology is unaffected by either coating. (c) Corresponding water contact angle measurements for the parent and coated calcites.

confer hydrophobicity without blocking the stone microstructure, thereby allowing masonry to ‘breathe’ and thus reducing salt efflorescence¹, criteria which polymers do not fulfill; indeed swellable polymers and siloxanes may actually further damage eroded stone¹⁴. Linseed oil was historically used to conserve York Minster¹⁵, but darkens limestone and reduces salt permeability, with concomitant crystallization and decay. In line with conservation principles, appropriate surface coatings should not irreversibly modify historic structures. Molecular insight into alternative, environmentally benign and sustainable, surface coatings is thus required to develop new treatments tailored to York Minster¹. Here we report on the remarkable protection afforded by self-assembled fatty acid and fluorinated mixed adlayers towards sulfation of well-defined limestone nanocrystals under carefully controlled dry and humid SO₂ treatments. Self-assembled monolayers of amphiphilic molecules offer ultra-thin conformal coatings able to control the wetting, adhesion and chemical resistance of limestone surfaces without impairing their porosity.

Results

Hydrophobic limestone (HP-calcite) was first synthesised via chemical surface modification¹⁶ of nanocrystalline calcite by immersion in a dilute oleic acid (C₁₇H₃₃COOH) aqueous solution. Super-hydrophobic materials exhibit low water and snow adhesion, and facile dirt removal, mimicking the ‘lotus effect’ whereby certain plant leaves employ surface roughness and wax-like crystals to confer self-cleaning properties¹⁷. A super-hydrophobic limestone (SHP-calcite) was therefore also created via functionalisation of the dry HP-calcite powder with a methanolic solution of C₁₀H₄F₁₇Si(OMe)₃ (1H,1H,

2H,2H-perfluoro-decyltrimethoxysilane (FAS))¹⁸, adapting one-pot methodologies that have never been exploited to confer sulfate resistance. XRD and SEM (Figs. S1 and S2) confirmed the parent limestone phase and morphology were unperturbed by either surface treatment, with 5–7 μm rhombohedral calcite nanocrystallites retained. The integrity of these surface coatings, and their composition and coverage was quantified by XPS (Table 1). Successive grafting with oleic acid and FAS increased the surface carbon concentration by 80 and 24% over that of untreated limestone (Fig. 1b), associated with attachment of alkyl (285 eV binding energy) and CF₂ functional groups (292 eV and 689.4 eV, Fig. S3). FAS partially displaces the pre-adsorbed oleic acid, resulting in a 5 : 1 mixed oleic:FAS adlayer. The fractional oleic acid monolayer coverage can be estimated for the most thermodynamically stable (1014) facet of calcite¹⁹, assuming a surface density of 4.9 Ca²⁺ per nm², and suggests ~0.3 ML are present on HP-calcite, versus 0.1 ML on SHP-calcite. TGA exhibited negligible weight loss due to decomposition of either pure oleic acid or FAS/oleic adlayers, consistent with their presence as ultra-thin surface coatings (Fig. S4). Fig. 1c reveals a sharp increase in surface hydrophobicity determined by contact angle measurement following oleic acid, and subsequent FAS, adsorption. Pure limestone is highly hydrophilic and unable to stabilise a H₂O droplet due to rapid surface wetting. In contrast HP- and SHP-calcites gave water contact angles of 91.3 and 164.1° respectively (Table 1): <90° indicates hydrophilicity; 90–149° hydrophobicity; and >150° superhydrophobicity¹⁷, as anticipated following grafting of non-polar alkyl and fluorocarbon functions.

The impact of these hydrophobic adlayers on subsequent limestone reactivity towards pure SO₂ and humid SO₂ (SO₂/H₂O)

Table 1 | XPS surface composition and contact angles for parent and surface modified calcite samples

Sample	Surface composition/at%					Oleic acid/ML ^a	FAS/ML ^a	Contact angle/°
	O	Ca	C	F	Si			
Calcite	48.4	15.1	36.5	-	-	-	-	0
HP-Calcite	26.5	7.6	66.0	-	-	0.3	-	91.3
SHP-Calcite	35.8	11.1	48.3	4.5	0.3	0.1	0.02	164.1

^a Calculated from CH_x:Ca and CF₂:CH_x ratios from deconvoluted XP spectra see ESI for details.

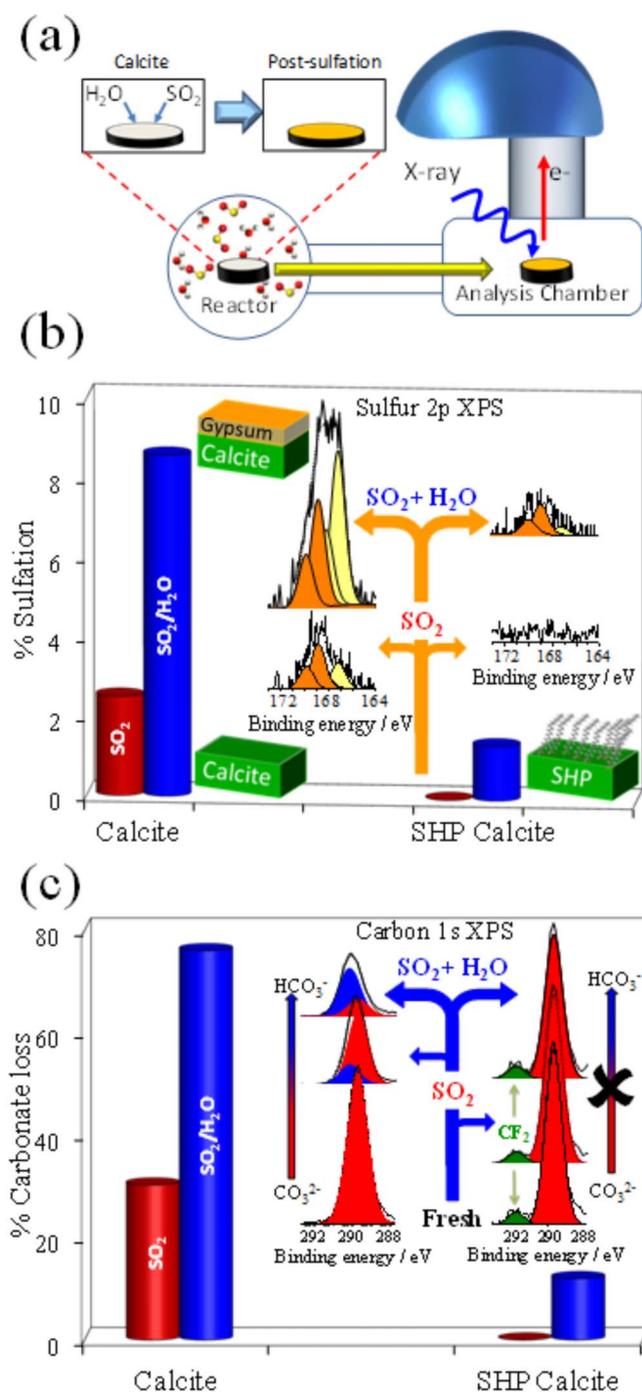
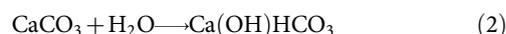
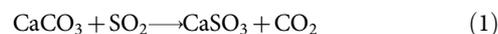


Figure 2 | In-situ XPS of calcite and SHP-calcite surfaces following in-situ exposure to SO₂ or 100 mTorr SO₂ + 18 Torr H₂O for 18 h.

(a) Schematic of the custom built in-situ XPS system used for SO₂/H₂O reactions. (b) Percentage sulfate formation based on S 2p spectra and (c) loss of carbonate based on C 1s spectra. Insets show the resulting fitted S 2p and C 1s XP spectra illustrating the impact of SHP coating on retarding sulfation and carbonate loss.

atmospheres was subsequently explored by *in-situ* XPS. Samples were exposed within the reaction chamber of a custom designed XPS system (Fig. 2a) to high concentrations of SO₂ with and without the presence of water vapor: i.e. either (i) 100 mTorr SO₂, or (ii) 100 mTorr SO₂ + 18 Torr H₂O vapour, for 18 hrs. Thus representing aggressive dry and wet treatments with 1000 ppm SO₂ prior to transfer into the analysis chamber. Fig. 2b and c show the deconvoluted S 2p and C 1s XP spectra, and corresponding quantification of sulfur

species on the surface as well as loss of carbonates. These data demonstrate a striking resistance of SHP-calcite to sulfation compared with the untreated parent limestone. The sulfur XP spectra in Fig. 2b show the formation of two surface sulfoxy species, with 2 p_{3/2} binding energies of 167.2 (SO₂) and 168.9 eV (SO₂/H₂O), attributable to CaSO₃·0.5H₂O and CaSO₄·0.5H₂O²⁰ respectively. Surface sulfation of untreated calcite is also enhanced more than three-fold in the presence of H₂O. The carbon spectra of untreated limestone show a concomitant significant loss of surface CO₃²⁻ (289.5 eV) following reaction with SO₂ or H₂O/SO₂, and the emergence of a new 290 eV feature characteristic of HCO₃⁻; the latter favored by SO₂/H₂O treatment. In contrast, surface carbonate in the SHP-calcite appears completely stable. These observations are consistent with the proposed reaction of SO₂ and H₂O with limestone (and passivation thereof by SHP) via:



We attribute the stability of our mixed oleic acid/FAS superhydrophobic adlayer to inhibition of H₂O adsorption, and thus formation of surface HCO₃⁻ (2) and subsequent reaction with SO₂ (3). Direct site-blocking of Ca²⁺ via coordination to COO⁻ would also prevent (1) under anhydrous conditions.

The ability of these hydrophobic adlayers to protect limestone against sulfation under aqueous acid conditions was further explored by ex-situ XRD and XAS to quantify reactively-formed crystalline and amorphous Ca compounds. Parent calcite, HP-calcite and SHP-calcite powders were stirred in 0.1 M H₂SO_{4(aq)} for 1 min, then rapidly filtered and dried prior to analysis. Inter-conversion of crystalline calcite (23.1, 29.4, and 39.5°) to gypsum (20.7, 23.4 and 29.1°) was monitored by XRD from the area of their respective reflections and quantified in Fig. 3a. All fresh samples exhibited identical diffraction patterns characteristic of pure calcite (Fig. S5). The principal (104) reflection of the fresh parent calcite at 29.4° completely disappears upon treatment with 0.1 M H₂SO₄, coincident with the appearance of the principal gypsum reflection at 29.1°. In contrast, HP and SHP-calcite materials show strong resistance towards acid sulfation, respectively forming only 24 and 17% nanocrystalline gypsum. Since XAS is an averaging technique probing the local chemical environment, it offers complementary insight into the overall extent of limestone sulfation via loss (growth) of both crystalline and amorphous calcite (gypsum) phases. Calcium K-edge X-ray Absorption Near Edge Spectroscopy (XANES) provide characteristic fingerprints for the Ca²⁺ coordination environment in calcite and gypsum²¹. XANES analysis of the parent calcite, HP-calcite and SHP-calcite after treatment with 0.1 M H₂SO₄ are shown in Fig 3b. Linear combination fitting to reference compounds shows that sulfated HP- and SHP-calcite retain approximately five times as much calcite as unfunctionalised sulfated limestone (Fig 3c), with the latter amorphous. There is good agreement between the amount of crystalline gypsum measured by XRD and that observed by XANES, suggesting the reactively-formed gypsum is largely nanocrystalline. Small amounts of Ca(OH)₂ were also required to achieve good XANES fits, although this phase was undetected by XRD indicating this may be surface-localised. The enhanced resistance of HP- and SHP-calcites towards wet sulfation is maintained even under a harsher 1.0 M H₂SO_{4(aq)} treatment sufficient to fully convert the parent calcite to gypsum.

Discussion

The impact of hydrophobic coatings on calcite sulfation can be accounted for by the interplay between acid-initiated Ca²⁺ dissolution and consequent gypsum precipitation (Fig. 4). Under acidic pH,

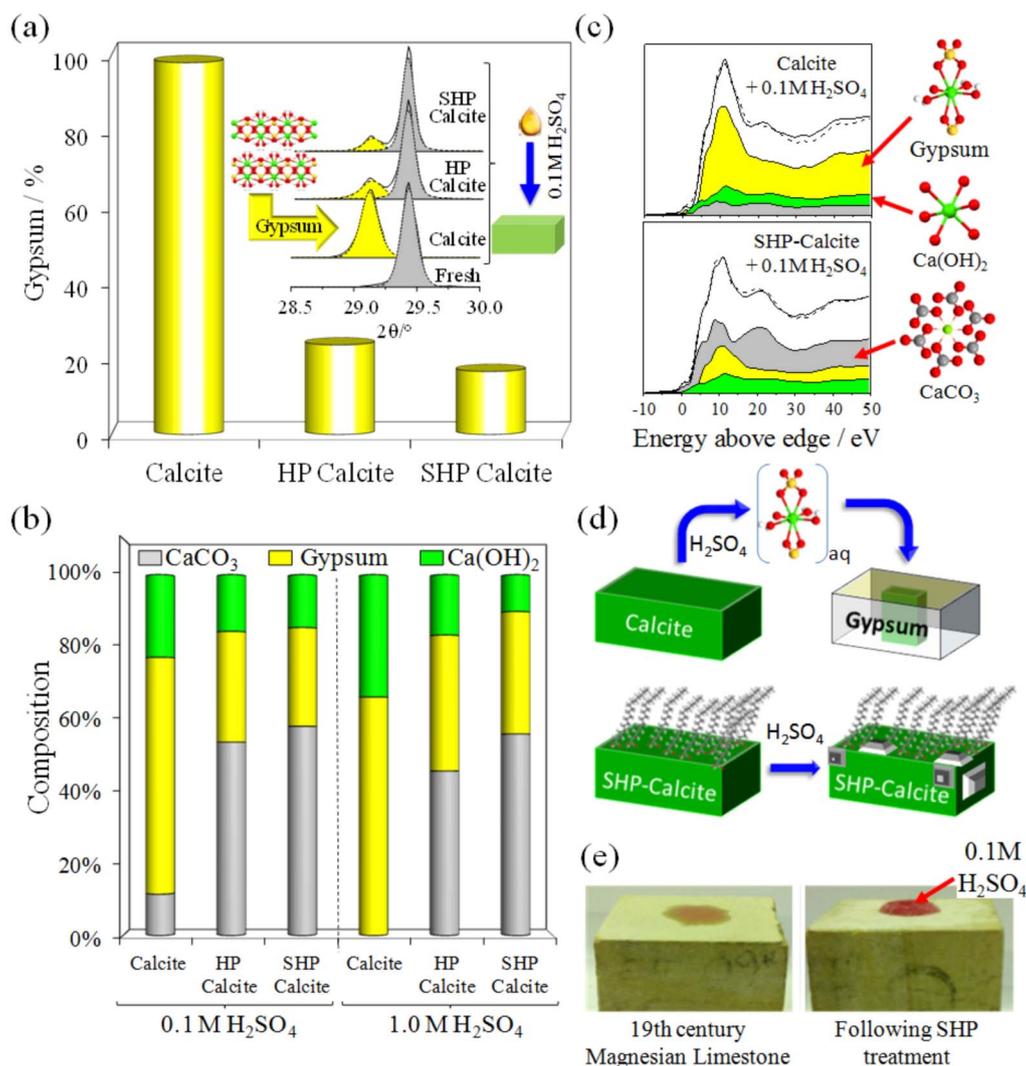


Figure 3 | Impact of hydrophobic coatings on protecting calcite against sulfation under aqueous SO_4^{2-} environments. (a) Quantification of powder XRD and (b) fitted Ca K-edge XANES of fresh and HP-/SHP-calcite treated with H_2SO_4 for 1 min. (c) exemplar least squares fits of calcite and SHP-calcite Ca K-edge XANES to standard compounds (crystal structures of $CaCO_3$, $Ca(OH)_2$, and $Ca(SO_4)_2 \cdot 2H_2O$ (gypsum) shown for reference). (d) Cartoon illustrating calcite dissolution and subsequent gypsum deposition, and role of hydrophobic coating in site-blocking/repelling acid sulfation. (e) Photograph of H_2SO_4 repellent, SHP-coated 19th century magnesian limestone from the East Front of York Minster (artificially coloured with methyl red to aid the eye).

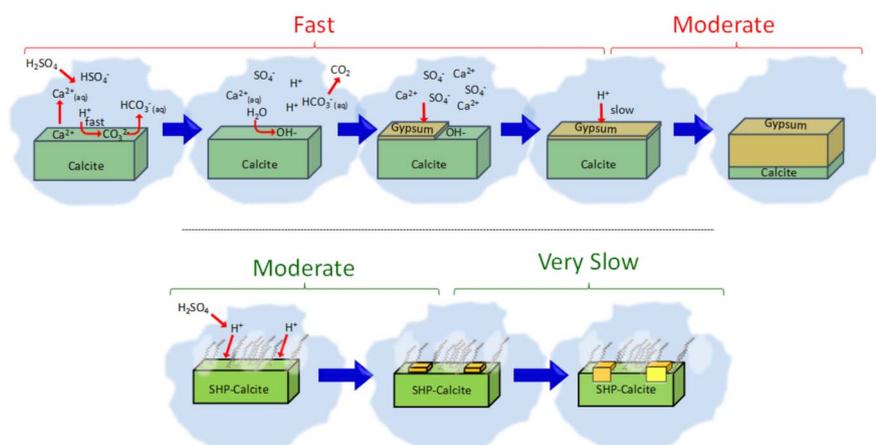
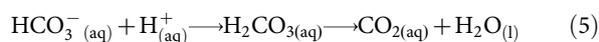
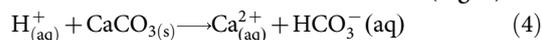


Figure 4 | Proposed model for gypsum formation over calcite and SHP-calcite following exposure to H_2SO_4 .



dissolved $\text{Ca}^{2+}(\text{aq})$ will precipitate as a gypsum overlayer onto the residual calcite as the solubility limit is reached¹, passivating the surface and slowing further Ca^{2+} dissolution^{22,23}. This work shows that hydrophobic coatings retard gypsum formation, likely through inhibiting H^+ attack of the underlying calcite. However, since our coatings do not fully encapsulate the parent calcite crystallites, small amounts of gypsum still form upon immersion in 1 M H_2SO_4 , possibly as islands between hydrophobic oleic acid/FAS domains as illustrated in Fig-3d.

Gypsum formation from calcite is proposed to proceed in two steps: acid initiated dissolution via reactions (4) and (5); followed by precipitation of gypsum crystallites onto remaining calcite nucleation sites (6), as the solubility limit for Ca^{2+} and SO_4^{2-} ions is reached²³. Formation of a gypsum overlayer will retard subsequent further H^+ penetration and associated Ca^{2+} dissolution (Fig. 4)²².



We propose the SHP coating hinders the initial H^+ attack and Ca^{2+} dissolution in reaction 4, via site-blocking and increased surface hydrophobicity. However, limited calcite dissolution and subsequent deposition of small gypsum islands may occur in regions scattered in between Oleic acid/FAS protected areas (recall the overall Oleic acid/FAS surface coverage is ~ 0.12 ML), consistent with the partial surface sulfation observed for SHP-calcite. Growth of such gypsum islands would be restricted by their lateral domain sizes, which would be expected to be independent of acid strength (provided the SHP coating remained intact), resulting in common surface gypsum concentrations for both 0.1 or 1.0 M H_2SO_4 treatments - as observed.

The practical application of a SHP coating to protecting historic limestone was finally assessed using 19th century magnesian limestone obtained from York Minster. Fig 3e shows photographs of untreated and treated stone exposed to 0.1 M H_2SO_4 ; wetting of the SHP-treated surface is significantly reduced, which should prevent long-term sulfate permeation. In conclusion, oleic acid and FAS self-assembled monolayers can be used to generate hydrophobic and super hydrophobic coatings able to protect calcite against both gas and aqueous phase sulfation. Such coatings could have a significant impact on stone conservation, affording readily applied, conformal barriers able to protect historic limestone from weathering by gas phase and particulate sulfur oxide pollutants.

Methods

HP-calcite was synthesised by dispersing 20 g CaCO_3 in 45 ml of deionised water at 75°C for 2 mins, after which 0.442 g of oleic acid was added and the slurry stirred for a further 30 min, then filtered and dried for 18 h in a vacuum oven at 80°C. SHP-calcite was prepared from a solution of 200 ml of ethanol containing 40 μl of deionised water and 1 g of 1H,1H,2H,2H-perfluorodecyl-trimethoxysilane (FAS) which was stirred for 1 h before adding 2 g of HP-calcite and stirring for a further 1 h. The resulting solid was filtered and dried for 18 h at 80°C.

In-situ gaseous sulfation was performed utilising a custom-designed Kratos Axis Ultra XPS system at Iowa University, in which samples were exposed in the reactor cell to 100 mTorr SO_2 , or simultaneously to 100 mTorr SO_2 and 18 Torr H_2O , prior to transfer of treated samples to the analytical chamber. Liquid phase sulfation was performed by immersion of 0.5 g of calcite sample in 100 ml solutions of 0.1 M H_2SO_4 or 10 ml of 1.0 M H_2SO_4 ($\text{Ca}:\text{SO}_4$ stoichiometry at 1:2) for 1 min, after which the sample was rapidly filtered and dried under vacuum. Ex-situ Ca and S K-edges fluorescence XAS measurements were performed on beam-line B18 of the Diamond synchrotron²⁴.

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Author contributions

K.W. and A.F.L. conceived the overall concept for the project. R.A.W. prepared, analysed and characterised the materials. J.W., G.C. and A.D. assisted with acquisition of XAS measurements on B18. V.G. conceived and designed the in-situ XPS system and oversaw measurements along with J.B. and G.R. who conducted the in-situ sulfation experiments with R.A.W. Overall data analyses, project planning and paper preparation were largely conducted by K.W. and A.F.L. with input from V.G. and J.B.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

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