JOURNAL OF
Materials
CHEMISTRY
Feature Article

New nanocomposites: putting organic function "inside" the channel walls of periodic mesoporous silica

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Received 3rd February 2000, Accepted 13th March 2000
Published on the Web 30th May 2000

Nature's accomplishments are inspiring chemists to design new materials based on biologically formed organic and inorganic structures that have been optimized over evolutionary timescales. A recent breakthrough in biomimetic materials chemistry has seen the fusion of organic and inorganic chemistry within the channel walls of periodic mesoporous organosilicas (PMOs). The incorporation of organic moieties in the walls of the liquid crystal templated mesoporous silica confers unique chemical, physical and mechanical properties upon the materials. In this Feature Article, we provide an overview of this new class of materials and propose a classification scheme that will distinguish the PMOs from other mesoporous organic–inorganic hybrid materials.

Traditionally, composites have been fabricated from preformed components in a process that organizes them in a matrix, and with a particular arrangement.[1] Integration is often a "top-down" procedure and so the structure and composition of interfaces between the constituent parts, which can have a profound effect on the properties of the composite, are not usually under molecular scale control. Moreover, the material may be divided into macroscopic domains with sizes on the order of micrometers or millimeters. An appealing solution to the interface problem is through biomimetic materials chemistry, which, by contrast, is purely synthetic and operates from the "bottom-up".[2–5] The idea is to co-assemble organic and inorganic precursors into a nanocomposite material with molecular level command over interfaces, structure, and morphology. In this regard the composites field is beginning to "take shape".[6] Specifically, self-assembling organic–inorganic hybrid materials are beginning to emerge in the literature, with "bottom-up" command of the interface between organic and inorganic components, structure control from angstroms to microns, composition control over a large portion of the periodic table, hierarchical construction and morphologies spanning all three spatial dimensions.[7] Such "designer" nanocomposite materials inspire interest in many fields, from biomaterials to pharmaceuticals, aerospace to energy, automotive to construction, electronics to photonics.

In this context, there is definitely a notable recent change in the nature of interfaces between materials used to achieve specific properties, functions and applications. It is also apparent that while methods for the preparation of well-defined interfaces between inorganic–inorganic and organic–organic materials are fairly mature, techniques for making well-defined molecular-scale interfaces between inorganic "hard" and organic "soft" materials are less familiar. The effects of their structure and quality on the properties of materials are just beginning to emerge. One could say that "hard" materials science is going "soft" through materials chemistry.

To amplify, composite materials combine the properties of two or more components that have been selected to maximize aspects of mechanical performance. Materials science traditionally evaluates different compositions and architectures to optimize properties like hardness, toughness, stiffness, strength, and damage tolerance. Classes of materials often used in composites include metals, ceramics, glasses, elastomers, and polymers. Fiber and laminate composite constructions are the most common, the designs of which are often based on the architecture of composites found abundantly in animals and plants. This is because Nature has solved the problem of designing and synthesizing composite materials with structures that have been optimized to make them hard, tough, and strong enough to house, protect, and brace living

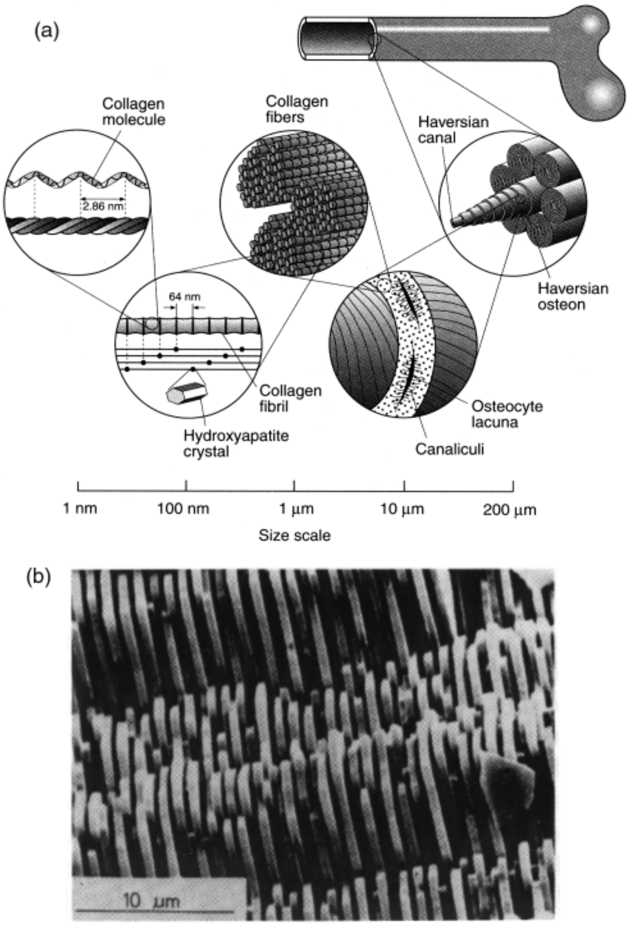


Fig. 1 Biomineralized inorganic crystals. (a) Scheme illustrating the complex hierarchical structure of bone. The integration of collagen and hydroxyapatite at several length scales gives bone its excellent structural properties. (b) Electron micrograph showing the microstructure of the nacre of abalone shell. The inter-digitated array of aragonite crystals in an organic polymer matrix (*ca.* 5 wt% polymer) creates a material that is twice as hard and more than 1000 times as tough as aragonite alone.[5f] (Part (a) was reprinted from P. Ball, *Made to Measure*, Princeton University Press, Princeton, 1997, p. 198; part (b) was reprinted from ref. 9, p. 500.)

DOI: 10.1039/b000950o

organisms.[8] Optimization of these properties serves to enhance the chances of survival. Since organisms have spent millions of years optimizing structural biomaterials for performance, durability, and appearance, it is reasonable that chemists interested in designing functional materials are developing a curiosity about how Nature has solved problems that are often encountered in materials science and technology.

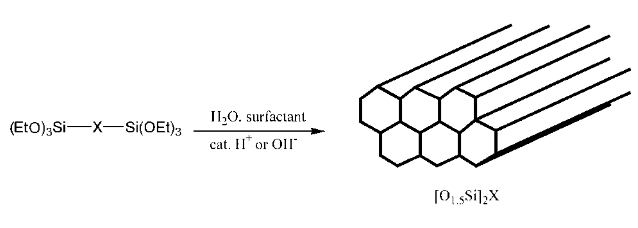
A contemporary challenge is technology transfer—identification of questions in materials chemistry and connecting them with answers from Nature. Synergism between Nature and materials chemistry should have considerable practical value. Take, for example, the coccolith microskeleton, the magnetotactic bacteria biogeomagnetic compass, the fish gravity and sonar device, the mollusc shell, and animal teeth and bone—they all exhibit miraculous shapes, hierarchical construction principles, functional specificity, and obvious practical utility, Fig. 1.[9] Their formation and impressive properties have inspired chemists to take a biomimetic approach to the synthesis of materials.

From the outpouring of materials research with a biomimetic theme it is clear that materials chemists have recognized the benefits to be derived from molecular level control of interfaces between inorganics and organics. The synergy between biological and chemical building methods is leading to new classes of hybrid materials with remarkable structures and properties that portend a myriad of new functions and utility.

The focus of this Feature Article is on a new class of nanocomposite materials that have emerged from a fusion of organic synthesis, sol–gel chemistry and supramolecular assembly. They are referred to as periodic mesoporous organosilicas, PMOs.[10,11] What is so unique about these materials is that organic functionality has for the first time been integrated "inside" the channel walls of a silica-based material that exhibits crystalline mesoporosity.[11–14]

Periodic mesoporous silica (also known as MCM-41) emerged in 1992 as the first demonstration of a new strategy for materials synthesis—liquid crystal templating.[15,16] Biology relies on templating methods for the formation of many structures, such as the crystallization of apatite in collagen to make bone, where the nucleation and growth is controlled by interfacial interactions between the organic and inorganic components (Fig. 1a). Using lyotropic liquid crystalline surfactants and phase separated block copolymers to template the assembly of an inorganic framework, materials composed of oxides, sulfides, phosphates, and other inorganic compositions have been made.[17,18] They boast monodisperse, hexagonally ordered channels with diameters tunable with angstrom control between 2–100 nm. This extraordinary size control makes these materials appealing as hosts for catalysts and nanomaterials, and in other applications such as molecular separation.

Adding organic groups to mesoporous silica, by post-synthetic grafting of $XSi(OR)_3$ compounds (X and R are organic groups), for example, yields new types of functional inorganic–organic hybrid composites.[19] These groups may also be incorporated during the synthesis by including $XSi(OR)_3$ groups as one of the silica sources in the preparation.[20] The incorporation of organic groups into mesoporous materials is an attractive route to forming new, functionalizable materials that may have specialized applications—"smart materials".



Scheme 1

Unfortunately, these routes to inorganic–organic hybrid mesostructures suffer from several drawbacks: there is a limit of *ca.* 25% $[XSiO_3]$ groups in the synthetic route before collapse of the mesostructure; the organic groups are inhomogeneously dispersed in the materials, often clumped at the pore mouth and particle surface of the mesoporous silica; and the organic groups occupy pore space. Moreover, by analogy with polymer science, the organic groups are "side chains" and probably have little influence on the mechanical properties of the resulting mesoporous inorganic framework.

In 1999, two other groups (Japan, USA) and we independently reported the synthesis of a new class of mesoporous inorganic–organic hybrid materials, PMOs.[11–14] These materials are formed by the condensation polymerization of $(RO)_3Si–X–Si(OR)_3$ precursors in the presence of a liquid crystalline template (Scheme 1). This yields well-defined hexagonal symmetry mesoporous materials with bridge-bonded organic groups *within* the walls of periodic mesoporous silica. Actually, the materials prepared by Stein *et al.* possessed wormhole structures rather than the ordered hexagonal-symmetry mesoporous structures.[14] Examples of PMOs brought to practice so far have X = methylene, ethane, ethylene, benzene, thiophene, acetylene, and ferrocene.[11–14,21]

There are many foreseeable advantages to these materials, where the organic groups have been incorporated directly into the framework. First, the organic groups are on the perimeter of the channels, not blocking or occupying pore volume. Second, the properties of the framework (*e.g.* optical, electronic, hydrophobicity) may be modified by changing the bridging organic group. By having the organic component in the "backbone" of the framework and not just as a "side group", the hardness and density of the PMO may be varied. Due to the flexibility of organic spacers, monoliths and films may be less prone to cracking. Third, the physical and mechanical properties of the mesoporous framework may be modified by chemical reaction with the bridging group in the framework (*e.g.* nucleophilic substitution) or with a stimulus (*e.g.* fluorescence quenching with an analyte). Fourth, a greater fraction of the organic species may be placed in the framework before loss of order in the mesostructure occurs. Fifth, the organic groups are homogeneously distributed in the material.

Hybrid PMOs with organic or organometallic groups in the framework may be useful for several applications. For example, by including chiral organics in the walls, molecular recognition in the size-tunable channel space may permit new types of asymmetric syntheses and chiral separations. Incorporation of lanthanide complexes in the wall may afford mesoporous lasing materials. If molecules with large hyperpolarizabilities are used as the bridging group and aligned in the wall, mesoporous materials with large nonlinear optical responses may be obtainable. Mesoporous materials with strained rings in the walls may be useful as a new class of explosives or initiators for ring-opening polymerization. There are many opportunities for periodic mesoporous organosilicas with "designer" functional organics "inside" the framework.

PMOs are distinct from organosilica-based xerogels, which are amorphous materials prepared from the condensation of $(RO)_3Si–X–Si(OR)_3$ precursors in the absence of a surfactant template.[22–24] Although xerogels have attracted attention for potential application in catalysis, their poly-disperse pore size distributions have limited their use where size and shape selectivity are desired.

To be specific, PMOs are a novel class of hybrid silica-based materials having ordered mesopores and "bridge bonded" organic functional groups located "within" the silica walls. To distinguish them from previously existing hybrid organosilica materials, in which "terminally bonded" organics are grafted to the silica wall and protrude into the mesopores, we have developed a simple classification scheme. The mesoporous hybrid materials are prepared by a generalized synthesis involving the surfactant-templated co-assembly of an appropriate surfactant, an acid or base catalyst, an aqueous or non-aqueous solvent, and a mixture of sol–gel precursors comprised of $(RO)_4Si$ and $[(RO)_3Si]_mX$, where R is an alkyl group, X represents an organic moiety, and $m \geqslant 1$. Thus, variations in the ratio of sol–gel precursors enable the synthesis of a family of mesoporous silica-based materials, denoted meso-$(SiO_2)_p([SiO_{1.5}]_mX)_{(1-p)}$, where $0 \leqslant p < 1$ ($p = 1$ refers to the pure silica end member, MCM-41). We denote the cases in which the organic groups are terminally bound ($m = 1$) or bridging ($m > 1$) as Class I and Class III hybrid materials, respectively. The compositions can be continuously tuned between end members, meso-SiO_2 and meso-$([SiO_{1.5}]_mX)$. Moreover, the imbibed surfactant template can be removed from as-synthesized material by either solvent extraction, ion exchange or calcination techniques to create hybrid materials denoted meso′-$(SiO_2)_p([SiO_{1.5}]_mX)_{(1-p)}$ having ordered mesopores that are devoid of surfactant and contain spatially accessible X groups.

An extension of these methods facilitates the synthesis of Class II and IV multi-functional hybrid materials containing more than one type of bridging functional group, X and Y. This yields the family of materials denoted meso-$(SiO_2)_p([SiO_{1.5}]_mX)_{(1-p-q)}([SiO_{1.5}]_nY)_q$, where $0 \leqslant p < 1$ and $0 < q < 1$. Specifically, materials prepared with two different terminally-bonded organic groups ($m = 1$ and $n = 1$) are Class II and materials prepared with two different bridge-bonded organic groups ($m > 1$ and $n > 1$) are Class IV. An example of a Class IV hybrid brought to practice in our laboratory has X = ethylene and Y = ethane.

The synthetic method also applies to the synthesis of Class V multifunctional hybrid materials. These materials contain an organic group (X) bridging and located within the silica wall of the ordered mesopores and another organic group (Y) grafted to the wall and protruding into the ordered mesopores. This yields the new family of materials denoted meso-$(SiO_2)_p([SiO_{1.5}]_mX)_{(1-p-q)}([SiO_{1.5}]Y)_q$. An example of a Class V hybrid mesoporous material brought to practice in our laboratory has X = ethylene and Y = vinyl.[25]

The classification system has been summarized in Table 1 and Fig. 2. While we have only designated the cases of monofunctional and bifunctional organosilica mesostructures, one could theoretically incorporate any number of different bridging and terminally bound organic groups into the mesostucture to form polyfunctional organosilica hybrid mesostructures. We denote these as Class VI hybrids.

It is worth noting a subtle detail with regard to the synthesis of PMOs, that are both well ordered and exhibit minimal hydrolytic cleavage of the Si–C bond. The preparation of PMO materials involves the acid or base catalyzed hydrolysis of poly(trialkoxysilyl) organic precursors in the presence of a surfactant template. The presence of the organic moiety greatly influences the nature of the hydrolysis reaction and a number of new factors become important in the synthesis of these materials. Certain materials, such as the bis-silylated ethylene, methylene, and ethane precursors show great stability to strongly acidic or basic conditions and readily form PMOs. In more complicated bridging organic precursors, however, aqueous hydrolysis can result in significant cleavage, as well as a decrease in the degree of order in the material. To obtain a satisfactory PMO made with benzene or thiophene in an aqueous synthesis, a different approach to the hydrolytic polycondensation needed to be developed.[11] A notable divergence involved mixing an acidic aqueous cetylpyridinium chloride solution with 2,5-bis(triethoxysilyl)thiophene (or 1,4-bis(triethoxysilyl)benzene) briefly at room temperature. The resulting mixture was neutralized with $NaHCO_3$, then dilute NH_4F was added and the slurry held at room temperature. Filtering and washing yielded a white powder that showed only a small amount of Si–C bond cleavage and the PXRD pattern and TEM images showed good hexagonal order (Fig. 3).

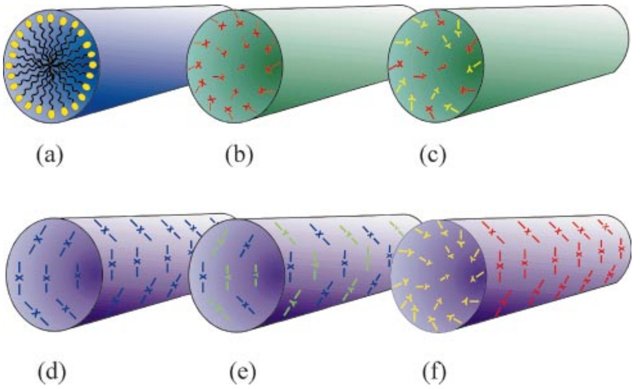


Fig. 2 Scheme illustrating a single channel of each class of the mesoporous hybrid organosilica materials. (a) Mesoporous SiO_2 (MCM-41) with surfactant inside the channels. (b) Class I hybrid with one terminal organic group (X). (c) Class II hybrid with two terminal organic groups (X and Y). (d) Class III hybrid with one bridging organic group (X). (e) Class IV hybrid with two bridging organic groups (X and Y). (f) Class V hybrid with one bridging (X) and one terminal (Y) organic group.

The preparation of "organic–inorganic walled" PMOs needs to be optimized on an individual basis. This can be achieved by varying such parameters as surfactant concentration, catalyst, temperature, as well as examination of non-aqueous routes to ordered materials. Another possibility is to change the rate of condensation by substituting ethoxy substituents with other alkoxy groups. For example, using a bis(trimethoxysilyl) organic precursor instead of the bis(triethoxysilyl) analog is expected to increase the rate of condensation over the rate of cleavage of the Si–C bond.

In the case of periodic mesoporous silica, the morphology of the material often dictates its function and utility.[26] In this regard, the PMOs are expected to be no exception. Non-ionic surfactant-based, lyotropic liquid crystal templating has been successfully utilized for synthesizing oriented film and monolith morphologies of the PMOs, Fig. 4.[27] This is an important step forward in the utilization of these materials.

As with any new class of materials, one would expect to find unusual reactivity in PMOs that are intellectually challenging to identify and allow further materials design. In this regard, we

Table 1 Classification scheme for hybrid mesoporous organosilica materials

	meso-$(SiO_2)_p([SiO_{1.5}]_mX)_{(1-p-q)}([SiO_{1.5}]_nY)_q$				
Class	Description	*p*	*q*	*m*	*n*
	Mesoporous silica	1	0	—	—
I	Terminally-bonded monofunctional	<1	0	1	—
II	Terminally-bonded bifunctional	<1	<1	1	1
III	Bridge-bonded monofunctional	<1	0	>1	—
IV	Bridge-bonded bifunctional	<1	<1	>1	>1
V	Mixed bridge-bonded and terminally-bonded	<1	<1	>1	1

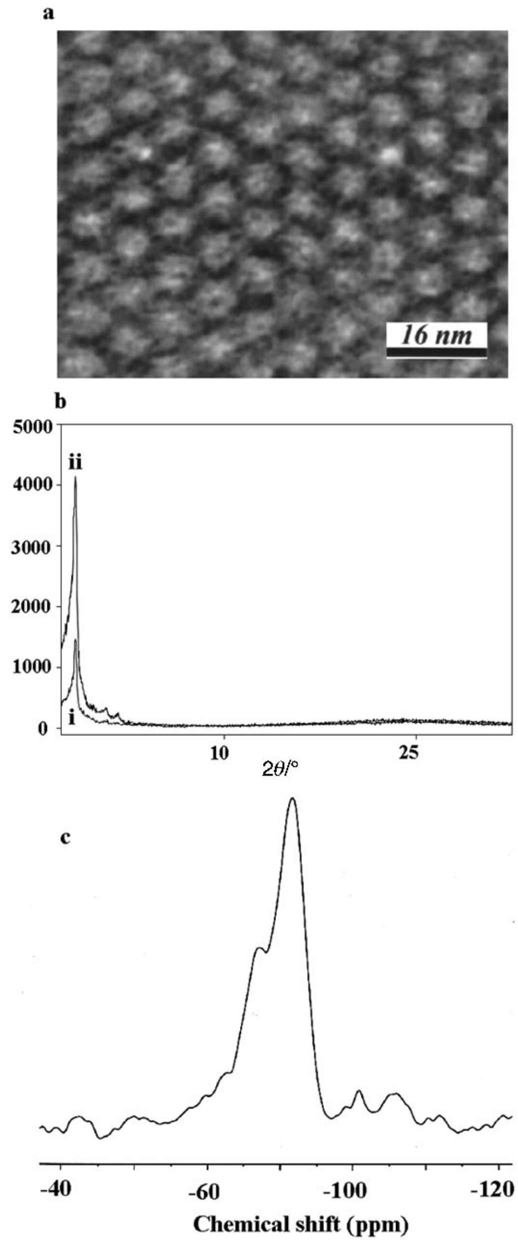


Fig. 3 (a) Transmission electron micrograph (TEM) image of a region of mesoporous ethenesilica. (b) Powder X-ray diffractogram of the same material shows 4 peaks, indicative of a highly ordered mesoporous material (i) before and (ii) after surfactant removal. (c) Solid-state ^{29}Si NMR spectrum of mesoporous ethenesilica with surfactant removed. The absence of Q sites in the spectrum ($Q = [SiO_4]$ sites) confirms that the Si–C bond remained intact during the surfactant extraction procedure.

have recently reported the synthesis and characterization of a methylenesilica PMO, which is isoelectronic with mesoporous silica, SiO_2.[21] When calcined at 500–600 °C, the organic groups are still present in the material. Using non-quaternary suppression (NQS) with a ^{13}C CP-MAS solid-state NMR experiment, we identified terminal methyl groups in the material. These result from the hydrolytic cleavage of Si–CH_2 bonds to form Si–CH_3 terminal groups. Mesoporous methylenesilica retained its well-ordered hexagonal structure at this temperature, and was still hexagonally organized at 900 °C, well after all of the organic groups had been removed.

The calcination of the methylenesilica PMO may give up to 50% terminal organic species in the mesostructure. This is a new and interesting route to Class I hybrid materials containing terminal organic groups as synthetic routes to those materials usually give amorphous products if the amount of organic exceeds 25%. By incorporating designer organics in the PMO, it may be possible to tune the terminal organic group obtained after hydrolysis.

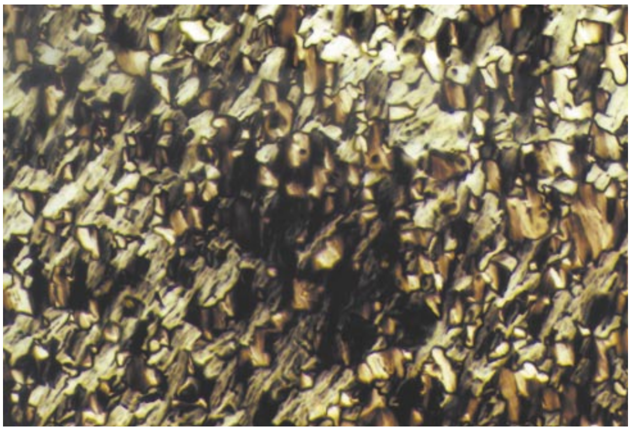


Fig. 4 Polarized optical microscope image of a PMO film with bridging thiophene groups shows a fan texture characteristic of a hexagonal liquid crystalline phase.

Moreover, the methylenesilica PMO is stable to 900 °C, after the organic group has been eliminated. This indicates that the silica framework has undergone a healing mechanism with the elimination of the methylene spacers. This occurs with a concomitant 12% contraction in the unit cell of the hexagonal mesostructure between room temperature and 700 °C. Calcination of PMOs with larger organic groups may permit the formation of well-organized mesoporous silica with very small channel diameters, a target with great catalytic potential.

All of these new classes of functional hybrid mesoporous organosilica materials have now been synthesized and structurally characterized in the form of powder, film and monolith samples. Patterning PMOs using soft lithography and micromolding methods is an obvious and appealing extension, and a way forward to the realization of functional and practical PMO devices.[28,29]

Our future research will be expanding the compositions of PMOs to incorporate a spectrum of organic and organometallic moieties, then to further develop the "chemistry of the channel walls". We anticipate that these new composites, with tunable framework structures, may find utility in various applications, ranging from chiral separation to chemical release to sound proofing to electronic packaging.

Acknowledgements

We gratefully acknowledge funding from the Natural Sciences and Engineering Research Council of Canada (NSERC) for our work on PMOs. MJM thanks NSERC for a postgraduate scholarship (1995–99) and postdoctoral fellowship (1999–2001, MIT). GAO acknowledges the Canada Council for the award of an Isaac Walton Killam Foundation Fellowship (1995–97).

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