

Model study of initial adsorption of SO₂ on calcite and dolomite

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Abstract

The rate of calcareous stone degradation is to a significant extent controlled by their surface chemistry with SO₂. Initial surface sulphite is converted to a harmful gypsum upon, e.g. NO₂ catalysed oxidation. However, it has been observed by scanning electron microscopy that the lateral distributions of gypsum crystals differ between calcitic and dolomitic marbles. The first-principles density functional theory is employed to understand the origin of these fundamentally different morphologies. Here, the stability differences of surface sulphite at calcite CaCO₃ (s) and dolomite Ca_xMg_{1-x}CO₃ (s) are determined. A qualitative difference in surface sulphite stability, favouring the former, is reported. This is taken to imply that calcitic micro-crystals embedded in a dolomitic matrix act as sinks in the surface sulphation process, controlled by SO₂ diffusion. The subsequent formation of gypsum under such conditions will not require SO₄²⁻ (aq) ion transport. This explains the homogeneous distribution of gypsum observed on the calcitic micro-crystals in dolomite. In contrast, sulphation on purely calcitic marbles never reaches such high SO₂ coverage. Rather, upon oxidation, SO₄²⁻ (aq) transport to nucleation centres, such as grain boundaries, is required for the growth of gypsum crystals.

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1. Introduction

Calcareous stones comprise a major component in historic buildings and monuments, many of which have suffered severe damage due to sulphur induced deterioration. Air born SO₂ is known to adsorb on the calcareous stone surface, whereby a thin film of calcium sulphite is formed in humid air, i.e. CaSO₃·1/2H₂O (s) [1,2]. While this surface species does not reduce the strength of the stone, upon oxidation, e.g. by ozone or by molecular oxygen in the

presence of NO₂ which serves as a catalyst, gypsum, mainly CaSO₄·2H₂O (s), is formed. The harmful effects of gypsum formation with respect to the resistance of marbles to weathering are well documented [3]. Aesthetic properties of marbles and tradition are two main reasons for the continued use of this material also in new buildings. Thus, it becomes important to find properties by which marbles of different morphologies and chemical compositions may be classified with respect to resistance to gypsum formation induced deterioration.

Surface chemical differences of natural stones at the air–surface interface are decisive to their rates of degradation. In case of the carbonates, the initial formation of calcium sulphite hemi-hydrate amounts

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to the replacement of a CO_2 molecule for SO_2 in that $\text{CO}_3^{2-}(\text{surf}) + \text{SO}_2(\text{g}) \rightarrow \text{SO}_3^{2-}(\text{surf}) + \text{CO}_2(\text{g})$. It becomes important to investigate the stability difference of surface sulphites at calcite $\text{CaCO}_3(\text{s})$ and dolomite $\text{Ca}_x\text{Mg}_{1-x}\text{CO}_3(\text{s})$ calcareous stones, since these are the most common rock-forming carbonates, accounting for more than 90% of the natural carbonates.

Laboratory tests to quantify the absorption of SO_2 at calcareous stone surfaces [4], and to monitor by means of diffuse reflectance infrared spectroscopy the initial sulphation and subsequent sulphation upon, e.g. catalytic oxidation of $\text{S(IV)}\text{--}(\text{VI})$ in the presence of NO_2

[5] at dry and humid conditions have been undertaken previously.

Recently, using SEM, we have observed that there are differences in the lateral distributions of gypsum micro-crystals on calcitic and dolomitic marbles. Thus, on pure calcitic marble, such as Carrara Bianco Venato Gioia, gypsum tends to form predominantly at grain boundaries and triple-grain junctions (Fig. 1). In contrast, on dolomitic marbles, such as Thassos marble, in addition to gypsum growth at pores and cracks, gypsum crystals were found to predominantly cover the surfaces of purely calcitic micro-crystals present in the dolomitic marble matrix (Fig. 2).

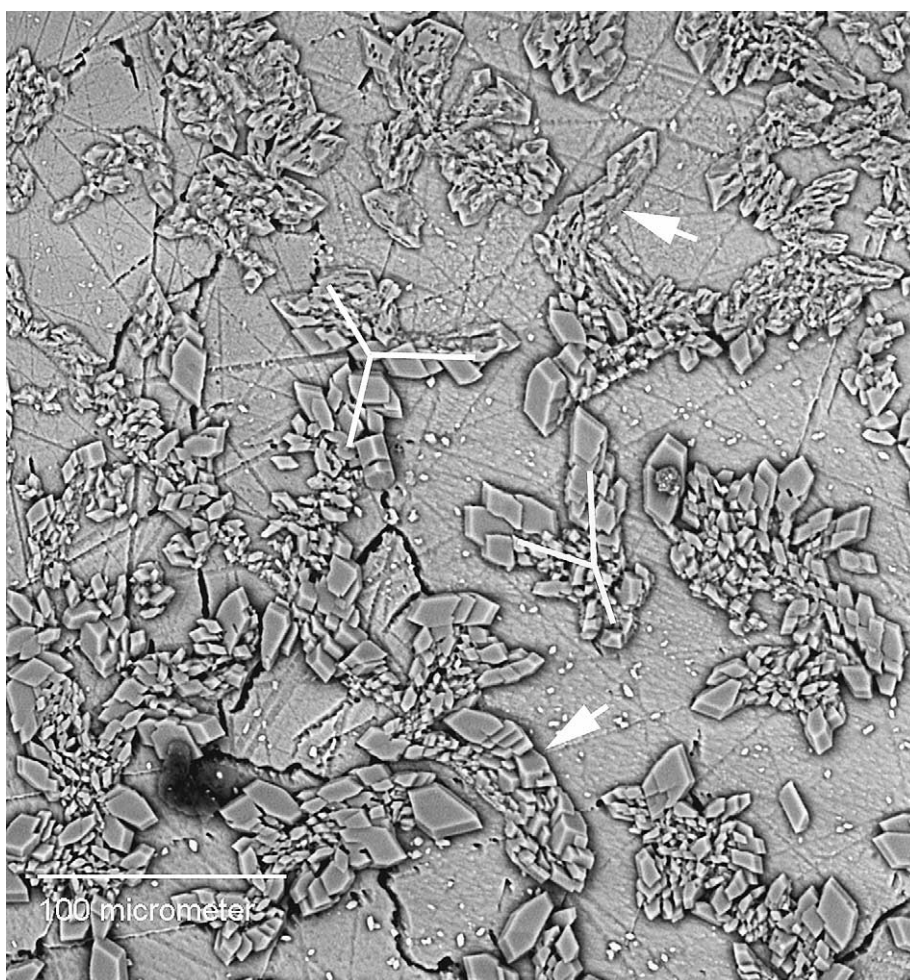


Fig. 1. Lateral distribution of gypsum on pure calcitic marble. The main occurrence of gypsum at triple-grain junctions and grain boundaries is marked by lines and arrows, respectively.

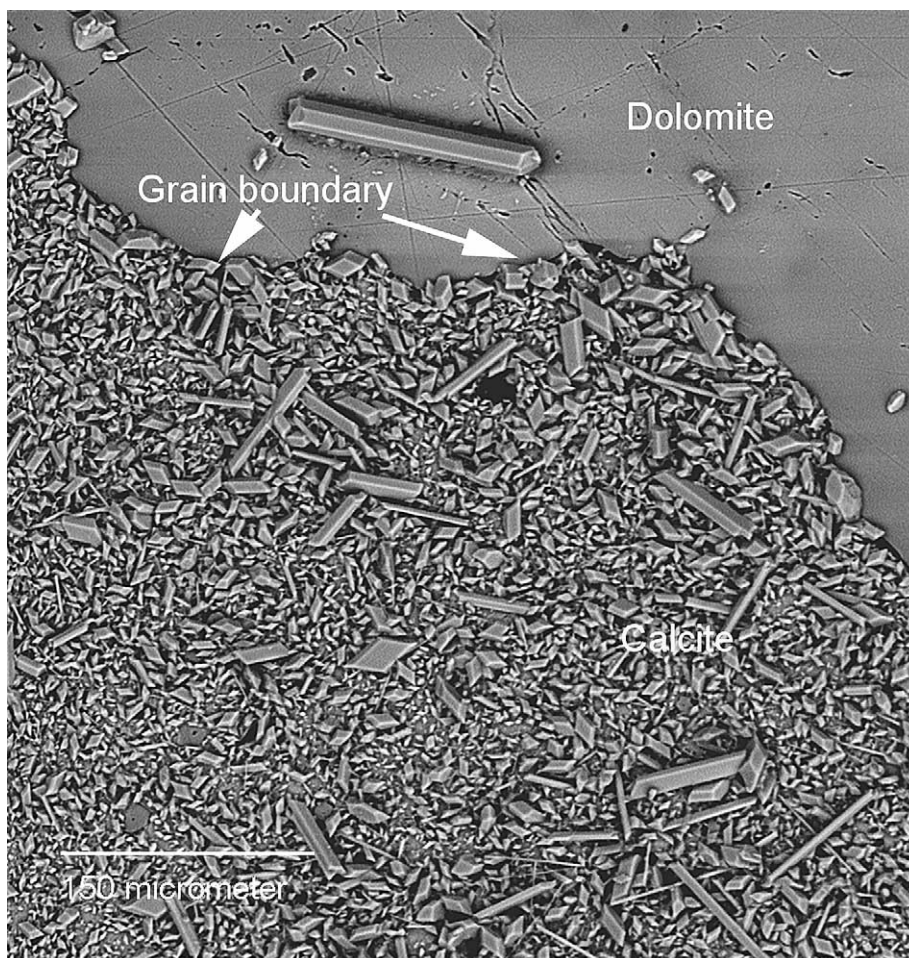


Fig. 2. Pure calcitic micro-crystals present in the dolomitic marble are totally covered by gypsum crystals of various sizes whereas dolomitic micro-crystals are almost free of gypsum.

The understanding of the origin of the fundamentally different morphologies of the gypsum-calcite system in calcitic marble matrix as compared to dolomitic marble matrix is sought here by means of first-principles density functional theory. In particular, differences in the initial sulphation process are reported.

2. Modelling

Density functional theory has been applied to unravel fundamental aspects of the sulphation of marbles. The computational procedure involves selecting an

appropriate crystal plane, i.e. being electro-neutral in that the sum of positive and negative charges is equal. In this study, the 110 surface was selected. The selected unit cell possesses two symmetry inequivalent surface CO_3^{2-} ions (cf. Figs. 3a,b and 4a,b), each of which have been subjected to replacement by SO_3^{2-} . The surface reaction corresponds to detachment of CO_2 (g) from a surface O^{2-} site and the attachment of an SO_2 molecule. The so-called slab-type calculations have been undertaken meaning that the surface has been modelled by means of a semi-infinite slab, where periodic boundary conditions were imposed. All ions at the surface were subject to geometry optimisation, whereas the geometries of

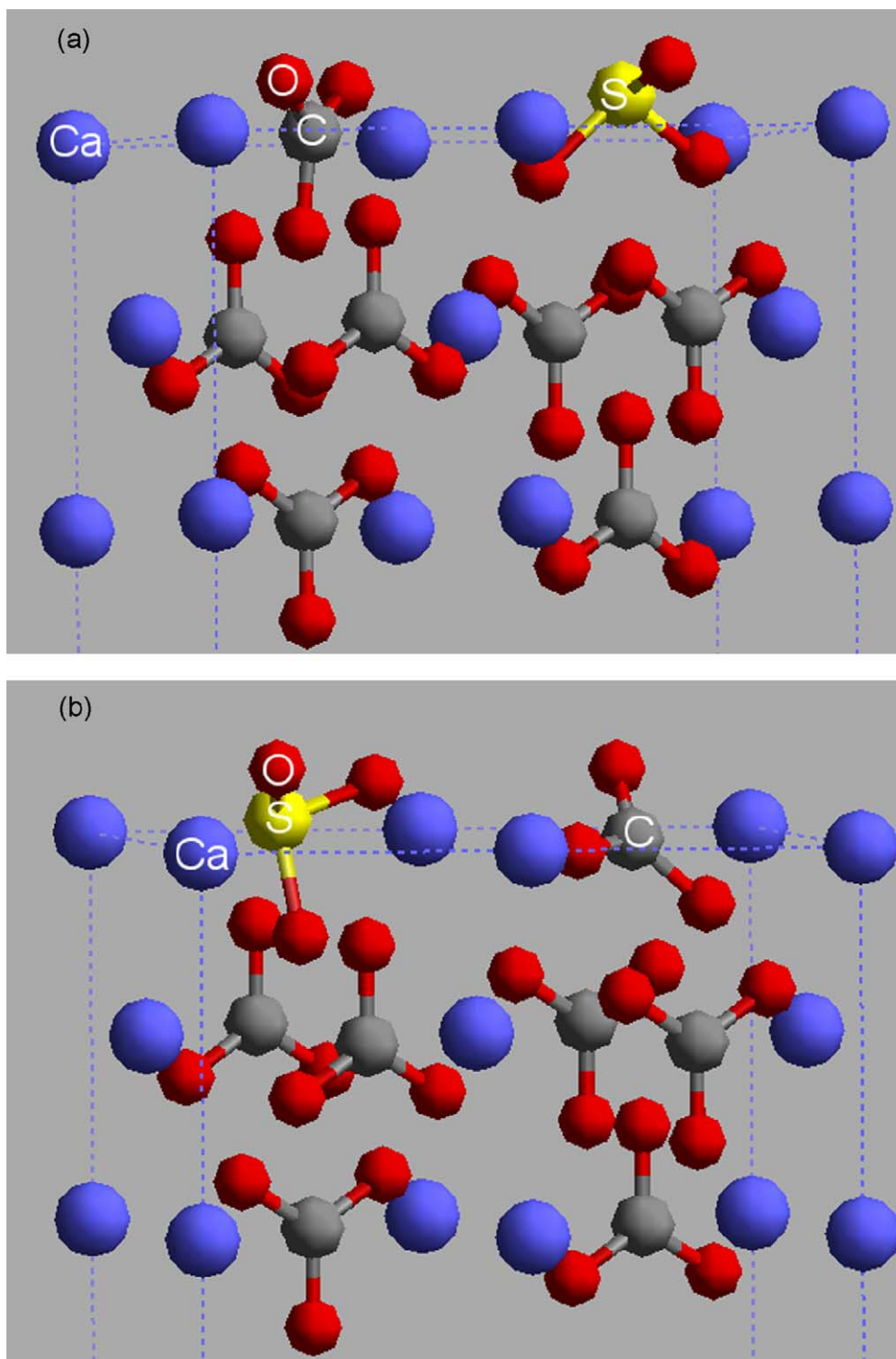


Fig. 3. Substitution of CO₂ by SO₂ on calcite: (a) site I and (b) site II.

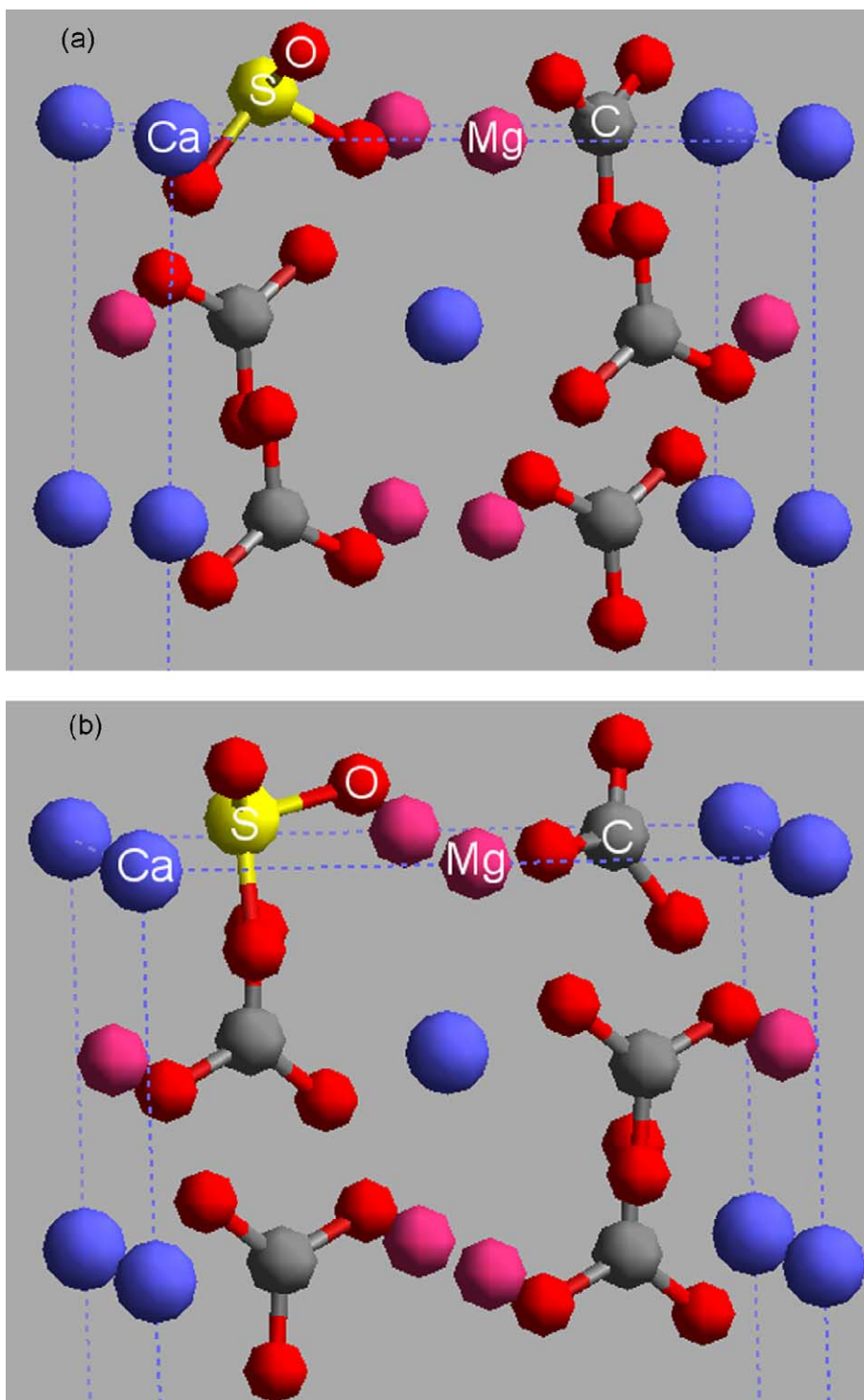


Fig. 4. Substitution of CO_2 by SO_2 on dolomite: (a) site I and (b) site II.

the subsurface ions were kept frozen in their bulk positions. The Perdew–Burke–Entzerhoff generalized gradient approximation improvement to the local density approximation, the GGA-PBE density functional [6], as implemented in the plane-wave based CASTEP program package [7] inside Cerius² [8]. The Vanderbilt non-local ultra-soft effective core potentials [9] were applied, meaning that the valence electrons are described explicitly whereas the core electrons are described effectively. A 300 eV kinetic energy cut-off was employed consistently in the present work. This cut-off value determines how well the valence regions in the immediate vicinity of the atomic cores are described. This description has been validated independently and extensively in two previous studies on the surface nitration of BaO (s), and on the CO oxidation on Co₃O₄ (s) [10,11].

3. Results and discussion

The binding energies for the surface CO₃^{2−} ions and surface SO₃^{2−} ions for the two symmetry inequivalent sites in the unit cell are listed in Table 1. Structural properties of the surface carbonates and sulphites, and M–O bond distances are displayed in Table 2. In all cases, the substitution of CO₂ for SO₂ at an O^{2−} site is preferred, but it has been calculated that greater exothermicity is associated with the replacement in the CO₃^{2−} ion, which has two oxygens pointing into the surface (site I) as compared to the CO₃^{2−} ion, which has only a single oxygen pointing into the surface (site II). The differences between the two exothermicities are approximately 57 and 45 kJ/mol on calcite and dolomite, respectively, and thus gives the magnitude of the stabilisation energy for the preferred site. While comparing the absolute stabilities related to the formation of half a monolayer of sulphite on calcite as compared to dolomite, we find

Table 1
Calculated binding energies for sulphite on calcite and dolomite

	Binding energy (kJ/mol)	
	Site 1	Site 2
Calcite	130	71
Dolomite	73	26

Table 2
Calculated bond lengths for carbonate and sulphite on calcite and dolomite

	Bond length (Å)	
	Calcite	Dolomite
C–O (site I)	1.247; 1.325; 1.328	1.269; 1.309; 1.312
C–O (site II)	1.284; 1.285; 1.314	1.276; 1.285; 1.325
S–O (site I)	1.536; 1.552; 1.557	1.511; 1.551; 1.571
S–O (site II)	1.518; 1.521; 1.566	1.511; 1.530; 1.573
Reference sulphite		
Ca–O (site I)	2.283 2.330	2.397 2.366
Ca–O (site II)	2.190 2.129	2.225 2.155

Ca–O shortest bond lengths are presented for reference minerals and after sulphation process.

substantial enhancement in the former. Thus, 130 kJ/mol exothermicity for the substitution at site I of calcite should be compared to 73 kJ/mol at the same site of dolomite. Similarly, 71 kJ/mol exothermicity at site II on calcite, should be compared to 26 kJ/mol at the same site on dolomite. Regarding the structural information, the single most important property to focus at is the degree of symmetry breaking in the C–O and S–O bond distances. Whereas three fairly equivalent distances are observed in the bulk, obviously, it is the anisotropic environment of a surface site, which is the cause of the variations in bond distances observed within one and the same surface anion, and enhanced IR activity with the lowering of molecular symmetry is expected.

How would the above results contribute to the understanding of the reason for the difference in the lateral distribution of gypsum on calcitic and dolomitic marbles? It is expected that initial sulphation would occur fairly equally on the dolomitic and calcitic crystal surfaces, whereas with time the 110 surface of calcite would act as a sink for dolomitic surface sulphite in a mixed calcite calcite/dolomite material. Subsequently, e.g. NO₂ catalysed oxidation of sulphite to sulphate would result in uniformly distributed gypsum crystals on the calcitic micro-crystal. In contrast, on pure calcitic marble, the surface concentration of sulphite never reaches the high levels attained on the dolomitic marble. Rather, formation of sulphate

ions would be followed by migration of these ions in the surface water film to grain boundaries, cracks and triple-grain junctions where gypsum would form. The cause for difference in lateral gypsum distribution between dolomitic and pure calcitic marbles would thus be found in the difference in surface concentrations, being in the high and low coverage limits, respectively.

4. Conclusions

The differences in lateral gypsum distributions between dolomitic and calcitic marbles are to a significant extent controlled by their surface chemistry with SO_2 . Implementation of the first-principles density functional theory gives explanation to the origin of these fundamentally different morphologies. The stability of surface sulphite at calcite CaCO_3 (s) is two times higher than that of dolomite $\text{Ca}_x\text{Mg}_{1-x}\text{CO}_3$ (s). This is taken to imply that calcitic micro-crystals embedded in a dolomitic matrix act as sinks in the surface sulphation process, controlled by SO_2 diffusion. The subsequent formation of gypsum under such conditions will not require further SO_4^{2-} (aq) ion transport. This is taken to explain the homogeneous distributions observed on the calcitic micro-crystals in dolomite. In contrast, sulphation on purely calcitic marbles never reaches such high SO_2 coverage. Rather, upon oxidation, SO_4^{2-} (aq) transport to

nucleation centres, such as grain boundaries, is required for gypsum crystal growth.

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