Smithsonian Institution
Scholarly Press

SMITHSONIAN CONTRIBUTIONS TO MUSEUM CONSERVATION • NUMBER 6


Conservation of the Exterior of the National Museum of the American Indian Building

Edited by
Jane Sledge, A. Elena Charola, Paula T. DePriest, and Robert J. Koestler

SERIES PUBLICATIONS OF THE SMITHSONIAN INSTITUTION

Emphasis upon publication as a means of "diffusing knowledge" was expressed by the first Secretary of the Smithsonian. In his formal plan for the Institution, Joseph Henry outlined a program that included the following statement: "It is proposed to publish a series of reports, giving an account of the new discoveries in science, and of the changes made from year to year in all branches of knowledge." This theme of basic research has been adhered to through the years by thousands of titles issued in series publications under the Smithsonian imprint, commencing with Smithsonian Contributions to Knowledge in 1848 and continuing with the following active series:

Smithsonian Contributions to Anthropology
Smithsonian Contributions to Botany
Smithsonian Contributions to History and Technology
Smithsonian Contributions to the Marine Sciences
Smithsonian Contributions to Museum Conservation
Smithsonian Contributions to Paleobiology
Smithsonian Contributions to Zoology

In these series, the Smithsonian Institution Scholarly Press (SISP) publishes small papers and full-scale monographs that report on research and collections of the Institution's museums and research centers. The Smithsonian Contributions Series are distributed via exchange mailing lists to libraries, universities, and similar institutions throughout the world.

Manuscripts intended for publication in the Contributions Series undergo substantive peer review and evaluation by SISP's Editorial Board, as well as evaluation by SISP for compliance with manuscript preparation guidelines (available at www.scholarlypress.si.edu). For fully searchable PDFs of all open access series and publications of the Smithsonian Institution Scholarly Press, visit Open SI at http://opensi.si.edu.

SMITHSONIAN CONTRIBUTIONS TO MUSEUM CONSERVATION • NUMBER 6

Conservation of the Exterior of the National Museum of the American Indian Building

Edited by
Jane Sledge, A. Elena Charola,
Paula T. DePriest, and Robert J. Koestler

Smithsonian Institution
Scholarly Press
WASHINGTON D.C.
2017

ABSTRACT
Sledge, Jane, A. Elena Charola, Paula T. DePriest, and Robert J. Koestler. Conservation of the Exterior of the National Museum of the American Indian Building. *Smithsonian Contributions to Museum Conservation*, number 6, viii + 66 pages, 56 figures, 5 tables, 2017.— The Smithsonian's National Museum of the American Indian building on the National Mall in Washington, D.C., has a significant problem with dark staining on its facade. This volume brings together papers from studies undertaken by the Smithsonian's Museum Conservation Institute to understand the staining problem, suggest procedures for the 2011 cleaning intervention, and propose test studies for the development of a maintenance plan for the building.

Cover images (from left): Detail of the north facade of the National Museum of the American Indian, September 2004, photo by John Steiner, Smithsonian Institution; detail of the National Museum of the American Indian west facade showing dark streaking, April 2010, photo by Melvin J. Wachowiak and E. Keats Webb, Smithsonian Institution.

Published by SMITHSONIAN INSTITUTION SCHOLARLY PRESS
P.O. Box 37012, MRC 957
Washington, D.C. 20013-7012
www.scholarlypress.si.edu

Library of Congress Cataloging-in-Publication Data
Names: Sledge, Jane, editor. | Charola, A. Elena, editor. | DePriest, Paula T. (Paula Teresa), 1957– editor. | Koestler, Robert J. (Robert John), 1950– editor. | Smithsonian Institution Scholarly Press, publisher.
Title: Conservation of the exterior of the National Museum of the American Indian building / edited by Jane Sledge, A. Elena Charola, Paula T. DePriest, and Robert J. Koestler.
Other titles: Smithsonian contributions to museum conservation ; no. 6. 1949-2359
Description: Washington, DC : Smithsonian Institution Scholarly Press, 2017. | Series: Smithsonian contributions to museum conservation, ISSN 1949-2359 ; number 6 | Includes bibliographical references and index.
Identifiers: LCCN 2016037519
Subjects: LCSH: National Museum of the American Indian (Washington, D.C.) | Museums—Conservation and restoration—Washington (D.C.) | Limestone—Biodegradation—Washington (D.C.) | Stone buildings—Conservation and restoration—Washington (D.C.) | Building materials—Environmental aspects—Washington (D.C.) | Cultural property—Protection.
Classification: LCC E76.86.N37 C66 2017 | DDC 973.04/970074753—dc23 | SUDOC SI 1.57:6
LC record available at https://lccn.loc.gov/2016037519

ISSN: 1949-2367 (online); 1949-2359 (print)

Publication date (online): 9 January 2017

♾ The paper used in this publication meets the minimum requirements of the American National Standard for Permanence of Paper for Printed Library Materials Z39.48–1992.

Contents

Preface

The National Museum of the American Indian building on the National Mall in Washington, D.C., is distinctive. It embodies the spirit of nature and is evocative of the first people who settled western mesas. The design is stylish, subtle, and suggestive. The buff Kasota stone, a dolomitic limestone, was chosen for most of the exterior facade because of its warm earth tones and its resemblance to the mesa landscape. No other building on the Mall can be compared to it.

The natural weathering process of the building's exterior has already begun. The process is usually a slow one caused by the dissolution and migration of iron oxide compounds—the same compounds that give the Kasota stone its yellowish color—on the exterior surface. Eventually, over centuries, this process would result in a reddish, orange, or brown surface layer, as found on the quarry-weathered stones used for the blocks at the base of the building (stones referred to as "roughback"). Apart from this geochemical process, colonization of the stone by various microorganisms, such as bacteria, algae, and fungi, would lead to the deposition of organic materials, which may or may not be visible and may speed up the weathering process depending on environmental conditions at the site.

Eleven years after the museum's inauguration and with the building stone weathering naturally, there are some areas where disfiguring dark streaking has occurred so rapidly that two cleaning interventions have been required. The main cause of this staining is the growth of microorganisms, referred to as "biocolonization," on certain areas where water flows or drips over the stone surface during rain events.

This publication brings together all the information compiled by the Smithsonian's Museum Conservation Institute, which investigated the origin of the staining problem, including papers on the "spirit" of the building; its construction history; characterization of the Kasota stone and its susceptibility to biocolonization; a correlation of the dark streaking pattern with design features; identification of the main colonizing microorganisms found in the most severely stained areas, including the dark deposits of biological material that accumulate on surfaces subjected to frequent water flows; discussion of cleaning procedures, including documentation of the cleaning carried out in 2011; and recommendations for preventing or mitigating future staining.

This volume also illustrates many of the benefits provided by an interdisciplinary approach when confronting the problems that can affect buildings.

Jane Sledge, Associate Director, National Museum of the American Indian
A. Elena Charola, Research Scientist, Museum Conservation Institute
Paula T. DePriest, Deputy Director, Museum Conservation Institute
Robert J. Koestler, Director, Museum Conservation Institute

Acknowledgments

Many groups and individuals provided valuable assistance during this project, specifically the staffs of the National Museum of the American Indian (NMAI), the Museum Conservation Institute (MCI), and the Smithsonian Office of Facilities, Engineering and Operations (OFEO). We also thank Duane Blue Spruce, Kathleen Fleming, Alexandra N. Harris, Tanya Thrasher, Erin Weinman, Katherine Fogden, and John Bixler (all of NMAI) and Jamil Burnett, Sharon Park, and David Grimes (all of OFEO). We give special thanks to Melvin Wachowiak (MCI) (deceased) for help with the photography and to then contractor Elizabeth Keats Webb (now imaging specialist at MCI) for web page design. Finally, the support from Francine Lewis and Beverly Smith is gratefully acknowledged, as is the invaluable help provided by Ann N´Gadi.

The National Museum of the American Indian: An Introduction

A. Elena Charola and Robert J. Koestler*

The Smithsonian's National Museum of the American Indian (NMAI) was inaugurated in September 2004. Its juxtaposition to the National Air and Space Museum on the south side of the National Mall in Washington, D.C., presents a stark contrast in architectural styles. NMAI's softly curving exterior and golden-hued stone were chosen to evoke the American Southwest, where many Native American people make their home.

THE PROBLEM

In 2006, only two years after inauguration of the NMAI building and six years after the beginning of its construction, it was noted that the building had developed blackish streaks in localized areas—mostly on the north facade—that were at first thought to be the result of dust and urban pollution accumulation. The streaks were aesthetically unacceptable, and their cleaning was undertaken (Grissom and Charola, "Keeping the National Museum of the American Indian Building Clean," this volume). However, the soiling problem recurred, and as a new cleaning intervention was being planned in 2009, the Smithsonian's Museum Conservation Institute (MCI) was asked to investigate the reason for the resoiling so soon after the first cleaning. A careful survey and examination of the building facade showed that the soiling was concentrated in areas that had the highest amount of water flowing across their surfaces (Grissom and Charola, "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building," this volume). The frequent wetting of the stone surfaces encouraged biocolonization of the stone.

Biocolonization of building surfaces results from the deposition of spores, bacteria, and algae present in the air onto surfaces. It is enhanced when stone surfaces are rough and frequently wetted (Warscheid, 1990). Once microorganisms settle on the surface, they require appropriate conditions (i.e., light, nutrients, and water) to flourish. Nutrients are supplied by dust and other organic materials, such as carbon particles and hydrocarbons from vehicular traffic (Scheerer et al., 2009), or they may be biological in origin, for example, pollen and bird droppings. The stone surface roughness provides many crevices to entrap the food sources and to provide protected niches for the microorganisms while its finer porosity retains water for long periods of time. Under these favorable conditions microorganisms will flourish and form communities, often composed of multiple species. Once a community develops, the extracellular polymeric substances secreted by the microorganisms serve to anchor them to the stone and protect

Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746, USA.

* Correspondence: A. E. Charola, charolaa@si.edu

Manuscript received 17 January 2012; accepted 23 May 2016.

them from desiccation. The community forms what is generally known as a "biofilm" (Gorbushina, 2007).

The biofilm on the NMAI's Kasota limestone (a calcitic dolomite) is composed of fast-growing, autotrophic (photosynthetic) algae, mixed with fungi (DePriest and Charola, this volume). The extensive colonization on the horizontal surfaces serves as a steady source of microorganisms to wash down the vertical faces of the stone every time it rains. Because of the unique facade structure, water flows down preferred pathways, resulting in preferential colonization and, ultimately, black staining in specific vertical streaks. Areas that receive a lot of water, such as those beneath scuppers, the outlets for draining water from the building's roofs, have shown the highest biocolonization levels and, in some instances, exhibit stone flaking. Although, in general, much attention has been focused on the visible streaking on the building, issues such as the induced deterioration by fairly constant water flow from the scuppers has not been considered.

ADDRESSING THE PROBLEM

The streaking problem was initially considered to be a simple soiling issue induced by air pollution and was treated by localized cleaning (carried out in 2006; see Grissom and Charola, "Keeping the National Museum of the American Indian Building Clean," this volume). In April 2009, a workshop on identifying and cleaning biocolonized surfaces was convened by MCI to discuss the latest approaches in this field, and as a serendipitous side problem, we talked about the staining on the NMAI building (Charola et al., 2011). At this meeting, participants felt that the soiling of NMAI was probably caused by biocolonization in the stone. By late 2009, after the rapid reappearance of staining cleaned in the 2006 intervention, NMAI asked for MCI's assistance in discovering the nature of the stains. The MCI called in four participants from our 2009 biocolonization workshop from different European research teams to return in 2010 to make a detailed examination of the stained areas of the building. The subsequent reports provided not only identification of the microorganisms but also suggestions on how to deal with the staining (Cappitelli et al., 2010; May et al., 2010; Salvadori, 2010; Warscheid, 2010). Subsequently, Cappitelli et al. and Salvadori, with collaboration of colleagues, combined their results into a journal article (Capitelli et al., 2012).

Following these studies, the use of a biocide—a chemical that can destroy or inhibit microorganisms—was recommended for subsequent cleanings. The biocide, a quaternary ammonium salt, served both as a surfactant (i.e., a chemical that changes the surface tension of water such as a detergent or wetting agent) and a biocide and was used in the second, localized cleaning campaign in 2011 (Grissom and Charola, "Keeping the National Museum of the American Indian Building Clean," this volume). Although it is recognized that biocides can significantly decrease the growth of microorganisms on stone and consequently reduce their detrimental aesthetic, physical, and chemical effects, their action is time limited (Krumbein et al., 1993). Recolonization is inevitable and depends on the substrate and environment of the building in question (Young, 1998; Young and Urquhart, 1998; Delgado Rodrigues et al., 2011).

Furthermore, there are concerns that residues of any surfactants used during the cleaning may remain in the stone and serve as nutrients for microorganisms (Warscheid and Braams, 2000). Several studies have investigated this issue, but most have been carried out with specific microorganisms under laboratory conditions (Leznicka et al., 1991; Krumbein and Gross, 1992), although some in situ evaluations have also been attempted (Tiano et al., 1995; Young et al., 2003; Pinna et al., 2008) with varying results, depending on the substrate, biocolonization species, and environmental conditions.

The problem of soiling from biocolonization, similar to that resulting strictly from air pollution, is a continuous problem. Although air pollution has significantly decreased following the Clean Air Act of 1970 and its subsequent amendments (U.S. Environmental Protection Agency, 2016), for the microorganisms and biological material present in the air, such as spores and pollen, no control is practical. Thus, removal of the existing biocolonization can only be considered a temporary mitigation of the soiling problem, and other, longer-term control methods need to be developed and tested for each specific site on the building.

APPROACHES TO A SOLUTION

Since microorganisms and dust settlement cannot be eliminated, periodic intervention is required to keep the building at an aesthetically acceptable level and avoid the development of thicker biological deposits that can actually induce deterioration, such as flaking of the stone surface (DePriest and Charola, this volume). Although the use of a biocide application can be effective in inhibiting recolonization, there is concern that long-term repeated use of the same compound may induce development of biocide-resistant microorganisms (Salvadori and Charola, 2011) or colonization by other, more invasive species (Agarossi et al., 1988). However, other approaches can either reduce biocolonization or complement the use of a biocide, for example, the application of water repellents to reduce the amount of water absorbed by a stone surface, which has been effective in limiting recolonization in some cases (Riecken et al., 1998). Nonetheless, even after a water repellent has been applied, rebiocolonization has still been observed 5 and 20 years after its application (Bläuer Böhm, 2005); other disfiguring effects may happen, too, such as the formation of zebra stripes on the stone surface as the water repellent unevenly wears away (Charola et al., 2008; Salvadori and Charola, 2011).

A potentially effective and minimally intrusive technique to control recolonization is the use of metal strips, such as zinc, appropriately located above the problem areas (as shown by Wessel, 2003, 2011). The success of this approach is based on the careful positioning of the metal strips so that water flows over them and then flows across the whole stained surface. As the water flows over the metal strips, zinc ions are carried down the face of the stone and deposited in the stone, inhibiting the growth of microorganisms. Successfully implementing this technique on an irregular surface, such as the NMAI building, requires experimenting with placement of the strips, which was done for selected areas in early 2012, after the 2011 cleaning (Grissom and Charola, "Keeping the National Museum of the American Indian Building Clean," this volume). So far, four years after placement of the strips, microbial soiling appears to have been inhibited in the zinc-enriched water runoff areas.

Another promising method to control biocolonization is the use of photocatalytic materials, such as titanium dioxide, applied to the stone surfaces. Although there have been successful applications of this methodology (Fonseca et al., 2010; Quagliarini et al., 2013a), it may not always be effective because photocatalytic materials require a specific quality and quantity of light in order to be activated (Quagliarini et al., 2013b). Further complicating matters, they might overwhiten surfaces and/or change the rate of biofilm formation and/or secretion of organic materials (Maurer-Jones et al., 2013).

The inclusion of nanoparticles of copper or zinc oxides in formulations, such as water repellents or consolidants (Szabó et al., 2004), is yet another recent approach. However, it requires further refinement before application to cultural heritage (Baglioni et al., 2012; Ranogajec et al., 2012). A related approach is based on the inclusion of silica nanoparticles into a consolidant or a water repellent, which produces a nanoroughening of the surface, mimicking nature's approach for shedding water, like what occurs on lotus leaves or petals of a rose (de Ferri et al., 2011; Pinho et al., 2014). Given the unusual shape of the NMAI building, there may not be a single solution to all of its staining problems.

BALANCING MEANING AND THE SOLUTION

The condition of a building's exterior is a result of its history, including past interventions. Although documentation of conservation or restoration actions on museum objects is standard practice, this is seldom the case for architectural heritage. Most interventions are carried out by contractors, and the general work is described in a service contract, but the details are left to the interpretation of the contractor. Often, there is no requirement to document in full the treatment used. The current publication addresses this issue for the Smithsonian's NMAI, and it should help us develop the most effective and efficient maintenance protocols for the building (Koestler et al., this volume).

Any conservation intervention needs to have a clear objective and must be in harmony with the value and significance of the object in question. Cleaning interventions, in particular, are perceived as a straightforward application of detergent, water, and scrubbing by which any soiling is removed. However, because this type of intervention is irreversible as it removes small particles of the stone surface, it should be used only as a last resort. For the NMAI building, it is important to consider what the building represents, which is the suggestion of American Southwest rock formations, and its landscaping aims to echo that originally found in the same area. The building was envisioned as "a 'clump of rock' carved as wind and water would do" (Grissom et al., this volume), which would reflect the harmony and balance between nature and design as well as the equilibrium native people had achieved with nature. Its design was to "embody and communicate the museum's mission to both Native and non-Native visitors." (Grissom et al., this volume) and reflect the vision of the various Native tribes that are rooted in place and culture. Even if total elimination of colonizing microorganisms were feasible, it might not be desirable. A balance between the aesthetics of the building and its equilibrium with nature is the ultimate objective.

REFERENCES

Agarossi, G., R. Ferrari, M. Nonte, C. Gugliandolao, and M. Maugeri. 1988. "Changes of Microbial System in an Etruscan Tomb after Biocidal Treatments." In *6th International Congress on Deterioration and Conservation of Stone*, ed. J. Ciabach, pp. 82–91. Torun: Nicolaus Copernicus University Press.

Baglioni, P., R. Giorgi, and D. Chelazzi. 2012. Nano-materials for the Conservation and Preservation of Movable and Immovable Artworks. *International Journal of Heritage in the Digital Era,* 1(Suppl. 1):313–318. http://dx.doi.org/10.1260/2047-4970.1.0.313.

Bläuer Böhm, C. 2005. "Auswirkungen von hydrophoben Fassadenmaterialen auf die Erhaltung und Pflegefähigkeit von Baudenkmälern" [Behavior of hydrophobic materials for façades with regard to the conservation and maintenance of monuments]. In *Klimastabilisierung und bauphysikalische Konzepte*, ed. M. Exner and D. Jakobs, pp. 117–128. Munich and Berlin: ICOMOS Hefte der Deutschen Nationalkomitees XLII. [International Council on Monuments and Sites, Journals of the German National Committee XLII]

Cappitelli, F., O. Salvadori, D. Albanese, F. Villa, and C. Sorlini. 2012. Cyanobacteria Cause Black Staining at the National Museum of the American Indian Building, Washington, D.C., USA. *Biofouling* 28(3):257–266.

Cappitelli, F., F. Villa, and C. Sorlini. 2010. Molecular Characterization of the Microflora Dwelling on Stained Areas of the NMAI Building. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29556.

Charola, A. E., J. Delgado Rodrigues, and M. Vale Anjos. 2008. Disfiguring Biocolonization Patterns after the Application of Water Repellents. *Restoration of Buildings and Monuments,* 14(5):365–372.

Charola, A. E., C. McNamara, and R. J. Koestler, eds. 2011. *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series*. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press. http://dx.doi.org/10.5479/si.19492359.2.1.

de Ferri, L., P. P. Lottici, A. Lorenzi, A. Montenero, and E. Salvioli-Mariani. 2011. Study of Silica Nanoparticles – Polysiloxane Hydrophobic Treatments for Stone-Based Monument Protection. *Journal of Cultural Heritage,* 12:356–363. http://dx.doi.org/10.1016/j.culher.2011.02.006.

Delgado Rodrigues, J., M. Vale Anjos, and A. E. Charola. 2011. "Recolonization of Marble Sculptures in a Garden Environment." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series*, ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 71–85. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

DePriest, P., and A. E. Charola. 2017 (this volume). "Biological Colonization and 'Ink Strokes' on Buildings." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 39–44. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Fonseca, A. J., F. Pina, M. F. Macedo, N. Leal, A. Romanowska-Deskins, L. Laiz, A. Gómez-Bolea, and C. Saiz-Jiménez. 2010. Anatase as an Alternative Application for Preventing Biodeterioration of Mortars: Evaluation and Comparison with Other Biocides. *International Biodeterioration and Biodegradation,* 64:388–396. http://dx.doi.org/10.1016/j.ibiod.2010.04.006.

Gorbushina, A. A. 2007. Life on the Rocks. *Environmental Microbiology,* 9(7): 1613–1631. http://dx.doi.org/10.1111/j.1462-2920.2007.01301.x.

Grissom, C. A., and A. E. Charola, 2017 (this volume). "Keeping the National Museum of the American Indian Building Clean." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 45–58. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

———. 2017 (this volume). "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 27–38. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Krumbein, W. E., S. E. Diakumaku, K. Petersen, and T. Warscheid. 1993. "Interactions of Microbes with Consolidants and Biocides in the Conservation of Rocks and Mural Paintings." In *Conservation of Stone and Other Materials*, vol. 2, *Prevention and Treatments*, ed. M.-H. Thiel, pp. 589–596. London: E & F Spon.

Krumbein, W. E., and M. Gross. 1992. "Interaction of Biocides with Cultures of Biodeteriorating Microbiota in Agar Diffusion and Rock Cube Tests." In *7th International Congress on Deterioration and Conservation of Stone*, ed. J. Delgado Rodrigues, F. Henriques, and F. Telmo Jeremias, pp. 501–509. Lisbon: Laboratório Nacional de Engenharia Civil.

Leznicka, S., J. Kuroczkin, W. E. Krumbein, A. B. Strzelczik, and K. Petersen. 1991. Studies on the Growth of Selected Fungal Strains on Limestones Impregnated with Silicone Resins (Steinfestiger H and Elastosil E-41). *International Biodeterioration,* 28:91–111.

Maurer-Jones, M. A., I. L. Gunsolus, B. M. Meyer, C. J. Christenson, and C. L. Haynes. 2013. Impact of TiO_2 Nanoparticles on Growth, Biofilm Formation, and Flavin Secretion in *Shewanella oneidensis. Analytical Chemistry,* 85:5810–5818.

May, E., R. Inkpen, and C. Hughes. 2010. Biocolonization of the NMAI Building and Image Analysis Methods for Its Evaluation. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29557.

Pinho, L., A. Pedna, P. Frediani, and M. J. Mosquera. 2014. "Reversible Flourinated PLA/SiO_2 Nanocomposites as Hydrophobic Coatings for Stone." In *Hydrophobe VII International Conference on Water Repellent Treatment and Protective Surface Technology for Building Materials*, ed. A. E. Charola and J. Delgado Rodrigues, pp. 199–203. Lisbon: Laboratorio Nacional de Engenharia Civil.

Pinna, D., B. Salvadori, and O. Salvadori. 2008. "Bioreceptivity of Stone Samples Treated with Protectives." In *11th International Congress on Deterioration and Conservation of Stone*, ed. J. W. Lukaszawivz and P. Niemcewicz, pp. 1027–1034. Torun: Nicolaus Copernicus University Press.

Quagliarini, E., F. Bondioli, G. B. Gofreddo, A. Liciulli, and P. Munafò. 2013a. Smart Surfaces for Architectural Heritage: Preliminary Results about the Application of TiO_2-Based Coatings on Travertine. *Journal of Cultural Heritage,* 13:204–209. http://dx.doi.org/10.1016/j.culher.2011.10.002.

———. 2013b. Self-Cleaning Materials on Architectural Heritage: Compatibility of Photo-induced Hydrophilicity of TiO_2 Coatings on Stone Surfaces. *Journal of Cultural Heritage,* 14:1–7. http://dx.doi.org/10.1016/j.culher.2012.02.006.

Ranogajec, J., S. Paµaliµb, H. Hirµenberger, and S. Vujovic. 2012. Protection of Cultural Heritage Objects with Multifunctional Advanced Materials. *International Journal of Heritage in the Digital Era,* 1 (Suppl. 1):255–258. http://dx.doi.org/10.1260/2047-4970.1.0.255.

Riecken, B., M. Cartens, and R. Mansch. 1998. "Durability of a Hydrophobic Product for Natural Stones against Combined Microbiological and Chemical Stress and an Artificial Weathering Procedure." In *Hydrophobe II: Water Repellent Treatment of Building Materials*, ed. F. H. Wittmann, pp. 137–151. Freiburg: Aedificatio Publishers.

Salvadori, O. 2010. Microscopic Characterization of the Biocolonization on the NMAI Building. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29558.

Salvadori, O., and A. E. Charola. 2011. "Methods to Prevent Biocolonization: An Overview of Current Research for Architectural and Archaeological Heritage." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series*, ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 37–50. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

Scheerer, S., O. Ortega-Morales, and C. Gaylarde. 2009. "Microbial Deterioration of Stone Monuments." In *Advances in Applied Microbiology*, vol. 66, ed. A. S. Laskin, S. Sanastian, and G. N. Gadd, pp. 97–138. New York: Elsevier.

Szabó, T., J. Németh, and I. Dékäny. 2004. Zinc Oxide Nanoparticles Incorporated in Ultrathin Layer Silicate Films and Their Photocatalytic Properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 230:23–35. http://dx.doi.org/10.1016/j.colsurfa.2003.09.010.

Tiano, P., P. Accolla, and L. Tomaselli. 1995. Phototrophic Biodeteriogens on Lithoid Surfaces: An Ecological Study. *Microbial Ecology,* 29:299–309. http://dx.doi.org/10.1007/BF00164892.

U.S. Environmental Protection Agency. 2016. Reviewing National Ambient Air Quality Standards—Scientific and Technical Information. https://www3.epa.gov/ttn/naaqs/ (accessed July 17, 2016).

Warscheid, T. 1990. Untersuchungen zur Biodeterioration von Sandsteinen unter bersondere Berücksichtigung der chemoorganotrophen Bakterien [Studies on the biodeterioration of sandstones with regards to chemoorganotrophic bacteria]. Doctoral thesis, University of Oldenburg, Oldenburg, Germany.

———. 2010. Evaluation and Treatment of Microbial Biofilms on the NMAI Building. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29559.

Warscheid, T., and J. Braams. 2000. Biodeterioration of Stone: A Review. *International Biodeterioration and Biodegradation,* 46:343–368.

Wessel, D. P. 2003. "The Use of Metallic Oxides in Control of Biological Growth in Outdoor Monuments." In *Art, Biology and Conservation*, ed. R. J. Koestler, V. Koestler, A. E. Charola, and F. Nieto-Fernandez, pp. 536–551. New York: The Metropolitan Museum of Art.

———. 2011. "Field Observations on the Effectiveness of Zinc Strips to Control Biocolonization of Stone." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series*, ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 109–112. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

Young, M. E. 1998. Algal and Lichen Growth Following Chemical Stone Cleaning. *Journal of Architectural Conservation,* 3:48–58. http://dx.doi.org/10.1080/13556207.1998.10785225.

Young, M. E., and D. C. M. Urquhart. 1998. Algal Growth on Building Sandstones: Effects of Chemical Stone Cleaning Methods. *Quarterly Journal of Engineering Geology,* 31:315–324. http://dx.doi.org/10.1144/GSL.QJEG.1998.031.P4.04.

Young, M. E., D. C. M. Urquhart, and R. A. Laing. 2003. Maintenance and Repair Issues for Stone Cleaned Sandstone and Granite Building Facades. *Building and Environment,* 38:1125–1131. http://dx.doi.org/10.1016/S0360-1323(03)00084-2.

Design and Construction of the National Museum of the American Indian Building: Focus on the Exterior Stone

Carol A. Grissom,[1]* *Amy Ballard,*[2] *Justin Estoque,*[3] *Debra Nauta-Rodriguez,*[4] *and Michael Dobbs*[5]

The National Museum of the American Indian (NMAI) is unlike any other building on the National Mall. With its curving, undulating stone exterior and its unique landscaping, it expresses the culture of its constituents more than any other Smithsonian building and is the first building on the Mall that announces the twenty-first century (Figure 1).

In 1916, retired Standard Oil executive George Gustav Heye established the Museum of the American Indian in New York City for his collection of Native American artifacts. The collection contained more than 800,000 objects as well as 86,000 photographic negatives and 40,000 books. Over the years, the building that housed the collection became unsuitable for the proper maintenance of the collection, and a new home was needed. In 1989, the U.S. Congress authorized the creation of the National Museum of the American Indian in Washington, D.C., as part of the Smithsonian complex. This act allowed for the transfer of the Heye's collection to the Smithsonian, with the stipulation that a presence would be maintained in New York City. In consequence, the National Museum of the American Indian encompasses the George Gustav Heye Center (part of the U.S. Custom House) in New York City as well as a Cultural Resources Center for collection storage and research in Suitland, Maryland, but it is the building for exhibits and public programs that opened in 2004 on the National Mall that is referred to here as the National Museum of the American Indian.

DESIGN PHILOSOPHY

It was crucial that Native American people be engaged and involved in all aspects of the new museum on the Mall, especially the programming and the design. In 1991, the Smithsonian hired the architectural firm Venturi, Scott Brown to organize a series of consultations with Native people throughout the United States, Canada, and Central and South America to determine what was important to them in a new museum. Some of the comments from the tribes were the following: "Say who we are visually." "A living museum—not formal and quiet." "We want to welcome people—that should be in the entrance." "It should be a natural experience to go there—one should feel the love of Indian people for who they are. These things are alive and part of today" (Venturi, et al., 1993).

[1] Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746, USA.

[2] Smithsonian Facilities, Office of Planning, Design and Construction, Historic Preservation Branch, P.O. Box 37012, MRC 511, Washington, D.C. 20013-7012, USA.

[3] National Museum of the American Indian, Smithsonian Institution, P.O. Box 37012, MRC 590, Washington, D.C. 20013-7012, USA.

[4] Smithsonian Facilities, Office of Planning, Design and Construction, P.O. Box 37012, MRC 511, Washington, D.C. 20013-7012, USA.

[5] Michael Dobbs, SmithGroup JJR, 1700 New York Avenue, NW, Suite 100, Washington, D.C. 20006, USA.

* Correspondence: C. A. Grissom, grissomc@si.edu

Manuscript received 17 January 2012; accepted 23 May 2016.

FIGURE 1. Left: a view of the east-facing entrance facade of the building. Right: the north facade where the cataract and pool are found. Photos by Eric Long, Smithsonian Institution.

Venturi, Scott Brown also interviewed Smithsonian management and a wide variety of the museum's staff members to solicit their views on what a workable museum should be; the latter included everyone from curators to maintenance crews, exhibit designers, and security guards. The interview process took three years to complete and contributed greatly to the success of the project. These consultations evolved into a programming document, "The Way of the People," that informed the architects about what Native peoples wanted in "their museum" (Ewing and Ballard, 2009:132).

The founding director of the museum, W. Richard West Jr., is a member of the Cheyenne and Arapaho tribes. He came to the Smithsonian from a New Mexico legal firm, where he represented Native American rights. He was the perfect man for the job because he crossed two worlds—the Anglo and the Indian—with great ease. West defined three elements of the new museum's mission: (1) represent and interpret Native culture as a living, vibrant phenomena, (2) interpret Native cultural inheritance and contemporary lives through performance and creative art (West, 2004), and (3) "support cultural preservation in the Native community because it is in the United States' vital interest to do so" (Venturi, et al., 1993).

It was essential that the design for the new building on the National Mall embody and communicate the museum's mission to both Native and non-Native visitors. Every tribe has its own traditional building type, generally with forms, materials, and technologies closely reflecting climatic and site conditions as well as tribal social structures. In other words, designs are deeply rooted in place and culture, and it was important to convey this concept in the new Mall building. At the same time approval had to be gained from a large group of Smithsonian stakeholders and the web of design review agencies in Washington, D.C. Also, it was important that an architect be found who could design a building that would reflect the past and present as well as look to the future of indigenous people of the Western Hemisphere.

The Smithsonian hired the Philadelphia firm Geddes Brecher Qualls Cunningham, which assembled a formidable team of Native American designers. The primary architect was Douglas Cardinal (Canadian Blackfoot), who studied architecture at the University of Texas. Growing up in western Canada and living in Texas gave him a respect and love of windswept plains evident in his architecture. Cardinal walked the streets of Washington and the Mall to get a feel for the city. He also relocated his office from Ottawa to Washington, met with Smithsonian and regulatory review staff, and organized a consultation process of his own, a three-day "vision session." The ideas that came from this vision session were not limited to design but encompassed ways of life: how do people deal with each other, with nature, the world? Cardinal invited tribal elders such as the late Lloyd Kiva New (Cherokee Nation), a respected artist from New Mexico, to attend and give ideas to augment "The Way of the People." The elders blessed the site and drew inspiration from it by walking every inch. The session confirmed that the entrance to the building should face east, following many traditional Native dwellings whose entrances are oriented to greet the morning sun; the design should include references to Native cosmology; and the building should contain as much natural material as possible and be welcoming to everyone. Cardinal believed that the new museum "should endeavor to be a spiritual act and should be demanded from all those contributing to the design the very best of their endeavors." He designed the building from the inside out, placing human needs at the heart of the design process. The center of the Potomac—a large interior gathering space—was to become the heart of the building from which everything else grew. At the same time, rather than designing something that is merely functional, Cardinal paid close attention to the building's visual form. He envisioned the exterior as a "majestic curvilinear symbol representing the nurturing female forms of Mother Earth" (Cardinal, 2016), and it appears solid and timeless but also undulates with sensuality—it is alive and dynamic.

A unique team of Native experts worked with Cardinal on the design. Ramona Sakiestewa, a noted Hopi weaver, was asked to develop design schemes for the museum's interior and also worked with the designers on the color palette. Johnpaul Jones, an architect and landscape architect from Seattle and a member of the Cherokee and Choctaw tribes, collaborated with Donna House, a Navajo and Oneida botanist, in the landscape design that surrounds the building. Jones and House felt it was important to use indigenous plants throughout the landscape and honor the host tribes of the D.C. region upon whose land the museum was being built by recalling the landscape that existed prior to European contact. The plantings include elm trees, cattails, wild rice, water lilies, and manna grass. The plantings in the crop area to the south are carefully selected as examples of Native American resources for culinary, artistic, and medicinal purposes (Ottesen, 2011).

Cardinal and his team were very aware of the other buildings on the National Mall, and they wanted to respect that tradition and context. Also, they had to incorporate height and setback limitations, as well as views that needed to be respected, the most important being the view to and from the U.S. Capitol. Since it had been decided that the main entrance would face east, it would therefore face the U.S. Capitol. Cardinal envisioned the building as a "clump of rock" carved as wind and water would do. As a result, the building's volume, curving forms, and rough and smooth textures evoke a natural rock formation that has been carved by wind and water while still relating to the context of the National Mall. To complement the dome of the National Gallery of Art across the Mall, the architect designed a lower stepped dome for the Potomac with an opening at its center that brings in light and sun and serves as a focal point above.

The water elements are a crucial feature of the landscape and contribute to the architecture of the building. As Johnpaul Jones (Jones and Jones Architects, personal communication to A.B.) wrote, "Indigenous people of this country consider water as an important welcoming element; a natural element that offers itself to us freely. Since most of the visitors coming to NMAI come from the northwest direction we thought that here is where the water should welcome folks. The physical design idea was to make it look like the water flowed out of the rock layers of the stone building into small pools and then flowed over a lower stone projection as a series of waterfall, cascading to a lower pool, and then flowing along the north side of NMAI to the east end of the building where it magically flows into the east site wetland area" (Figure 2).

Jones also reveals a secret about another water feature: "There is a wonderful little detail that you can only see in action on a rainy day at the NMAI; it is just around the corner to the right as you face the waterfall . . . on the west face of the waterfall area." The rain from the roof is drained "down a vertical hidden pipe and appears at a stone element that spins the water in a spiral before it flows into another pipe which leads to the wetland area, where it is cleaned up by the wetland plants and sent on its way to the Potomac River."

A FOCUS ON STONE

Natural stone is fundamental to the design concept of the NMAI, which Cardinal referred to as an "abstraction of the rock that formed this continent" and "spirit mountain" (Forgey, 2004) and the design team identified as a "rock formation carved by wind and water, a formation emerging from the earth rather than being set down upon it" (Blue Spruce, 2008:17). These visions were realized in large part by cladding the curvilinear building with the warm earth tones of buff-colored Kasota limestone supplied by Vetter Stone (Figures 1, 3). Johnpaul Jones recalls, "Originally we considered using the same stone that was used for the exterior of the East Building of the National Gallery of

FIGURE 2. Two views of the cascade and fountains at the northwest corner of the building. Photos by Eric Long, Smithsonian Institution.

FIGURE 3. Entrance (left) and north facade (right) during the building's inauguration, September 2004. Photo by John Steiner, Smithsonian Institution.

Art, but there wasn't enough of it available. So we chose instead a creamier colored Kasota stone that is quarried in Minnesota."

In addition to the Kasota limestone installed on the facade, a range of other stones were used throughout the building. The cascade portion of the watercourse is made of Golden Sand limestone imported from Mexico, selected to match the Kasota limestone but more resistant to abrasion by water; this stone was also used at the base of the building where it is in contact with water (Figure 2). Exterior paving and a bench in the Potomac are made of American Mist granite quarried by Rock of Ages in Morgantown, Pennsylvania, and fabricated by Granicor of St. Augustin, Quebec. Thermal-finish Mount Airy granite decorates the curbs of planters along the site's perimeter and exterior stair treads. Thermal-finish Missouri Red granite surrounds the maple floor at the center of the Potomac. A single block of red Seneca sandstone, a local stone used for the facade of the Smithsonian Castle, is at the center of the floor, the "hearth and heart of the building." Polished Cambrian Black is used in the museum store and café, polished Giallo Sahara marble is used on countertops in the public restrooms, and honed Calizza Capri limestone is used for interior handrails and the cap of the monumental stair (Stinnard, 2005).

CONSTRUCTION

After a decade of planning, groundbreaking for the mall building occurred on September 28, 1999, and was followed shortly afterward by site excavation. The construction contract was awarded on June 20, 2001, to the Clark Construction Group of Bethesda, Maryland, and Table Mountain Rancheria Enterprises of Friant, California, who were overseen by architects of record Polshek-SmithGroup and Smithsonian staff.

Although the building is clad with stone, it is primarily constructed with poured concrete floors, columns, and shear walls (Figure 4; see also figure 7 in Grissom and Charola, "Survey and Documentation of Darkening and Streaking on the National

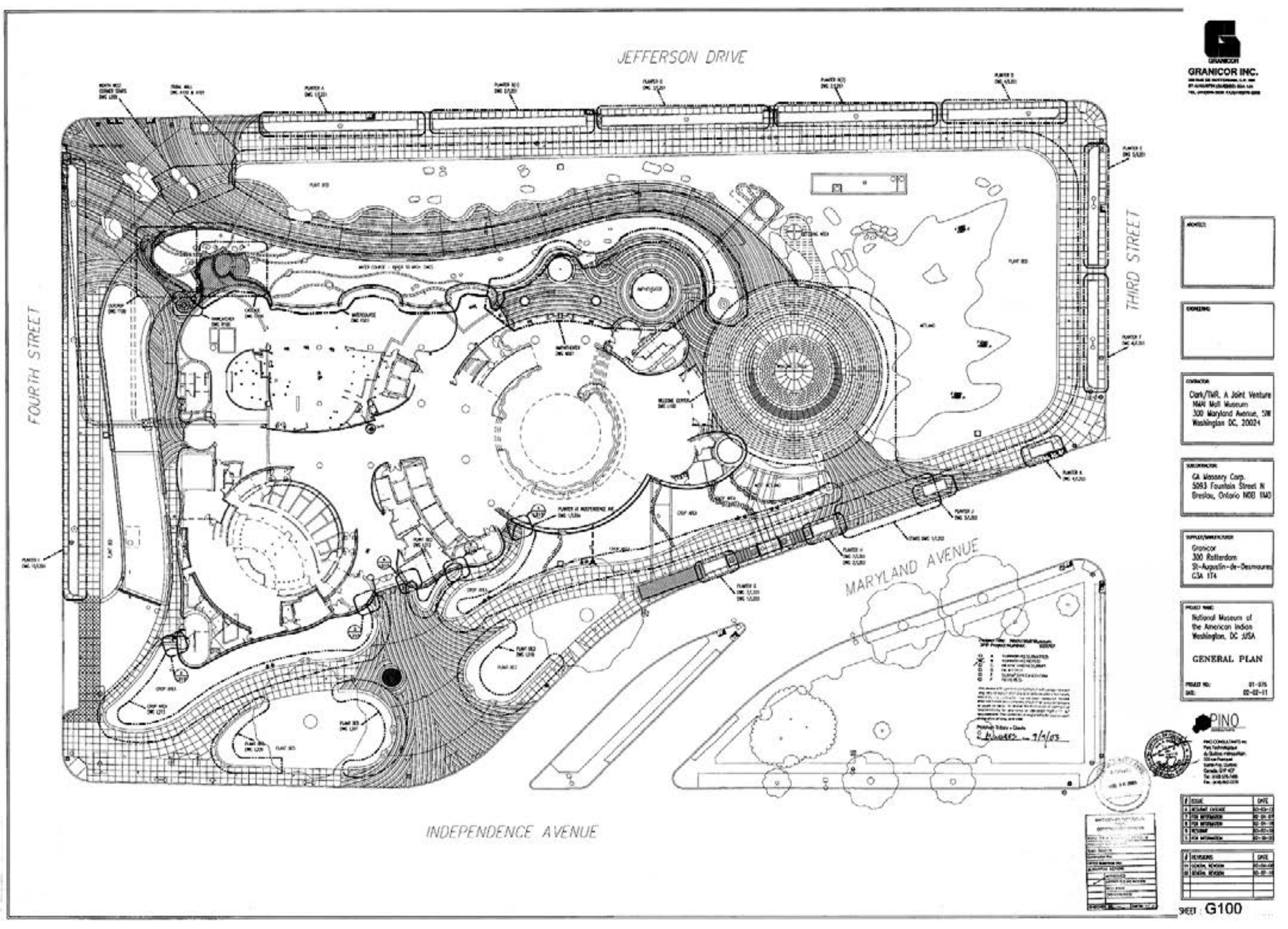

FIGURE 4. General plan. Site plan by Polshek, Toby + Davis, Jones & Jones, and Granicor Inc., G100, February 2, 2001 ©2016 Smithsonian Institution.

Museum of the American Indian Building," this volume). To support the museum building, Clark drove over a thousand friction-resistant piles of epoxy-coated steel (H310-section) 15 m into bearing strata (McCraven, 2002) upon which they constructed the building's framing, using flat-plate construction of reinforced concrete floors to keep floor-to-floor heights to a minimum. In this way, the number of floors (six plus two mezzanines) was maximized while the building's height remains within the capital's building height restriction of 40 m (130 feet). Frame columns were offset between floors, allowing more flexibility to accommodate interior requirements while maintaining the structural integrity of the frame (Portland Cement Association, 2016).

Construction of the building was complicated by the design's curvature throughout: curves number over 1,000, with little repetition. For pouring the concrete walls, an innovative adjustable radius formwork made by Conesco Doka was used, forming concave or convex walls with radii as tight as about 3 m. Nearly 5-m-high serpentine formwork panels, which sat on 2.4-m-wide climbing platforms, were positioned by a crane for each pour (McCraven, 2002). Grout-filled concrete block walls in some locations completed the structure. Steel framing was used in only two locations: to bear the weight of the cantilevered entrance portico and to support the precast glass-fiber-reinforced concrete dome crowning the nearly 40-m-diameter Potomac space.

Buff Kasota limestone, technically a dolomitic limestone, was supplied from the more than 200 ha Vetter Stone quarry near Mankato, Minnesota (Figure 5). Instead of using the panelized stone systems common for construction today, 50,000 blocks were custom cut at the quarry with over 150 different curves, both convex and concave (Granitto, 2005).

"Although in some ways the building looks as though it was carved by nature, it shows a human hand as well" (Blue Spruce, 2004:72). Although all blocks measure approximately 10 cm in thickness, three different ways were employed to fashion the stone for different parts of the building or architectural elements:

1. "Splitface" stones covering the majority of the facade were made from over 700 m^3 (25,000 ft^3) of Vetter Stone's Northern Buff Kasota limestone using hydraulic chisels to create curved blocks with the desired irregular

FIGURE 5. A view of the Vetter Stone quarry, Mankato, Minnesota. Photo by Duane Blue Spruce, Smithsonian Institution.

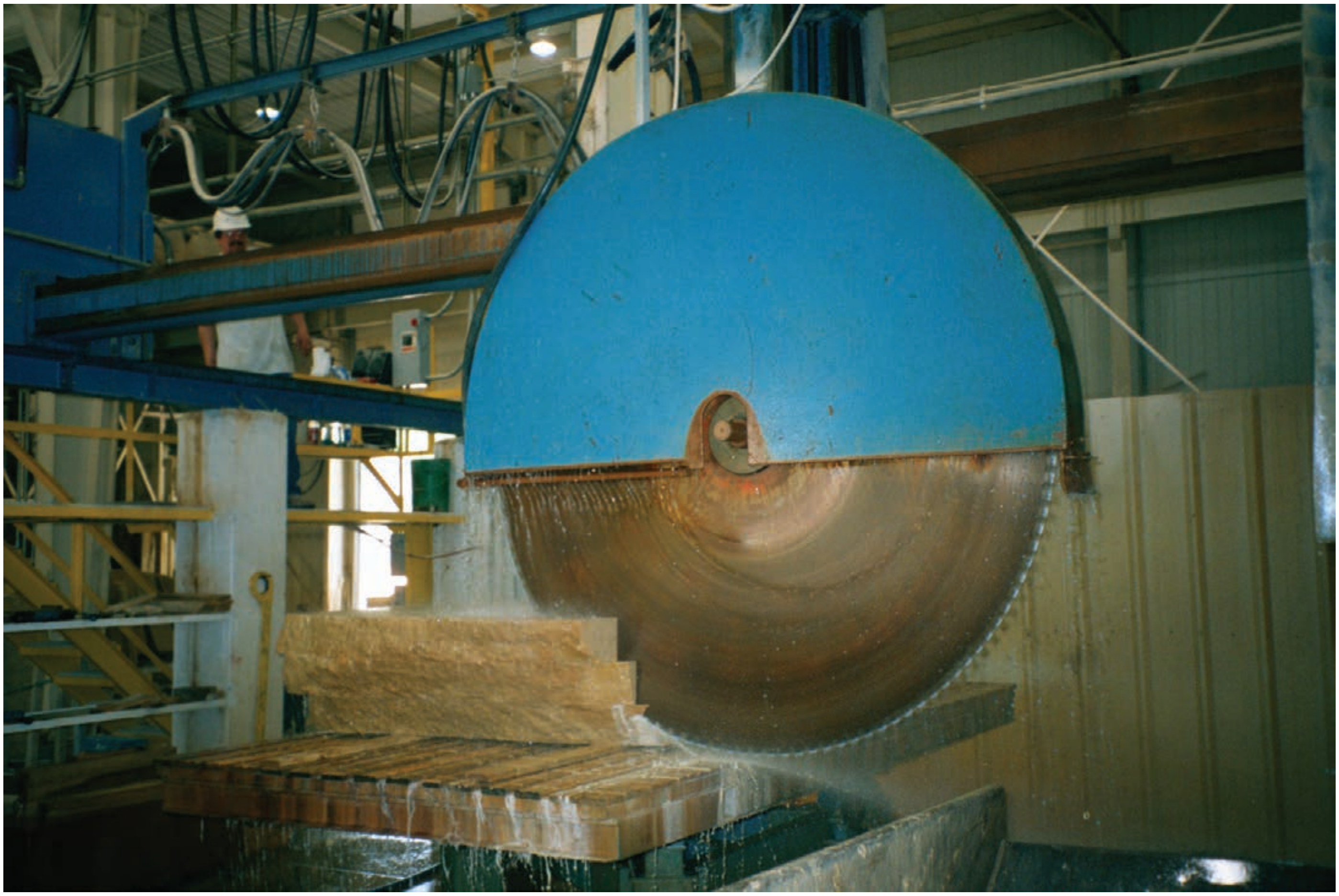

FIGURE 6. Saw at Vetter Stone. Photo by Duane Blue Spruce, Smithsonian Institution.

surfaces of natural stone. Thus, the facade is in marked contrast to that of the flat ashlar masonry of other buildings on the National Mall. Sawed to four course heights (15, 20, 30, and 40 cm) and a range of widths (Figure 6), blocks were arranged irregularly on the facade to create the appearance of natural stone formations. These blocks were laid "in the bed," as is most common for building stones, that is, with bedding planes horizontal.

2. "Roughback" stones, also known as "quarry creek" and "fleuri cut," are the highly decorative blocks of Golden Buff Kasota limestone at ground level. These blocks were cut as large as possible and often span splitface coursing just above them; block sizes and placement are also more irregular than for splitface blocks. Exterior surfaces of the blocks reflect naturally weathered horizontal surfaces of quarry beds colored by iron deposits in rusty hues ranging from yellow to red to dark brown, and they are highly textured by trace fossils. These blocks are installed with bedding planes vertical, in masonry parlance known as "face bedded." Since their surfaces reflect bedding planes, they are mostly planar, in contrast to the curved splitface blocks. Thus, roughback areas are characterized by ledges and faceting on the otherwise curved surfaces of the building. Remarkably, however, a few "tour de force" stones were obtained whose surfaces follow highly curved portions of the building, for example, the extraordinary nearly 3-m-wide block to the left of the main entrance (Figure 7).
3. "Tapestry" finish on Northern Buff Kasota limestone was used for sills, copings, and window surrounds requiring smooth surfaces. These stones were sawed and then sandblasted to remove saw marks for a smooth natural-looking finish (Figure 8). Blocks with this type of finish were also used for interior walls.

Installation of the stone began in April 2003 and was completed around April 2004. More than 40 masons employed by G-A (George & Asmussen) Masonry of Canada and Crestwood, Kentucky, individually installed each stone block, working closely with Vetter Stone.

FIGURE 7. Area to the left of the building's entrance, showing a nearly 3-m-wide roughback block in the third course, marked with an arrow, whose curvature follows that of the building. Photo by Carol Grissom, Smithsonian Institution.

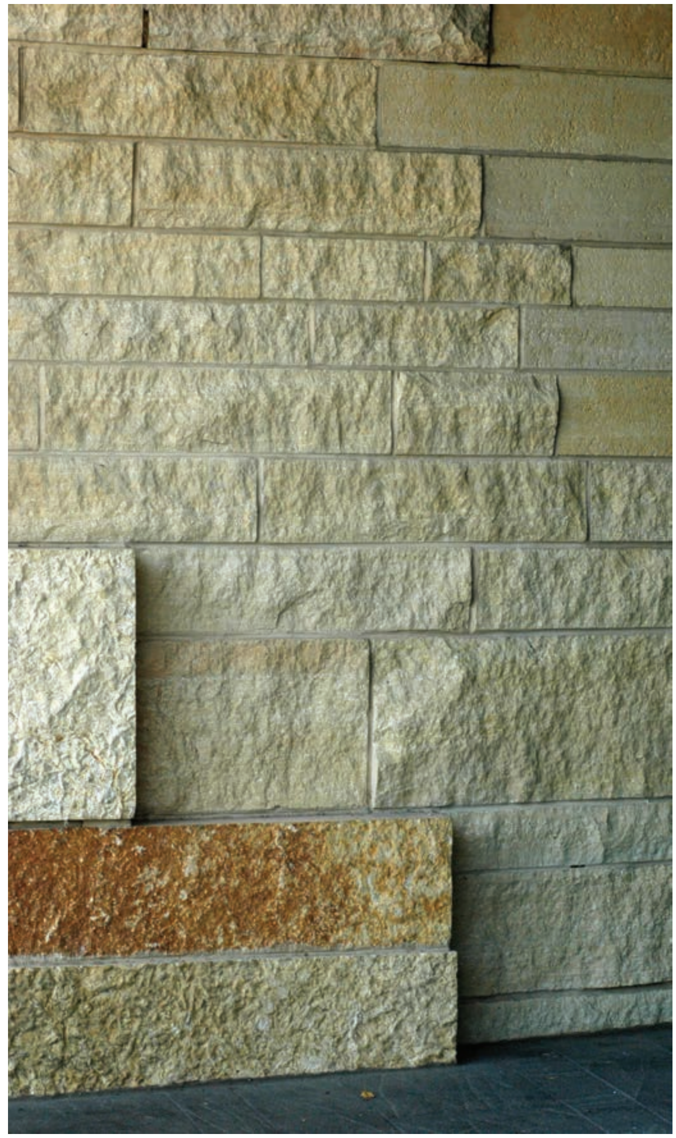

FIGURE 8. Detail of the three fabrication types for the Kasota limestone facade near the museum's entrance: large blocks of roughback stone at lower left, splitface blocks to the right and above, and smooth tapestry-finish blocks at upper right. Dark gray American Mist granite paving can be seen at the base of the wall. Photo by Carol Grissom, Smithsonian Institution.

Prior to installation of the stone blocks, a 5-cm-thick layer of polyurethane foam insulation was spray applied to the concrete structural masonry covered with a rubber blueskin moisture barrier (Figures 9, 10). Additional brown-colored insulation was then sprayed on top of the blueskin barrier, covering stainless-steel attachment hardware for the stone.

Each stone block was secured to the building with the hardware while leaving a vented 5-cm air gap between stone and insulation to provide an additional barrier for modulating the interior climate of the building. For splitface stonework, a course was laid on a custom-made stainless-steel shelf bracket bolted to the interior structure about every 3 m (Figures 9, 10). Blocks then laid on top of this course were secured with V-ties to hardware fixed to the interior structure. Roughback stones at the base of the building were secured with hardware at each side and by tiebacks at intervals on their top surfaces (Figures 11, 12).

Stone blocks were wet set with mortar in full depth, consuming nearly 3,000 tons of custom color-blended mortar, and 2,500 tons of core-fill grout were used for the concrete (CMU) block (Quikrete, 2016). An exception was made where rubberized flashing was placed atop the stainless-steel shelf brackets and under coping stones and sills. These joints were instead

FIGURE 9. Installation of splitface blocks at the southeast corner of the building. Note the blueskin moisture barrier, brown polyurethane foam, and shelf brackets at horizontal intervals. Photo by Michael Dobbs, SmithGroup.

FIGURE 10. North wall layers visible during construction: (from interior) concrete structural masonry, blueskin barrier, stainless-steel hardware at intervals with brown foam insulation over top, a 5-cm-wide air gap, and Kasota limestone. A shelf bracket is visible at the base of the brown foam insulated area. Photo by Michael Dobbs, SmithGroup.

FIGURE 11. Detail showing stainless-steel hardware used to attach the Kasota limestone, west facade. Photo by Michael Dobbs, SmithGroup.

caulked with silicone sealant. Open head joints, that is, vertical joints without mortar, serve as weeps at intervals above flashing, allowing any moisture trapped inside the air gap to escape.

CONCLUSIONS

Use of stone is integral to achieving design objectives for the National Museum of the American Indian. In particular, the buff-colored Kasota limestone facade provides the building with the warm tones and random surfaces of the natural world. At the same time, the internal concrete structure to which the stonework is attached provides the desired interior spaces, efficiently insulated by spray insulation and an air gap to help maintain climate control suitable for the museum's important collection of artifacts.

Acknowledgments

We give special thanks to Duane Blue Spruce, public spaces planning coordinator, National Museum of the American Indian; Eric Long, photographer, National Air and Space Museum;

FIGURE 12. Blocks of roughback stone at the base of the building during installation. Note the stainless-steel brackets that secure each stone at the sides and on top to the interior structure. Photo by Michael Dobbs, SmithGroup.

Johnpaul Jones, Jones and Jones Architects; and Pat Ponton, construction representative, Smithsonian Facilities, for their help with this article.

REFERENCES

Blue Spruce, D. 2004. *Spirit of a Native Place: Building the National Museum of the American Indian*. Washington, D.C.: National Museum of the American Indian in association with National Geographic Society.

———. 2008. "Honoring Our Hosts." In *The Land Has Memory*, ed. D. Blue Spruce and T. Thrasher, pp. 11–32. Washington, D.C.: Smithsonian Institution.

Cardinal, D. J. 2016. National Museum of the American Indian. http://www.djcarchitect.com/work/#/national-museum-of-the-american-indian/ (accessed July 20, 2016).

Ewing, H., and A. Ballard. 2009. *A Guide to Smithsonian Architecture*. Washington, D.C.: Smithsonian Books.

Forgey, B. 2004. Natural Wonder: Douglas Cardinal's Rough-Hewn Mountain of a Building Channels the Spirit of the Earth. *Washington Post,* September 17. http://www.washingtonpost.com/wp-dyn/articles/A27598-2004Sep16.html (accessed June 2, 2016).

Granitto, D. 2005. Gallery of Curves. *Masonry Construction*. http://www.masonryconstruction.com/projects/masonry-constructions-project-of-the-year_o (accessed May 28, 2016).

Grissom, C. A. and A. E. Charola. 2017 (this volume). "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 27–38. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

McCraven, S. C. 2002. Intense Geometry: The National Museum of the American Indian: Imitating the Natural Elements of Wind, Water, and Light Presents Design Challenges for the Contractor on a Very High-Profile Project. *Concrete Construction*, August. http://www.concreteconstruction.net/products/general-construction-equipment/intense-geometry_o (accessed July 20, 2016).

Ottesen, C. 2011. *A Guide to Smithsonian Gardens*. Washington, D.C.: Smithsonian Books.

Portland Cement Association. 2016. Case Studies: Concrete Cultural Buildings: National Museum of the American Indian. http://www.cement.org/concrete-basics/buildings-structures/case-histories/cultural-buildings/national-museum-of-the-american-indian (accessed July 20, 2016).

Quikrete. 2016. Construction of a New Museum. National Museum of the American Indian, Washington, D.C. http://www.quikrete.com/Media/case-studies/National-Museum-of-the-American-Indian.pdf (accessed June 2, 2016).

Stinnard, M. 2005. Natural Stone Reflects Indian Culture. *Stone World*, February 1. http://www.stoneworld.com/articles/83351-natural-stone-reflects-indian-culture (accessed June 2, 2016).

Venturi, Scott Brown and Associates. 1993. *The Way of the People: National Museum of the American Indian: A Detailed Architectural Program*. (3 vols.) Washington, D.C.: Smithsonian Institution Office of Design and Construction.

West, W. R. 2004. "As Long as We Keep Dancing." In *Spirit of a Native Place: Building the National Museum of the American Indian,* ed. D. Blue Spruce, pp. 47–65. Washington, D.C.: National Museum of the American Indian in association with National Geographic Society.

Composition and Characteristics of Kasota Limestone on the Exterior of the National Museum of the American Indian Building

A. Elena Charola, Edward P. Vicenzi, Carol A. Grissom, and Nicole Little*

Characterization of a building stone is fundamental to understanding deterioration mechanisms that may affect it during its service time. The most relevant properties are chemical and mineralogical composition, porosity, and microstructure, as well as its behavior with respect to water absorption and drying.

CHARACTERIZATION OF THE STONE

The stone used for cladding the exterior of the National Museum of the American Indian (NMAI) building is variously referred to in the building trade as Minnesota, Kasota, and Mankato limestone (Lent, 1925:11), but for consistency in this publication it will be referred to as Kasota limestone. In lithological terms, the stone is a dolomite, since it contains a significant amount of magnesium carbonate as well as calcium carbonate. Stratigraphically, it is a part of Ordovician age Oneota dolomite strata found in southeastern Minnesota (Lathram and Thiel, 1946).

Figure 1 shows two blocks that illustrate textural and color variation of the stone; differences in texture are more pronounced for the block on the right, where denser strata are interspersed with less dense layers. Color measurements were taken using a Minolta CR-300 Chroma Meter that uses the CIELAB 1976 system (Urland, 1999). The values measured for three samples ranged from 74.22 to 77.14 for L* (lightness), 1.90 to 3.01 for a* (red-green), and 14.91 to 22.22 for b* (yellow-blue). The Munsell notations for these values range from 2.5Y8/2 (white) to 2.5Y8/4 (pale yellow). The color results mainly from iron-bearing minerals present in the stone, expressed as approximately 1% of iron(III) oxide (Fe_2O_3) by weight (Table 1).

Most stone on the NMAI building is a relatively uniform buff color, and most blocks were cut and installed with bedding planes horizontal, as is customary for durability. For special decorative effect, more colorful blocks were used at street level, known variously as roughback, fleuri cut, or quarry creek stones (Grissom et al., this volume). These blocks were cut from the tops of buried beds that acquired thin surface layers of reddish brown, ochre, orange, and even gray coloration from deposition of iron- and manganese-rich solutions over time. The range of colors was also affected by variations in environmental

Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746, USA.

* Correspondence: A. E. Charola, charolaa@si.edu

Manuscript received 17 January 2012; accepted 23 May 2016.

FIGURE 1. Cut surfaces of two wetted blocks of NMAI Kasota limestone showing differences in color and texture. Photo by Carol A. Grissom.

conditions during deposition and diagenesis that produced different oxidation states of iron and manganese. These colorful surface layers are thin, delicate, and easily detached or eroded. Moreover, installation of the blocks with the colorful surface layers parallel to the wall makes them vulnerable to spalling off.

Table 1 shows results of atomic spectroscopy for Kasota limestone performed by Twin City Testing (unpublished data) for Vetter Stone and wet chemical analyses from geological literature (Bowles, 1918:155; Lathram and Thiel, 1946). On the basis of its chemical composition, the Kasota limestone is classified by geologists as a calcitic dolomite because of the relative percentages of calcium and magnesium (Carozzi, 1972:264).

Acid Attack Analysis

The NMAI Kasota limestone was characterized at the Museum Conservation Institute (MCI) by simple acid attack using a standard procedure (Teutonico, 1988:113–115). This approach is based on dissolution of the carbonate fraction of the rock, that is, dolomite, a calcium magnesium carbonate ($CaMg(CO_3)_2$), and calcite, a calcium carbonate ($CaCO_3$). Left behind is the insoluble fraction of the stone containing minerals such as quartz, feldspars, and clays. Table 2 presents results obtained from three samples left over from NMAI construction, each with a mass of approximately 100 g. Two samples, A and B (corresponding to 1A and 3E in C. Grissom and N. Little, Mankato Stone Analysis, unpublished report, February 2011) were obtained from stone stored at the Paul E. Garber facility located near the MCI at the Museum Support Center, whereas the third one, C, was provided by Tim Rose (TR in Grissom and Little, unpublished report) from the Department of Mineral Sciences within the Smithsonian's National Museum of Natural History, one of the Vetter Stone quarries' samples provided to the Smithsonian prior to construction. Results from Table 1 are included for comparison,

TABLE 1. Chemical analysis of stone from quarries near Kasota, Minnesota. The Twin City Testing (TCT) analysis was done on "glacier buff #21" from Vetter Stone's quarry near Kasota. Bowles (1918) analyzed stone from McClure and Widell quarries closer to Mankato, now owned by Mankato Kasota Stone Inc. Lathram and Thiel (1946) analyzed samples from Kasota (L&T-K) as well as Ottawa (L&T-O), about 16.1 km north of Kasota. Values are percentages by weight. A dash (—) indicates the compound was not found by the test.

Fractions	Compound	TCT[a]	Bowles	L&T-K	L&T-O
Carbonate (%)	$CaCO_3$	47.4	48.26	49.54	51.02
	$MgCO_3$	36.8	38.67	32.34	40.06
Acid insoluble (%)	SiO_2	9.97	7.35		
	Al_2O_3	1.45	4.51		
	Fe_2O_3	0.80	0.97		
	Mn_2O_3	0.09	—	13.18	8.99
	TiO_2	0.07	0.08		
	P_2O_3	—	0.06		
	K_2O	1.29	—		
	Na_2O	0.08	—		
Total		97.95	99.90	95.06	100.07

[a]Results as reported by the laboratory.

TABLE 2. Results for acid attack analysis of three NMAI Kasota limestone samples compared to results from studies of other stones quarried near Kasota (expressed as weight percent), where Vetter corresponds to the data provided by Vetter Stone; Bowles (1918); L&T corresponds to Lathram and Thiel (1946) and WJE corresponds to Wiss, Janney, Elstner Associates (WJE, 1997).

	NMAI samples			Other studies			
Residue	A	B	C	Vetter	Bowles	L&T	WJE
Carbonate (%)	86.50	87.40	82.50	84.20	86.93	81.88–91.08	90.4–92.0
Acid insoluble (%)	13.50	12.60	17.50	15.60	12.87	13.18–8.99	9.6–8.0
Total	100.00	100.00	100.00	99.80	99.80	95.06–100.07	100.0

as well as those for two samples taken from the Philadelphia Museum of Art built in 1928 from materials quarried at a location now owned by Vetter Stone. These were analyzed by Wiss, Janney, Elstner Associates, (WJE, Laboratory Studies, 1997:29). Results for the Kasota stone used in the NMAI building are similar to those in other studies.

X-Ray Powder Diffraction

The acid-insoluble residues were further analyzed at MCI using a Rigaku Micro X-Ray diffractometer for identification of crystalline materials. Table 3 lists X-ray powder diffraction (XRD) results for minerals identified in the residues, which had been separated into coarse- and fine-grain-size fractions, above and below 20 µm, respectively, during the acid analysis procedure. Figure 2 shows XRD patterns for the two fractions of one sample. Quartz was found to be the major component in all acid-insoluble residues, and in one coarse fraction it was the only mineral found. Minor amounts of alkali (K, Na) feldspars, such as orthoclase and microcline, were identified in all other samples. Feldspars were also identified by WJE (Laboratory Studies, 1997:23) by XRD analysis of the acid-insoluble fraction of stone from the Philadelphia Museum of Art, whereas petrographic analyses provided by Vetter Stone (H. Vetter, Vetter Stone Co., personal communication) identified plagioclase, (Ca, Na) feldspar, as a minor constituent in one of two samples from their quarry. Finally, XRD showed patterns consistent with traces of mica (possibly muscovite) or clays (possibly illite and/or palygorskite) in the fine fraction, labeled in the detail of the initial section of the XRD pattern at lower 2Θ angles and higher *d* values in Figure 2.

TABLE 3. Results from powder X-ray diffraction of coarse- and fine-grain-size fractions of acid-insoluble residues (AIR) for three samples of NMAI Kasota limestone.

Sample	Percent w/w per sample	AIR fraction	Percent w/w per fraction	Minerals present	Relative amount
A	1.1	Coarse	8	α-Quartz	Major
	12.4	Fine	92	α-Quartz	Major
				Orthoclase	Minor
				Microcline	Minor
				Clays or micas	Traces
B	0.9	Coarse	7	α-quartz	Major
				Orthoclase	Minor
				Microcline	Minor
	11.7	Fine	93	α-Quartz	Major
				Microcline	Minor
				Orthoclase	Minor
				Clays or micas	Traces
C	2.0	Coarse	11	α-Quartz	Major
				Orthoclase	Minor
				Microcline	Minor
	15.5	Fine	89	α-quartz	Major
				Microcline	Minor
				Orthoclase	Minor
				Clays or micas	Traces

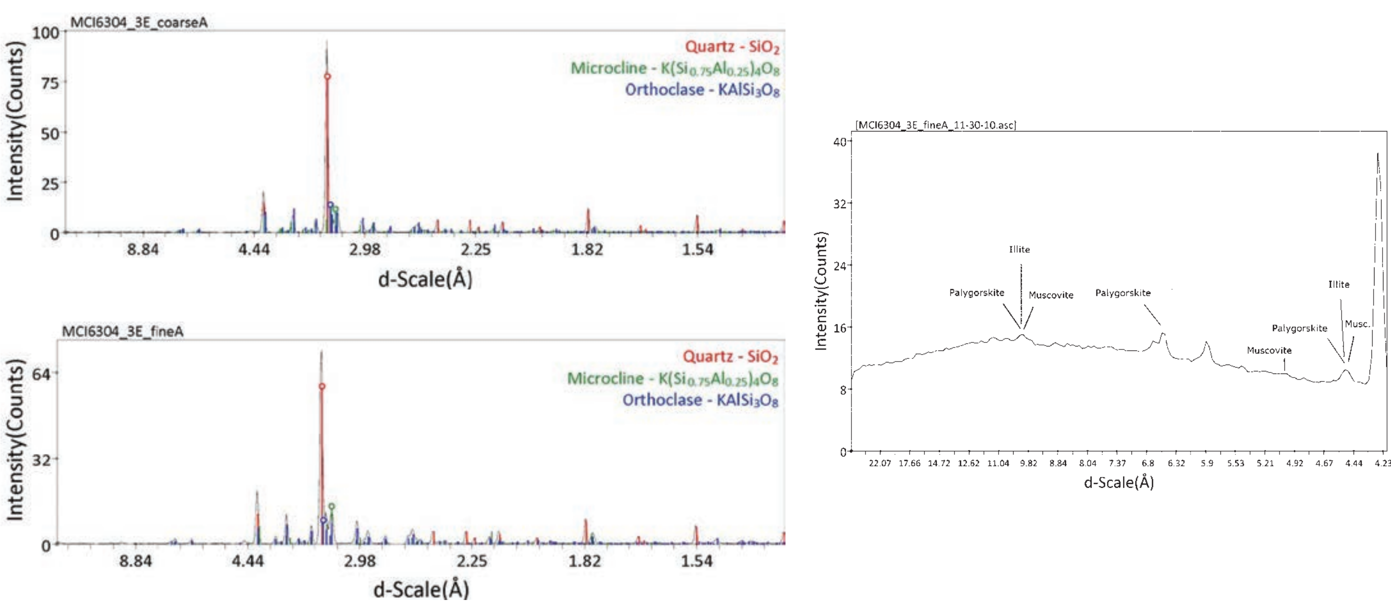

FIGURE 2. The XRD patterns for the acid-insoluble fractions of a NMAI Kasota limestone sample (B) expressed in terms of *d* spacing (distance between adjacent lattice planes). Top left: coarse-grain-size fraction. Bottom left: fine-grain-size fraction. Right: detail of the initial section of the pattern for the fine fraction, with peaks associated with mica or clay minerals identified.

Microscopic Examination

Polished thin sections were examined with Leica and Olympus polarizing light microscopes and an FEI Quanta 200F field emission scanning electron microscope (FE SEM). A Bruker 5030 energy-dispersive spectrometer attached to the SEM was used to collect hyperspectral X-ray images of analyzed regions.

A polished thin section examined with the Leica microscope gives an idea of the texture of the stone (Figure 3). Using this technique, the largest pores in the section measured over 1 mm in linear dimensions, and the smallest measured about 50 µm.

Higher magnification of a thin section shows the Kasota limestone pore structure more clearly (Figure 4). Rather than being held together by the matrix, the crystals are in contact with

FIGURE 3. This dark-field image of an entire thin section of NMAI Kasota limestone (sample 1b) is a mosaic of five image tiles. Pores appear black in this image, and areas with the largest pores are circled in red. The largest pores measure about 1 mm (1,000 µm) in linear dimension. Composite photo by Melvin J. Wachowiak, Smithsonian Institution.

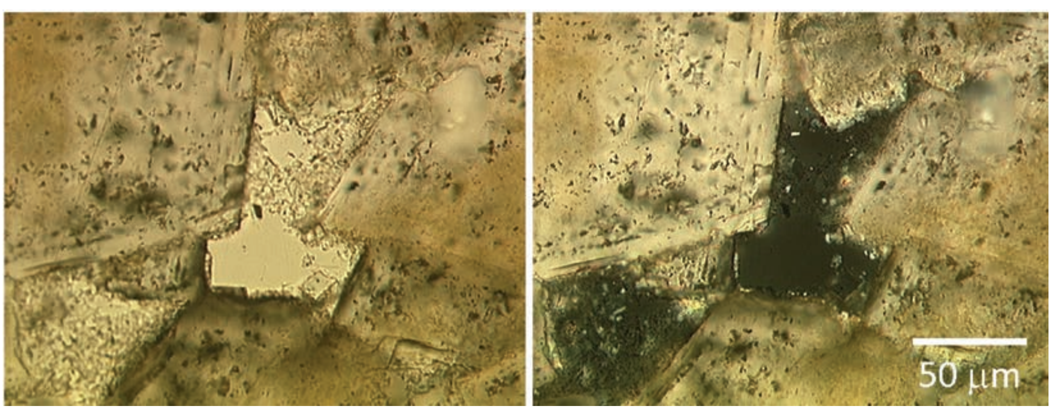

FIGURE 4. Thin section of NMAI Kasota limestone (sample 2B): left: plane-polarized light; right: crossed-polarized light. The large pore in the center between dolomite crystals is partly filled with fine-grained cement, which reduces its size. Dolomite crystals are about 100 µm in length, and the micritic calcite is <3 µm. Photos by Edward Vicenzi, Smithsonian Institution.

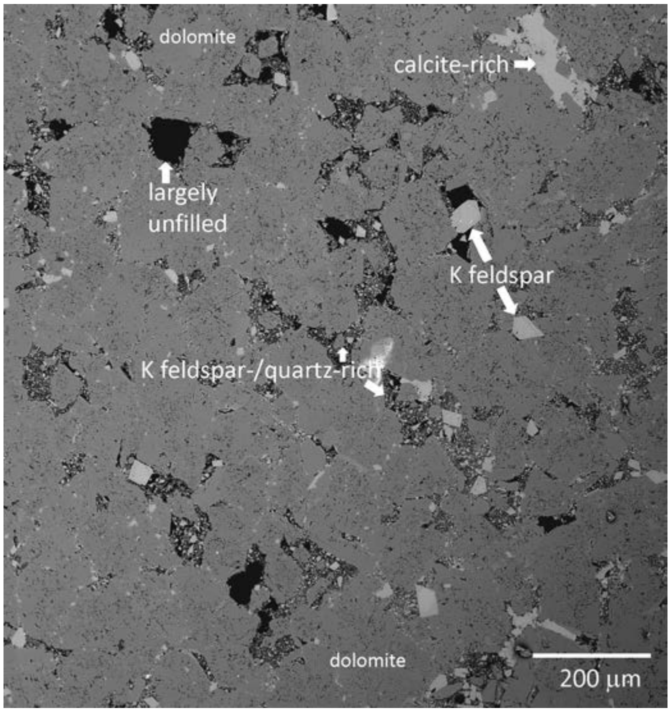

FIGURE 5. Overview backscattered electron image of Kasota limestone. Note that because the image intensity scales lighter with higher average atomic number in backscattered electron images, both calcite and K feldspar appear lighter than dolomite in the image. Image by Edward Vicenzi, Smithsonian Institution.

each other, creating a grain-supported structure. Note that the void between crystals is partly filled with fine-grained cement, referred to as micritic calcite (<4 µm), a recrystallized lime mud.

Cement that fills pores in the stone was further examined and analyzed using the FE SEM. Figure 5 illustrates the range of pore textures and mineral assemblages found in the stone. Some pores are largely unfilled, whereas others contain large euhedral (potassium) K feldspar crystals, with and without finer-grained K feldspar and quartz. Other pores appear to be almost completely filled with fine-grained calcite.

A series of false-colored X-ray images shown in Figure 6 illustrates heterogeneity within the Kasota limestone. Void spaces are black, whereas silicates (feldspars and quartz) are represented by blue, calcite by red, and dolomite by yellow or green. The images show that pores in the section range in size from about 10 to 400 µm in linear dimensions. In general, larger pores are partly filled, whereas smaller pores are mostly filled. Pores filled by both silicates and calcite were likely formed as the result of two successive generations of fluid precipitation, and these regions tend to have the least amount of void space remaining.

Figure 7 shows typical cement mineral assemblages at higher spatial resolution, which allows individual crystals to be distinguished. Large K feldspar crystals measure as much as 25 µm in

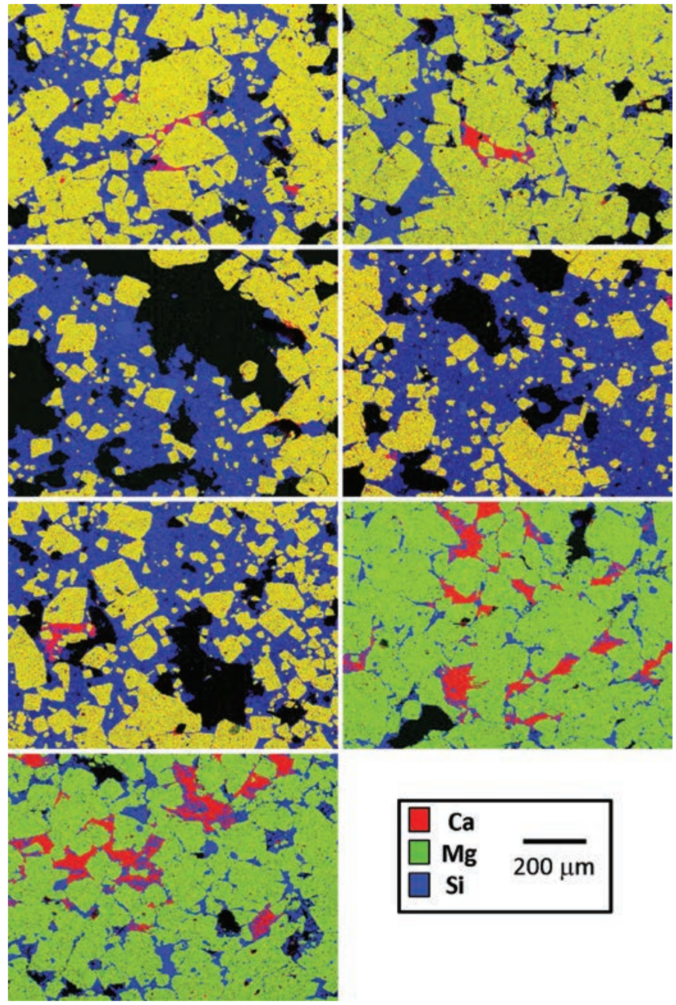

FIGURE 6. Composite X-ray images showing the heterogeneity of cement minerals at a moderate length scale. The false-colored images comprise three components: red (calcium), green (magnesium), and blue (silicon). Dolomite grains have a color spread from yellow to green stemming from automatic color scaling depending upon the total X-ray count rate of its two components (Mg + Ca). Where void space is high, the count rates were correspondingly low and shifted the intensity of green in dolomite to yellow. Images by Edward Vicenzi, Smithsonian Institution.

linear dimension. Smaller K feldspar and quartz crystals measure about 5 µm or less. Fine-grained calcite particles measure 1 µm or less, sometimes appearing as agglomerations. A few individual clay platelets are present, measuring 2 µm or less, but no mica was observed.

Water Absorption and Drying Characteristics

The behavior of any stone with regard to water absorption and loss is a function of its pore system, particularly pore

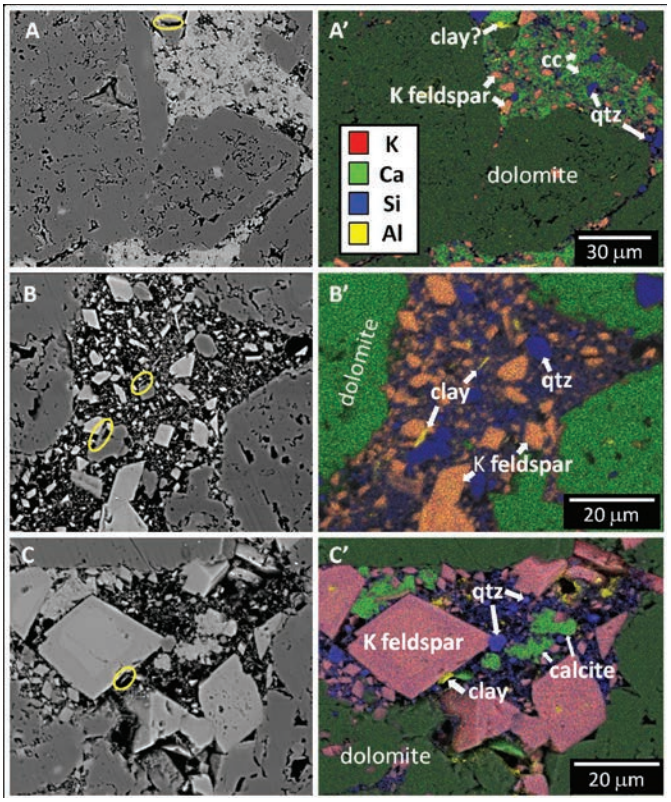

FIGURE 7. (A–C) Backscattered electron and (A′–C′) composite X-ray images of three varieties of natural cement in the NMAI Kasota limestone. The false-colored X-ray images comprise four components: red (potassium), green (calcium), blue (silicon), and yellow (aluminum). Aluminum-rich regions indicate volumetrically minor clay particles; yellow ellipses locate them on the backscattered electron images. Images by Edward Vicenzi, Smithsonian Institution.

sizes and their distribution. Porosity of stone with respect to water can be measured in several different ways. Total porosity can only be measured under vacuum, but measurement of open pores alone can be done at atmospheric pressure (Borelli, 1999). Apparent porosity (also referred to as percent absorption) is the percent absorption by weight of water in open pores. Open porosity is the percent absorption by volume of water in open pores.

For the present study, the apparent porosity was measured on two 5 × 5 × 5 cm Kasota limestone cubes from the NMAI construction (Kasota 1 and Kasota 2) following the procedure of ASTM C97-96 (American Society for Testing and Materials, 1996). Since it is unlikely that building stone would be completely saturated by water, however, the test was modified by reducing the immersion time from 48 to 24 hours. The open porosity percentage was calculated from the apparent porosity percentage following Borelli (1999). Table 4 shows that porosity values for the two Kasota limestone samples are within the

TABLE 4. Apparent and open porosity values measured for two NMAI Kasota limestone samples (calculated from data in Table 5), along with those reported by Wiss, Janney, Elstner Associates (WJE) and for the Oneota dolomite by Lathram and Thiel (1946; L&T). A dash (—) indicates that the data was not reported.

				L&T	
Porosity	Kasota 1	Kasota 2	WJE	Wabasha County	Houston County
Apparent (%)	4.66	4.45	2.7–4.2	0.62–2.64	1.31–2.57
Open (%)	12.11	11.58	—	1.72–6.73	3.55–6.68

values reported by Wiss, Janney, Elstner Associates for the Philadelphia Museum of Art (WJE, Laboratory Studies, 1997:22) but considerably higher than those reported in the literature for stones from other Oneota quarries (Lathram and Thiel, 1946), perhaps because they are a hundred miles or more from Kasota. The values for the Kasota stone fall at the high end of apparent porosity for dolomite rock, which ranges from 1.0% to 5.0% according to Winkler (1997:34).

To further characterize the porosity of the stone, the cubes were tested using a standard capillary water absorption method, UNI 10859 (Ente Nazionale Italiano di Unificazione, 2000). This test was followed by total immersion of the samples in water for 24 hours and drying at environmental conditions of 21°C and 45% relative humidity. Figure 8 shows the absorption and drying curves obtained from the test. Slight differences in the drying curves may reflect variations in texture and porosity between the two Kasota limestone samples and/or slight differences in environmental conditions since the samples were not run simultaneously. Data shown in Table 5 were derived from these curves.

For most inorganic porous materials, water absorption is a relatively fast mechanism, whereas drying takes a significantly longer time. For the two samples of NMAI Kasota limestone, about 25 hours of contact with water was required to nearly reach asymptotic values in the capillary absorption curves. This means that it would take about 25 hours of constant rain to saturate the building's stone to 95% of its fully immersed capacity. When the two samples were dried after immersion, on the other hand, it took four times longer (some 100 hours) to lose the same amount of water.

Pore size and pore size distribution are critical in determining both absorption and drying characteristics (Rousset Tournier, 2001). Macropores are defined as those with diameters above 1 mm, capillary pores are those with diameters ranging from 1 mm down to 1 µm, and micropores are those with diameters below 1 µm. When liquid water initially comes into contact with

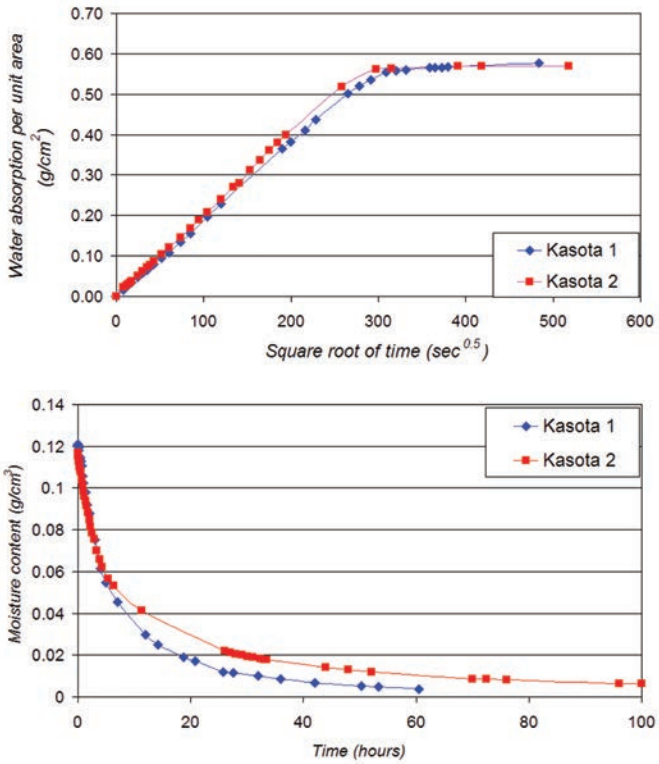

FIGURE 8. Water absorption and drying curves for two samples of NMAI Kasota limestone. Top: capillary absorption curves; bottom: drying curves.

TABLE 5. Water-related parameters for NMAI Kasota limestone. Values in parentheses are correlation factors for calculated slopes. A dash (—) indicates that the test was not extended to allow calculation of the final drying rate.</tab title>

Parameter	Kasota 1	Kasota 2
Capillary absorption coefficient (g cm^{-2} $s^{-0.5}$)	0.00191 (0.999)	0.00202 (0.999)
Water absorbed at asymptotic value (g)	14.44	14.25
Water absorbed after 24-hour immersion (g)	15.14	14.47
Initial drying rate (g cm^{-3} h^{-1})	0.0153 (0.997)	0.0151 (0.996)
Critical moisture content (g cm^{-3})	0.06	0.06
Final drying rate (g cm^{-3} h^{-1})	—	0.00008 (0.998)

stone, water will line the walls of macropores, whereas capillary pores and micropores are filled. Even when stone is totally immersed in water, macropores are never completely filled because air is trapped in them. When stone dries out, liquid water first evaporates from large pores open to the exterior (straight initial section of the drying curve in Figure 8). Then, below the critical moisture content, two transfer mechanisms operate simultaneously, capillary transport in smaller pores and water vapor diffusion from larger pores, to move it to the stone surface (curved section in Figure 8 because the contribution of each mechanism changes with time). At the final stage, the only transport mechanism is water vapor diffusion within the stone (straight final section in Figure 8; Charola and Wendler, 2015). This means that the Kasota limestone on the NMAI building could stay in the final drying stage for many days after a rain event.

Porosity of the Kasota limestone is nonhomogeneous because of the wide variety of pore sizes (Figures 3–7), and it is characterized by irregular connections between pores, which affect water transport and retention. The empty "structure," referred to as void tortuosity, depends on the type, shape, and size of mineral grains or crystals and their organization, best seen in Figures 6 and 7. The largest pores in the capillary range measure nearly 1.0 mm in the linear dimension (Figure 3); micropores can be seen at high magnification (Figure 7). Fractured surfaces offer a different view of the stone's texture and morphology (Figure 9): the largest capillary pores (about 1 mm) are surrounded by denser areas with lower porosity that will retain moisture

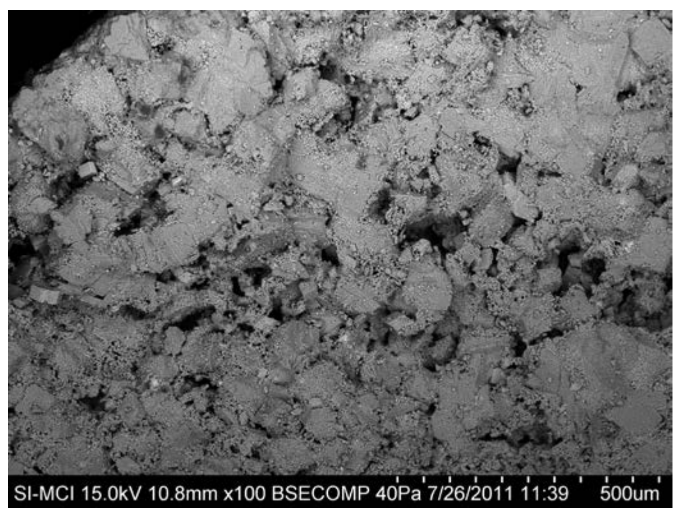

FIGURE 9. Backscattered electron micrograph of a fractured surface of NMAI Kasota limestone showing a range of texture and porosity. The pores are seen as black areas; a band of larger pores crosses the sample at the center of the photograph. Note the wide range of crystal and grain aggregate sizes from a few microns to about 2–3 mm length. Photo by Hanna Szczepanowska, Smithsonian Institution.

longer after rainfall. Shapes of pores also play a role in moisture retention. Long, flat pores found in the Kasota limestone between platy minerals or in cleavage plane fissures of dolomite and feldspar minerals also retain water longer. Moreover, capillary condensation can occur at relative humidity of around 90%; in other words, these pores may hold liquid water even if it is not raining.

It is rare that a building stone will be saturated with as much water as a test sample immersed in water for 24 hours, and it is unlikely that the initial drying rate will be constant in actuality. For the specific case of the NMAI building, drying was observed after a nightlong heavy rain, and it was seen that the north side dried significantly faster than the south side, a feature attributed to the prevailing WNW wind at the time. Furthermore, wind eddies were detected, apparently forming on account of the building's curved walls, and they clearly accelerated drying in localized areas.

DISCUSSION AND CONCLUSIONS

The Kasota limestone used for cladding on the NMAI building is classified as a calcitic dolomite; it is mostly grain supported and has an open porosity of 12%. The general color of the stone is tawny on account of iron(III)-bearing minerals. More highly colored surface layers on some stones at ground level are attributed to the deposition of iron and manganese minerals at the top of buried quarry beds.

The NMAI Kasota limestone is susceptible to dissolution by water, particularly if the water is acidic. The presence of carbon dioxide in the air results in the formation of carbonic acid in rain water, which can attack the stone's carbonate minerals, dolomite (calcium magnesium carbonate) and calcite (calcium carbonate). Although the solubility of calcite is only about one-twelfth that of dolomite when in equilibrium with a saturated solution at about 20°C, calcite dissolves at a faster rate in dolomite (Martinez and White, 1999). Therefore, calcite will be leached out first from Kasota limestone under normal weathering conditions. When found as micritic particles within pores, the large specific surface area (i.e., its surface to volume ratio) of calcite will increase its dissolution rate (Thomson and White, 1974: Charola and Koestler, 1985/1986).

The pore structure and surface roughness of stone affect the absorption of water, whereas pore sizes control water loss. Under laboratory conditions, it was found that drying a Kasota limestone sample took four times longer than wetting it. Although after a rain event the surface layer of the stone may appear dry, water can still be held within subsurface capillary pores and micropores. In addition, the splitface blocks comprising the majority of the stonework, made using hydraulic chisels (Grissom et al., this volume), introduced fissures and microcracks below the surface. This has made the blocks more susceptible to water retention and subsequent spalling from mechanisms such as freeze-thaw and biocolonization, as discussed in more detail by DePriest and Charola (this volume).

When considering regular cleaning, the susceptibility of Kasota limestone to aqueous dissolution is relevant because it leads not only to surface erosion but also to an increase in porosity and loss of mechanical strength. It is noteworthy in this context that Golden Sand limestone (with low apparent porosity of less than 1%) was used for the building's cascade because of its superior resistance to water flow, instead of the Kasota limestone (with much higher apparent porosity of about 4.5%; Grissom et al., this volume).

REFERENCES

American Society for Testing and Materials. 1996. Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone. ASTM C97-96. West Conshohocken, Pa.: American Society for Testing and Materials.

Borelli, E. 1999. *Porosity*. ARC Laboratory Handbook 2. Rome: International Centre for the Study and the Preservation of Cultural Heritage.

Bowles, O. 1918. The Structural and Ornamental Stones of Minnesota. *U.S. Geological Survey Bulletin,* 663.

Carozzi, A. V. 1972. *Microscopic Sedimentary Petrography*. New York: Robert E. Krieger.

Charola, A. E., and R. J. Koestler. 1985/1986. "SEM Study of the Deterioration of Monumental Stones in Vienna." In *Wiener Berichte über Naturwissenschaft in der Kunst*, ed. A. Vendl, B. Pichler, J. Weber, and G. Banik, vol. 2/3, pp. 176–185. Vienna: Hochschule für Angewandte Kunst.

Charola, A. E., and E. Wendler. 2015. An Overview of the Water-Porous Building Material Interactions. *Restoration of Buildings and Monuments,* 25(2–3): 55–65. http://dx.doi.org/10.1515/rbm-2015-2006.

Ente Nazionale Italiano di Unificazione. 2000. Beni culturali. Materiali lapidei naturali ed artificiali. Determinazione dell'assorbimento d'acqua per capillaritá [Cultural Heritage. Natural and Artificial Stone Materials. Determination of Water Absorption by Capillarity]. UNI 10859. Milan: Ente Nazionale Italiano di Unificazione.

DePriest, P., and A. E. Charola. 2017 (this volume). "Biological Colonization and 'Ink Strokes' on Buildings." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 39–44. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Grissom, C. A., A. Ballard, J. Estoque, D. Nauta-Rodriguez, and M. Dobbs. 2017 (this volume). "Design and Construction of the National Museum of the American Indian Building: Focus on the Exterior Stone." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 5–16. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Lathram, E. H., and G. A. Thiel. 1946. A Comparison of the Physical Properties and Petrographic Characteristics of Some Limestones and Dolomites of Southeastern Minnesota. *Journal of Sedimentary Petrology,* 16(2):72–85.

Lent, F. A. 1925. *Trade Names and Descriptions of Marbles, Limestones, Sandstones, Granites and Other Building Stones Quarried in the US, Canada and Other Countries*. New York: Stone Publishing.

Martinez, M. I., and W. B. White. 1999. A Laboratory Investigation of the Relative Dissolutions Rates of the Lirio Limestone and the Isla de Mona Dolomite and Implications for Cave and Karst Development on Isla de Mona. *Journal of Cave and Karst Studies,* 61(1):7–12.

Rousset Tournier, B. 2001. Transferts par capillarité et evaporation dans des roches—Rôle des structures de porosité [Capillarity and evaporation transfers in rocks—Role of the porosity structure]. Doctoral thesis, Université Louis Pasteur, Strasbourg, France.

Teutonico, M. J. 1988. *A Laboratory Manual for Architectural Conservators*. Rome: International Centre for the Study and the Preservation of Cultural Heritage.

Thomson, G., and R. White. 1974. The pH of Rain and the Destruction of Alkaline Stone. *Studies in Conservation,* 19:190–191. http://dx.doi.org/10.1179/sic.1974.017.

Urland, A. 1999. *Colour: Specification and Measurement*. Arc Laboratory Handbook 5. Rome: International Centre for the Study and the Preservation of Cultural Heritage.

Wiss, Janney, Elstner Associates (WJE). 1997. "Laboratory Studies." In Exterior Due Diligence Report for the Philadelphia Museum of Art. Jackson and Ryan. Houston, Tex.,1998

Winkler, E. M. 1997. *Stone in Architecture: Properties, Durability*. New York: Springer-Verlag.

Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building

Carol A. Grissom and A. Elena Charola*

Stonework on the facade of the National Museum of the American Indian (NMAI) has undergone changes since the building's inauguration in 2004. Some of these changes were expected from weathering and suit the aesthetic of the building, but some were unexpected darkening in color and disrupt this aesthetic. In 2010, darkened areas were surveyed and studied to understand the reasons for the changes before a major cleaning in 2011. High-quality photographs of the building were taken, construction drawings were examined, and the building was observed during and immediately after rainfall. In general, darkening occurred in areas that had the most water flowing over the stone surfaces and was correlated with design features and unusual environmental conditions.

Specifically, examination of the building showed that darkened areas could be categorized into six types related to architectural features that predicate flow and retention of rainwater:

A. general darkening on the top and sides of capstones both at the roofline and on balconies unprotected from rainfall by any overhangs
B. slight, relatively uniform darkening below capstones over which water flows evenly, most notably below the capstones at the roofline
C. localized dark streaking below capstones over which water flows unevenly, often channeled by joints between capstones
D. dark spots on blocks that protrude from the facade and catch water, both rough-back blocks at the base of the building and scattered individual blocks
E. very dark streaks below the Senator Daniel K. Inouye Terrace, where there is increased flow of water over sloping and multiple capstones
F. very dark, thick deposits on areas below scuppers that drain rainwater from roofs above (not visible from the ground)

It is a well-known phenomenon that upper parts of buildings are most wetted during rain events, often with surprisingly little wetting of facades below. On traditional buildings, cornices at the tops of facades are typically flashed with metal on horizontal surfaces and guttered to channel rainwater into drains, limiting moisture penetration of stonework below. On the NMAI building, capstones at the roofline and on balconies were not flashed on top but were isolated from blocks below with rubberized membranes on their undersides. Most of these capstones are level, confirmed by the pattern

Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746, USA.
* Correspondence: C. A. Grissom, grissomc@si.edu
Manuscript received 17 January 2012; accepted 23 May 2016.

FIGURE 1. Darkening of capstones on the roofline (type A) in 2010. Flow of water in both directions when poured onto the center of the middle stone shows that the stone is essentially level. Note the light areas next to joints where water repellent components of silicone sealants bled into the stone. Photo by Carol A. Grissom, Smithsonian Institution.

of draining in both directions when a small amount of water was poured onto the center of a capstone (Figure 1). Thus, capstones not only receive but retain significant amounts of rainwater and show general darkening on both horizontal and vertical surfaces. The wetting and darkening patterns within individual blocks are not completely uniform (type A, Figure 1) because of variations in porosity, texture, and roughness of the stone (Charola et al., this volume). In addition, minimal wetting and darkening occurs on stones next to joints where water repellent components of silicone sealants bled into the stone, also seen in other photographs in this chapter. Finally, areas of stone adjacent to an electrical conduit on inner sides of capstones and near a lightning rod are relatively clean (see Figure 1).

The traditional projection of cornices over facades (often several feet or more) minimizes the wetting of areas below by rainwater. On a free-standing wall around NMAI's loading dock west of the building, the capstones do not project at all (Figure 2), and the walls are completely wetted by rainwater (also,

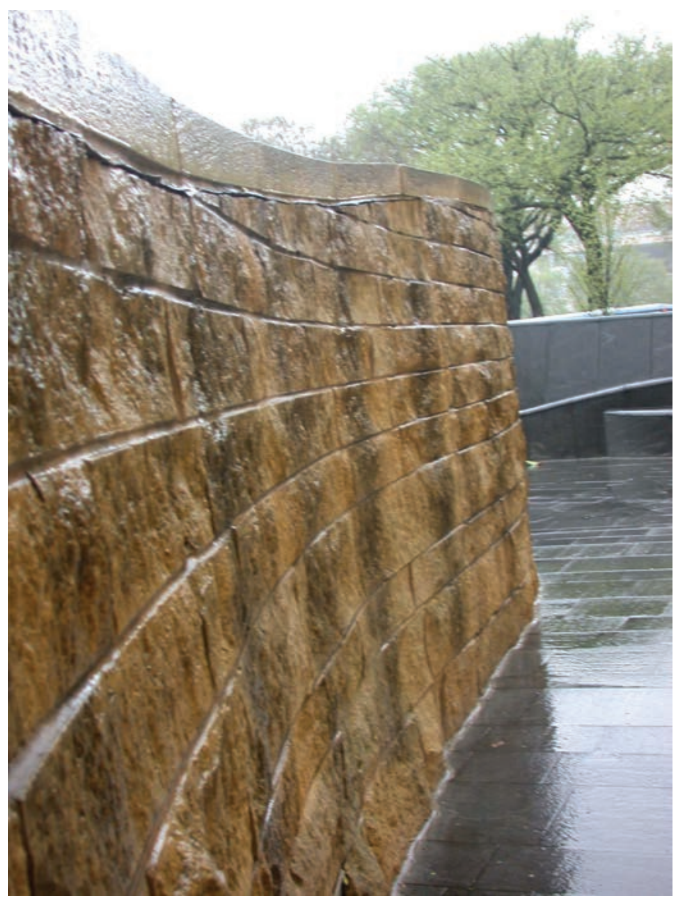

FIGURE 2. Wetting of the free-standing loading dock wall during a rainstorm in 2010. The absence of an overhang as well as the slope of the capstones and the wall results in overall wetting. Photo by Carol A. Grissom, Smithsonian Institution.

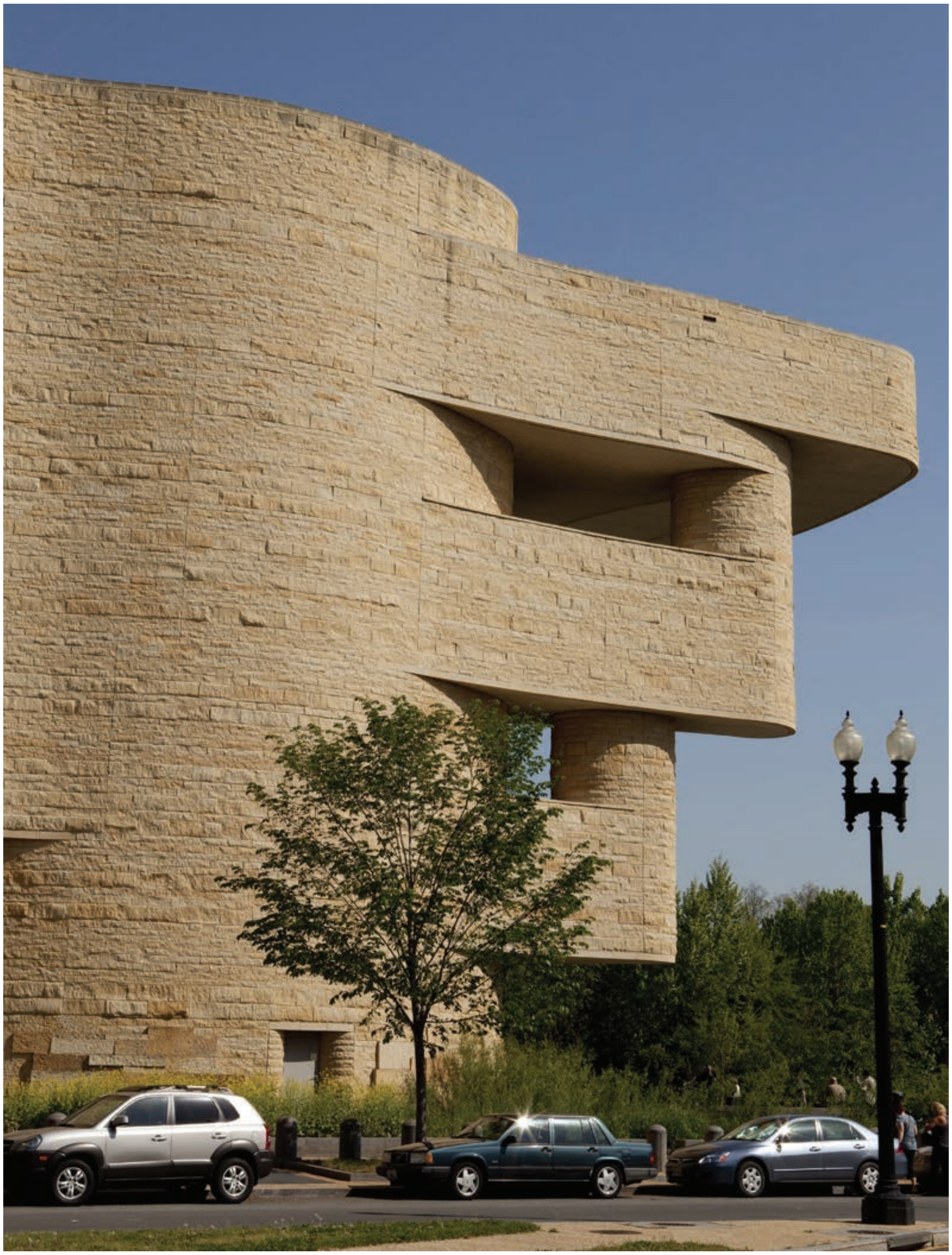

FIGURE 3. Slight, relatively uniform darkening (type B) immediately below the roofline of the south facade in contrast to clean-appearing areas below overhangs at right in 2010. Photo by Melvin J. Wachowiak and E. Keats Webb, Smithsonian Institution.

sloping capstones and walls are a factor in increasing the volume of water running over this wall). In all other locations, capstones project 3.8 to 5 cm over the NMAI facade. This relatively small amount of overhang contributes to the appearance of the building as a natural stone outcropping but reduces its protection of the facade. Below many capstones along the roofline of the facade, darkening was acceptable since it was barely noticeable and uniform on account of even water flow (type B, Figure 3). Below others, unsightly streaks formed, often where slightly recessed silicone sealant joints between capstones channeled water

FIGURE 4. Prominent dark streaks (type C) below the balcony's capstone joints above the cascade at the northwest corner in contrast to generalized darkening visible on the sides of capstones in 2010. Photo by Carol A. Grissom, Smithsonian Institution.

downward; capstone edges in the joints made water repellent by the sealant probably also increased water volume in these areas (see Figure 1; type C, Figure 4).

The NMAI building is distinguished by many gently curved "balconies," which protrude from the building but are not accessible (Figure 5). Most balconies are protected from rainwater by overhangs with the same curvature, such as those indicated by white arrows in Figure 5; as a result, they appeared clean in 2010. Other balconies, such as those indicated by red arrows in Figure 5, are unprotected by overhangs; they displayed dark deposits more clearly visible in the detail in Figure 6. In total, darkening was visible to some extent on capstones and stonework below seven unprotected balconies in 2010, identified on a plan of the building (Figure 7). Two of these balconies are on the south facade (Figures 5, 6); two are on the west facade (Figures 8, 9), and three are on the north facade (Figures 10, 11).

In many cases dark streaks occurred primarily below capstone joints on balconies (Figures 4, 8), but patterns of darkening were also affected by details of balcony construction. Balconies on the west facade were constructed with a single row of capstones abutting the building (Figures 8, 9). The slope and depth of the capstones gradually increase toward the center while capstone heights diminish in tandem. As might be expected, this seems to have increased the amount of water flowing toward the center and concentrated darkening toward the center on stonework below (Figure 9).

Other balconies were designed with parapet walls, tops of capstones sloping slightly inward, and internal drains. Nevertheless, darkening has occurred on facades just below, as seen in Figure 10. The deepest balcony is paved with multiple rows of stones, which can be seen from the interior of the building through windows on the fourth floor (Figure 11). Water is channeled through open joints between stones in the penultimate row into interior drains by inwardly sloping stones, but areas wetted during rain events were darkened, as was stonework on the facade below.

Stones that protrude to any extent from the facade and regularly retain water from rainfall are darkened. Roughback

FIGURE 5. Clean-looking stone below balconies protected by overhangs on the south facade (white arrows), in contrast to darkened stone below those that are not protected by overhangs (red arrows), in 2010. Photo by Melvin J. Wachowiak and E. Keats Webb, Smithsonian Institution.

FIGURE 6. Detail of dark streaking (type C) below the unprotected balcony on the left in Figure 5 in 2010. Photo by Melvin J. Wachowiak and E. Keats Webb, Smithsonian Institution.

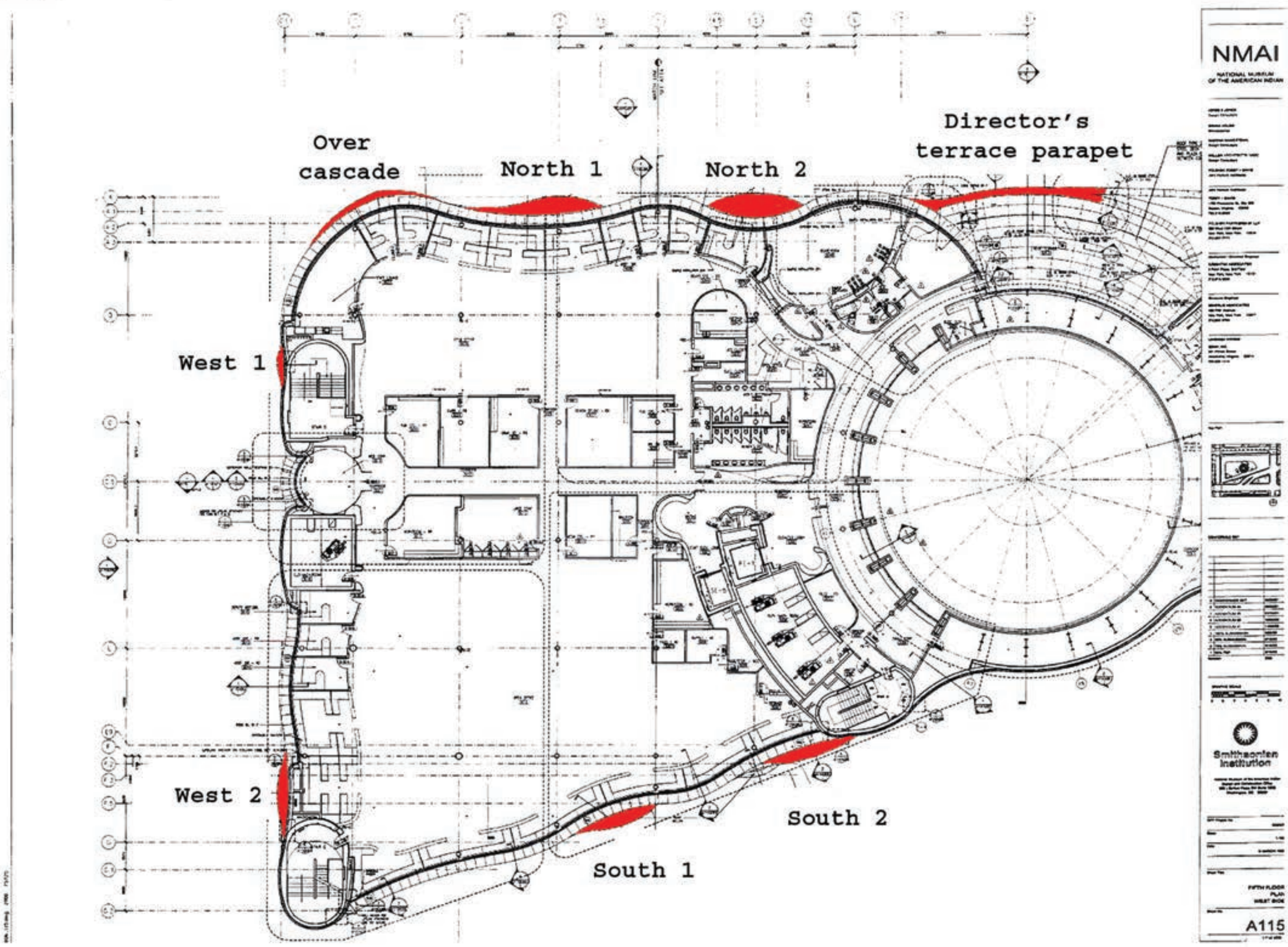

FIGURE 7. Plan of the NMAI building showing locations of seven unprotected balconies (in red) and the Director's Terrace parapet, now Senator Daniel K. Inouye Terrace, below which stonework was darkened in 2010. Carol A. Grissom, modified from Conformed Drawings, National Museum of the American Indian, vol. 2, A115, Fifth Floor Plan, West Side, 29 March 2001.

FIGURE 8. Dark streaking below a few capstone joints on west facade balcony 2 in 2010. Photo by Melvin J. Wachowiak and E. Keats Webb, Smithsonian Institution.

FIGURE 9. Generalized darkening below capstones toward the center of west facade balcony 1, probably from water flowing over the center capstones that are more sloped than those on the sides, in 2010. Photo by Melvin J. Wachowiak and E. Keats Webb, Smithsonian Institution.

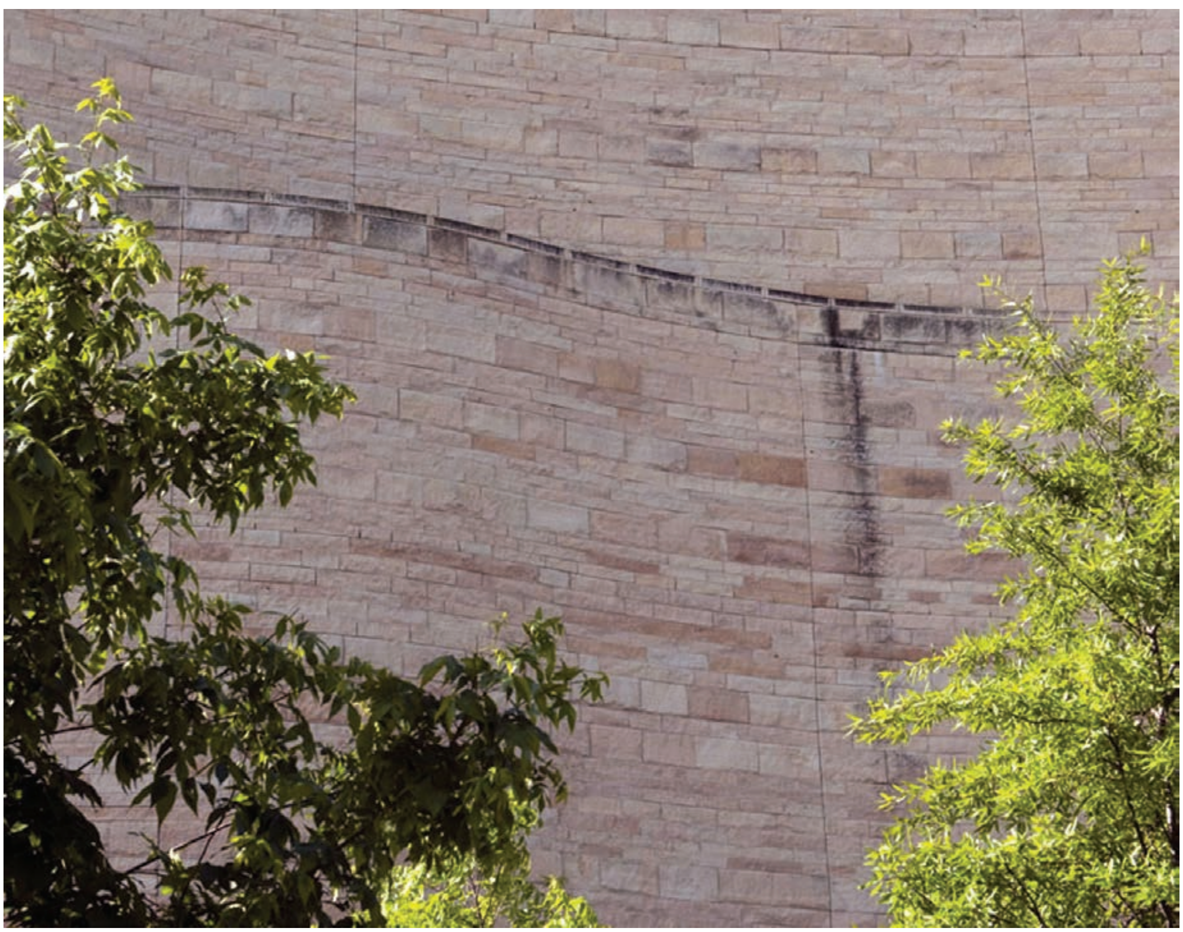

FIGURE 10. Darkening on stonework of the facade below north facade balcony 1, although the capstones slope slightly inward to drains, in 2010. Photo by Melvin J. Wachowiak and E. Keats Webb, Smithsonian Institution.

FIGURE 11. Dark deposits at the unprotected end of the deck of north facade balcony 2, seen from the fourth floor inside the museum, in 2010. Dark streaks occurred on the facade below, although the outermost stones slope inward on this balcony. Photo by Carol A. Grissom, Smithsonian Institution.

blocks at ground level, mainly on the south and west facades, project slightly from the building since their planar surfaces cannot conform to the curvature of the building. Darkening was found to be surprisingly varied on roughback blocks in 2010: they appear untouched in some locations (Figure 12) and darkened in others (type D, Figure 13). Several factors may be responsible. First, some areas dry far more quickly after wetting than others, in accordance with variable air flow patterns around the undulating stone exterior of the building. Second, darkening is often found near significant vegetation, where stones are in direct contact with the soil, regular watering occurs, and plants provide a barrier to evaporation. Third, some roughback stones have been periodically cleaned by NMAI staff, enabled by easy accessibility from the ground. In general, darkening on roughback stones was not as visually disturbing as on other areas of the building, perhaps because of lower contrast with the more highly colored stone surfaces. Scattered individual stones that project from the facade as part of the architects' intention to imitate the irregularities of stone outcroppings are also darkened. Examination during and immediately after rainfall showed that they were darkened where they were preferentially wetted, whereas nonprotruding stones were not wetted or darkened (type D, Figure 14).

The most disfiguring dark deposits visible on the building's facade are attributed to the unique construction of a large fifth-floor outdoor space, the Inouye Terrace (Figure 7, and type E,

FIGURE 12. Slight darkening of some highly colored roughback blocks next to paving in 2010. Photo by Carol A. Grissom, Smithsonian Institution.

FIGURE 13. Wetting and darkening of other roughback blocks (type D) with shielding vegetation nearby, such as these to the left of the Independence Avenue entrance to the building; photographed just after a rain event in 2010. Photo by Carol A. Grissom, Smithsonian Institution.

FIGURE 14. Wetting and darkening of the protruding block at the center (type D), photographed just after a rain event in 2010. Photo by Carol A. Grissom, Smithsonian Institution.

FIGURE 15. Dark streaks on the facade (type E) below the Inouye Terrace on the north facade in 2010. The red arrow indicates streaking compounded by runoff from both the terrace and an intersecting parapet wall. The blue arrow indicates streaking by increased runoff from stones sloping toward the intersection of the window sill and parapet wall. Photo by Melvin J. Wachowiak and E. Keats Webb, Smithsonian Institution.

FIGURE 16. (Left) Wetting of the area shown in Figure 15, photographed during a rain event in 2010; arrows are as in Figure 15. Photo by Carol A. Grissom, Smithsonian Institution.

Figure 15) Three factors are responsible for greater volumes of water flowing onto the facade below the terrace:

1. Across the terrace parapet wall, capstones slope 6° downward toward the facade, as shown by drawings (Vetter Stone Co., parapet detail, shop drawing 63, April 2, 2003, final approval) and confirmed by measurement of about 5° slope; thus, they shed more water onto the facade than horizontal capstones elsewhere on the building.
2. At the east end of the terrace (red arrow in Figure 15), water from terrace parapet capstones flows onto intersecting roof parapet capstones before falling onto the facade, which increases the amount of water flowing over the facade and results in intense dark streaking there. The oblique view in Figure 16 shows the two walls more clearly, as well as the near waterfall that occurs during rainstorms.
3. At the west end of the terrace, indicated by blue arrows in Figures 15 and 16, the terrace parapet wall intersects a windowsill, and large sloping capstones collect and funnel greater amounts of water over the facade (Figure 17).

Finally, at the top of the NMAI building, extremely dark and thick deposits were found on terrace walls below scuppers that drain rainwater from roofs above (type F, Figure 18). Since these areas are not visible from the ground, they have not been prioritized for attention, although they are significantly more unsightly. In addition, surface flaking indicates that the stone has sustained damage (Figure 19; see figure 3 in DePriest and Charola, this volume).

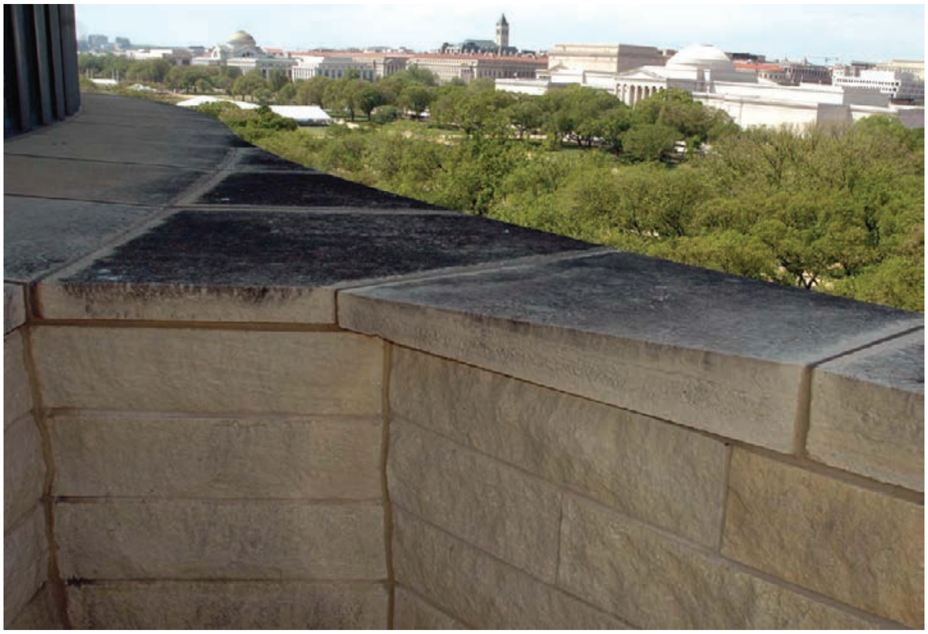

FIGURE 17. Darkening of capstones at the intersection of the Inouye Terrace parapet wall with the windowsill on the left in 2010. The large capstone displaying the darkest surface on the left slopes down and outward, whereas the stone to its right slopes toward it. During rainfall a large volume of water is funneled over these capstones onto the facade, contributing to the severe dark streaks seen in Figures 15 and 16. Photo by Carol A. Grissom, Smithsonian Institution.

FIGURE 18. Thick, dark deposits under scuppers (type F) that drain roofs atop the NMAI building with flows of large amounts of water in 2010. Photo by E. Keats Webb, Smithsonian Institution.

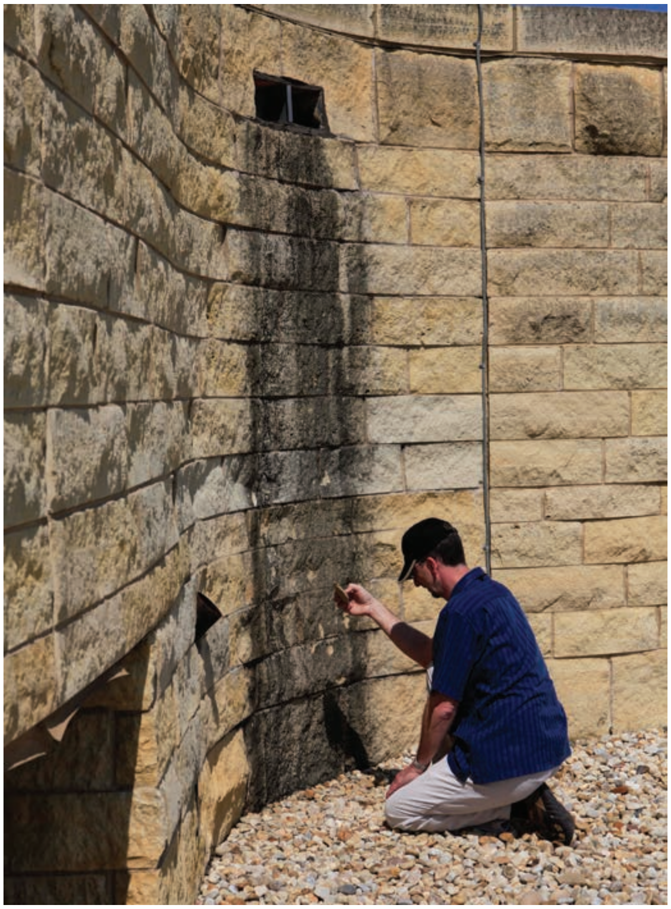

FIGURE 19. Light-colored spots in the thick, dark deposit under a scupper, detail of Figure 18, showing detachment and flaking of the stone in 2010. Photo by E. Keats Webb, Smithsonian Institution.

In summary, the locations of darkened areas on the NMAI building appear to correlate with areas of water flow over the building's facade; furthermore, the greater the water flow is, the more intense the darkening is. This variation suggests that the degree of darkening is a consequence of the building's design influencing water flow. The examination indicated that the darkening occurred where water preferentially flowed over stone surfaces, a necessary condition for biocolonization, as confirmed by further studies (DePriest and Charola, this volume). For the most part, darkened areas present a largely aesthetic problem. However, if not kept at an incipient stage, this could lead to the deterioration of the stone of this distinct building.

REFERENCES

Charola, A. E., E. P. Vicenzi, C. A. Grissom, and N. Little. 2017 (this volume). "Composition and Characteristics of Kasota Limestone on the Exterior of the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 17–26. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

DePriest, P., and A. E. Charola. 2017 (this volume). "Biological Colonization and 'Ink Strokes' on Buildings." In *Conservation of the Exterior of the National Museum of the American Indian Building,* ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 39–44. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Grissom, C., and A. E. Charola, 2017 (this volume). "Keeping the National Museum of the American Indian Building Clean." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 45–58. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Biological Colonization and "Ink Strokes" on Buildings

Paula T. DePriest and A. Elena Charola*

Biological organisms—whether plants, animals, fungi, or microbes—can cause damage and deterioration to buildings and building materials (Caneva et al., 1991, 2009). The damage may be direct, such as staining or chemical and physical/mechanical changes to the stone. Also, the organisms may indirectly create environmental conditions—such as increased moisture, nutrients, and organic material—that support the growth of other organisms capable of causing damage. The National Museum of the American Indian (NMAI) building on the National Mall has disfiguring streaking (see Grissom and Charola, "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building," this volume). Because of its rapid formation and pattern on the building, it does not appear to be from soiling with soot or city dust that is deposited by the prevailing winds. These streaks are good candidates for the biological stains that are known by the German name *Tintenstrich* (Jaag, 1945:236; Lüttge, 1997), literally "ink stroke," as illustrated in Figure 1. The NMAI building's inky stains follow water paths dripping over terrace ledges and protruding stones and down the face of the building (see figures 3–6 in Grissom and Charola, "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building," this volume). Without the decades required to build up organisms and organic debris that could support fungi or plant roots, the stain-producing organisms are most likely dominated by fast-growing, autotrophic (photosynthetic) algae or cyanobacteria (see Cappitelli et al., 2012; May et al., 2010). They live either on the surface of the stone face (epilithic organisms) or beneath the surface (endolithic organisms; see figure 2 in Cappitelli et al., 2012). Identifying the staining and its biological source is important for developing cleaning protocols and a preservation plan for this landmark building, as suggested by Warscheid (Warscheid, 2010; Warscheid and Leisen, 2011) and discussed elsewhere in this volume (see Grissom and Charola, "Keeping the National Museum of the American Indian Building Clean," this volume; Koestler et al., this volume).

The Kasota limestone facing stone of the NMAI building, finely porous and fissured from its rough cut (see Charola et al., this volume), is known to be susceptible to epilithic and endolithic colonization by photosynthetic algae, either the eukaryotic algae, known as green algae, or the unicellular or filamentous prokaryotic cyanobacteria, commonly known as blue-green algae (Pentecost and Whitton, 2000). The first report of endolithic organisms, by Diels (1914), was of algae and cyanobacteria growing inside white dolomitic rock in the Alps. The dolomite's transparent crystals, similar to calcite crystals found in limestones and marbles, and other transparent crystals such as quartz in sandstones and granites (Nienow et al., 1988a, 1988b) and gypsum in gypsum crusts

Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746, USA.
* Correspondence: P. T. DePriest, depriestp@si.edu
Manuscript received 17 January 2012; accepted 23 May 2016.

FIGURE 1. Characteristic *Tintenstrich* pattern on a structure at Angkor Wat, Cambodia. Note that the pattern follows the water drip lines. Reprinted with permission from Warscheid and Leisen (2011).

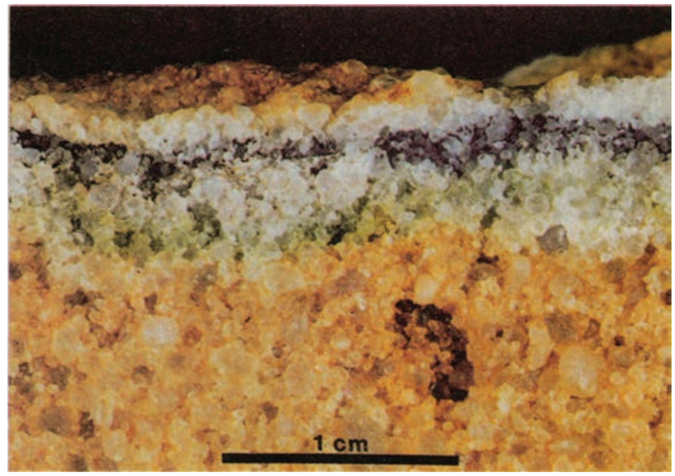

FIGURE 2. Cross section of sandstone from the Linnaeus Terrace, Asgard Range, Antarctica, showing black, white, and green zones of endolithic lichen under the surface. The black zone is pigmented fungi, the white zone is colorless fungi, and the green zone is algae. Reprinted with permission from Friedmann (1982).

on sandstones in Antarctica (Hughes and Lawley, 2003) allow sufficient light to penetrate into the stone to support the photosynthesis of both green algae and cyanobacteria. It has been found that light may penetrate to a depth of millimeters before it is attenuated and becomes a limiting factor for photosynthesis and growth (Horath et al., 2006). The depth of light penetration into stone may be increased by other factors such as the presence of water (Nienow et al., 1988b) and, in the case of quartz, the crystals' orientation (Hall et al., 2008; Hall, 2011).

Inside the stone, these microbes are protected from heat, drying, and excessive visible and UV light. The cyanobacteria in particular secrete a polysaccharide covering, referred to as an extracellular polymeric substance (EPS) or biofilm, which further protects them and other microbes in close proximity from desiccation. However, when the biofilm is swollen with water and physically pushing the rock crystals apart, the diffusion of CO_2 is significantly decreased, and the cyanobacteria's photosynthesis is reduced. Some marine cyanobacteria growing on carbonate rocks such as dolomite, limestone, and coral reefs may overcome a similar problem by driving the release of CO_2 by decomposing the stone (Garcia-Pichel et al., 2010). Over longer periods of time, the thin layers of water and dissolved organic acids released by the cyanobacteria held in capillary pores and micropores of the stone favor chemical dissolution of the carbonate minerals and decomposition of the stone with release of CO_2. Dissolved Ca^{2+} will eventually be redeposited as finely crystalline aggregates, referred to as micritic calcite (Viles, 1987), that may form surface crusts or fill the pores (see figures 4–7 in Charola et al., this volume). In these stones, cyanobacteria can create their optimal environment and even support a complex community of microbes: bacteria, green algae, fungi, and fungal-algal associations called lichens (Figure 2).

Cyanobacteria-mediated dissolution, transport, and reprecipitation of carbonate minerals, often referred to as boring (Golubic et al., 1975; Viles, 1987, 1995; Garcia-Pichel et al., 2010; Lombardozzi et al., 2012), are an important type of biological weathering and biodeterioration that can lead to disfiguring exfoliation or spalling of stone surfaces (Figure 3; see also figure 19 in Grissom and Charola, "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building," this volume). Pentecost (1992; as discussed in Pentecost and Whitton, 2000) reported that the 2 g of limestone fragments dislodged beneath a thick *Tintenstrich* would be equivalent to surface weathering of 3 mm/100 years. Both Hoppert et al. (2004) and Kolo et al. (2007) showed that on homogeneous carbonate rocks biological weathering leads to a gradual dissolution of the rock as some cyanobacteria and other microorganisms bore cavities, even directly into the calcite crystals. (In contrast, other microbes grow along crystal boundaries or in cracks and holes, avoiding the harder crystal surfaces; see figure 2d,e,f in Cappitelli et al., 2012). They also predicted that for endoliths, boring and reprecipitation of Ca^{2+} inside the rock may build mineral bridges that strengthen the structure, in contrast to epiliths, whose reprecipitation is on the colony surface and may lead to exfoliation (Figure 3; see the limestone block in figure 19 in Grissom and Charola, "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building," this volume, and the exfoliated fragment in figure 2b,e in Cappitelli et al., 2012). Hoppert et al. (2004:241) hypothesized that the mechanisms of endolithic colonization may "stabilize and preserve the rock surface morphology." Miller et al. (2010) proposed that pore size also influenced the ratio of

FIGURE 3. Exfoliation of the Kasota limestone from the NMAI building in the area below a scupper water drain on the east terrace wall beyond the Senator Inouye Terrace (see figure 18 in Grissom and Charola, "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building," this volume). The exfoliation or spalling is potentially a result of the blackish epilithic colonization.

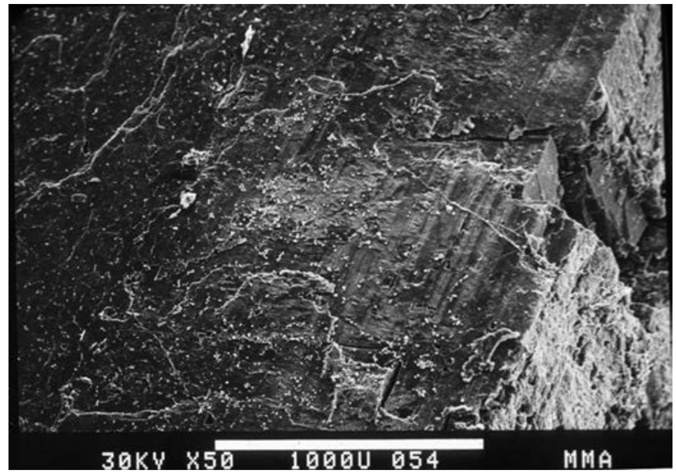

FIGURE 4. Fungi growing on the fractured surface of a single clear dolomite crystal used to evaluate damage by the biocolonization found at San Martín de Fuentidueña Apse. The vertical surface to the right was inoculated with the fungus, algae, and cyanobacteria, and the horizontal surface was exposed by fracturing five weeks after inoculation, showing biocolonization along a cleavage plane about 1 mm in depth. Reprinted with permission from Koestler et al. (1985).

epilithic to endolithic colonies on artificially colonized calcareous rocks; mainly endolithic colonization developed on rock with large intergranular porosity, whereas both epilithic and endolithic colonies developed on rock with fine to medium porosity, such as the NMAI building's Kasota limestone (see Charola et al., this volume). Also, Miller et al. (2010) observed other alterations of rock after cyanobacterial colonization, with possible neoformation of Fe-Mn oxides by the transformation of minerals present in the rock. For example, the original pyrolusite (MnO_2) was replaced by hausmannite ($Mn^{2+}Mn_2^{3+}O_4$) after biocolonization, and parallel changes were observed in the Fe oxides.

In comparison to cyanobacteria, fungi (see Cappitelli et al., 2012) may have more detrimental effects on the weathering and biodeterioration of carbonate rocks. Several studies address specifically fungal colonization on dolomitic limestones. Koestler et al. (1985) identified an ascomycetous fungus (likely *Trichothecium* sp.), along with a green chlorococcalean algae and a cyanobacteria (*Lyngbya* sp.), on the yellow dolostone (mostly calcitic dolomite) of San Martín de Fuentidueña, originally located in Segovia, Spain, but now at the cloisters of the Metropolitan Museum of Art in New York (Figure 4). Cámara et al. (2011) detected both epilithic and endolithic colonization by ascomycetous and basidiomycetous fungi, with green algae, cyanobacteria, and fungal-algal association, on dolostone samples from the Redueña quarry and also proposed that petrographic characteristics influenced endolithic growth (Cámara et al., 2008). In general, fungal filaments, hyphae, colonized existing pores, growing into the larger spaces regardless of whether they were inter- or intracrystalline. In low-porosity dolostone, endolithic growth was limited to preexisting fissures and cracks. For carbonate rocks, the fungal hyphae follow grain boundaries, apparently leaving bridges of biominerals, such as calcium oxalates like weddelite and whewellite, which are di- and monohydrates, respectively (Kolo et al., 2007). Kolo et al. (2007) detected other biominerals such as the magnesium oxalate dihydrate glushinskite and struvite, ammonium magnesium phosphate hexahydrate, and both magnesium and calcium carbonates, as well their mixture, dolomite. One of the results of the aggressive attack by fungi is the demicritization of the stone, that is, the dissolution of the fine micritic material, leaving the larger grains isolated and supported only by new biomineral bridges. This shows the large effect that fungi can have on the diagenesis of carbonate rocks.

The mere presence of microbes, cyanobacteria, algae, fungi, etc., produces visible stains on stone. All autotrophic plants and algae will have the photosynthetic pigments in shades of green to blue green, and some will have accessory pigments of orange, red, or even occasionally purple. Both autotrophic and heterotrophic organisms often have body structures that range from pale beige to dark brown. These are the colors that are expected and acceptable for nature and natural weathering of stone surfaces. However, two groups of pigments are especially dark and disfiguring on light stone surfaces. The first is melanins—a family of noncrystalline, light-absorbing (therefore blackish) aromatic compounds—which are both insoluble and resistant to decolorizing and cleaning (Butler et al., 2005). Melanins are thought to be protective against environmental stresses, such as UV radiation and oxidizing compounds, and to confer to fungi pathogenicity and virulence (Henson et al., 1999). The second is scytonemin, a dark yellow-brown, lipid-soluble pigment of the sheaths and biofilms of cyanobacteria (Garcia-Pichel and Castenholz, 1991; see figure 2g,i in Cappitelli et al., 2012, and figure 1 in May et al., 2010), the ink colorant of the *Tintenstrich* that intensifies in the driest sites (Pentecost and Whitton, 2000). Scytonemins, along with the colorless mycosporine-like amino acids (MAAs) of cyanobacteria, protect against UV radiation, specifically UV-A for scytonemin and UV-B for MAAs (Sinha and Häder, 2008). Intense UV-A radiation stimulates the production of scytonemin.

As cyanobacteria, fungi, and fungal-algal associations—called lichens—may form black crusts on the stone faces of buildings (Lewin, 2006; Gaylarde et al. 2007), distinguishing melanin from scytonemin staining requires identifying either the organisms or the staining compounds directly. Cyanobacteria, either unicellular-coccoid, clustered, or filamentous, are prokaryotic (lacking a true nucleus and cell organelles). Their cells have a somewhat uniform green pigmentation, although accessory pigments may tint them purple to blue, with a light speckling compared with the cells of eukaryotic (having a true nucleus) algae, in which the green chlorophyll is sequestered in large chloroplast organelles. Fungi are eukaryotic and heterotrophic—lacking chlorophyll and depending on carbohydrates from other organisms for their nutrition. Their cells, either in filaments or occasionally yeast shaped, have a distinctive chitinous cell wall. Cyanobacteria will produce an often thick, protective EPS or biofilms, whereas fungi excrete polysaccharides to adhere to surfaces and to form a pseudotissue layer or cortex as found in lichen associations. At present algae, cyanobacteria, and fungi are routinely identified with molecular-genetic methods, usually DNA sequencing of regions encoding the ribosomal RNA (= ribosomal DNA, rDNA) or the rDNA's internal transcribed spacer (Cappitelli et al., 2012). Although melanin, found in most organisms, is notoriously difficult to identify because of its amorphous form and range of molecular sizes, scytonemin, produced by only a few groups of cyanobacteria, has a defined structure and a known molecular mass of 544 Da (Sinha and Häder, 2008).

The hypothesis formulated was that the disfiguring stains on the NMAI building are of biological origin and not simply soiling. Because it developed rapidly, over a period of a few years, it is most likely the result of colonization by photosynthetic organisms that are limited only by the availability of light and water. The stone walls of the building analogous to a natural cliff, above any shading from trees or other vegetation, can reasonably be expected to be exposed to high light levels most of the year; adding water along paths determined by the complex surfaces of the building imitating intermittent streams produces the condition for biocolonization. If the organisms are cyanobacteria, then the stain is most likely scytonemin and not melanin, which is typically produced by fungal decomposers. Scytonemin production is known to increase under high UV-A illumination, as would be found on the upper areas of the building. The walls of the building, with their combination of carbonate stone, water tracks, and high light exposure, provide optimal conditions for development of a cyanobacterial *Tintenstrich*, in particular that of *Gloeocapsa* (Pentecost and Whitton, 2000), as reported by Cappitelli et al. (2012). If this hypothesis is supported by documentation of cyanobacteria producing scytonemin or the detection of scytonemin directly, then the challenge is to develop protocols to remove scytonemin and scytonemin-producing cyanobacteria and prevent or slow the recolonization and weathering of the building's facing stones.

REFERENCES

Butler, M. J., R. B. Gardiner, and A. W. Day. 2005. Degradation of Melanin or Inhibition of Its Synthesis: Are These a Significant Approach as a Biological Control of Phytopathogenic Fungi? *Biological Control,* 32:326–336. http://dx.doi.org/10.1016/j.biocontrol.2004.08.008.

Cámara, B., A. De los Ríos, M. A. Garcia-del-Cura, V. Galván, and C. Ascaso. 2008. Dolostone Bioreceptivity to Fungal Colonization. *Materiales de Construcción*, 58(280/290):113–124.

Cámara, B., A. De los Ríos, M. Urizal, M. Alvarez de Buergo, M. J. Varas, R. Fort, and C. Ascaso. 2011. Characterizing the Microbial Colonization of a Dolostone Quarry: Implications for Stone Biodeterioration and Response to Biocide Treatments. *Microbial Ecology,* 62:299–313. http://dx.doi.org/10.1007/s00248-011-9815-x.

Caneva, G., M. P. Nugari, and O. Salvadori. 1991. *Biology in the Conservation of Works of Art.* Rome: ICCROM.

Caneva, G., M. P. Nugari, and O. Salvadori. 2009. *Plant Biology for Cultural Heritage: Biodeterioration and Conservation*. Los Angeles: Getty Publications.

Cappitelli, F., O. Salvadori, D. Albanese, F. Villa, and C. Sorlini. 2012. Cyanobacteria Cause Black Staining at the National Museum of the American Indian Building, Washington, D.C., USA. *Biofouling,* 28(3):257–266.

Charola, A. E., E. P. Vicenzi, C. A. Grissom, and N. Little. 2017 (this volume). "Composition and Characteristics of Kasota Limestone on the Exterior of the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 17–26. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Diels, L. 1914 Die Algen-Vegetation der Südtiroler Dolomitriffe. Ein Beitrag zur Ökologie der Lithophyten. [Algae in South Tirol Dolomite Reefs. A Contribution to the Ecology of Lithotypes] Berichte der Deutschen Botanischen Gesellschaft 32:502–526.

Friedmann, E. I. 1982. Endolithic Microorganisms in the Antarctic Cold Desert. *Science,* 215(26):1045–1053. http://dx.doi.org/10.1126/science.215.4536.1045.

Garcia-Pichel, F., and R. W. Castenholz. 1991. Characterization and Biological Implications of Scytonemin, a Cyanobacterial Sheath Pigment. *Journal of Phycology,* 27:395–409.

Garcia-Pichel, F., E. Ramirez-Reinat, and Q. Gao. 2010. Microbial Excavation of Solid Carbonates Powered by P-Type ATPase-Mediated Transcellular Ca^{2+} Transport. *Proceedings of the National Academy of Sciences of the United States of America,* 107(50):21749–21754. http://dx.doi.org/10.1073/pnas.1011884108.

Gaylarde, C. C., B. O. Ortega-Morales, and P. Bartolo-Pérez. 2007. Biogenic Black Crusts on Buildings in Unpolluted Environments. *Current Microbiology*, 54:162–166. http://dx.doi.org/10.1007/s00284-006-0432-8.

Golubic, S., R. D. Perkins, and K. J. Lukas. 1975. Boring Microorganisms and Microborings in Carbonate Substrates. In *Study of Trace Fossils,* ed. R. Frey, pp. 229–259. New York: Springer-Verlag. http://dx.doi.org/10.1007/978-3-642-65923-2_12.

Grissom, C. A., and A. E. Charola. 2017 (this volume). "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 27–38. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

———. 2017 (this volume). "Keeping the National Museum of the American Indian Building Clean." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 45–58. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Hall, K. 2011. Natural Building Stone Composed of Light-Transmissive Minerals: Impacts on Thermal Gradients, Weathering and Microbial Colonization. A Preliminary Study, Tentative Interpretations, and Future Directions. *Environmental Earth Sciences,* 62:289–297. http://dx.doi.org/10.1007/s12665-010-0522-6.

Hall, K., M. Guglielmin, and A. Strini. 2008. Weathering of Granite in Antarctica: I. Light Penetration into Rock and Implications for Rock Weathering and Endolithic Communities. *Earth Surface Processes and Landforms*, 33(2):295–307. http://dx.doi.org/10.1002/esp.1618.

Henson, J. M., M. J. Butler, and A. W. Day, 1999. The Dark Side of the Mycelium: Melanins of Phytopathogenic Fungi. *Annual Reviews of Phytopathology,* 37:447–471.

Hoppert, M., C. Flies, W. Pohl, B. Guenzl, and J. Schneider. 2004. Colonization Strategies of Lithobiontic Microorganisms on Carbonate Rocks. *Environmental Geology*, 46:421–428. http://dx.doi.org/10.1007/s00254-004-1043-y.

Horath, T., T. R. Neu, and R. Bachofen. 2006. An Endolithic Microbial Community in Dolomite Rock in Central Switzerland: Characterization by Reflection Spectroscopy, Pigment Analyses, Scanning Electron Microscopy, and Laser Scanning Microscopy. *Microbial Ecology*, 51(3):353–364. http://doi.org/10.1007/s00248-006-9051-y.

Hughes, K. A., and B. Lawley. 2003. A Novel Antarctic Microbial Endolithic Community within Gypsum Crusts. *Environmental Microbiology, 5:555–565.* http://dx.doi.org/10.1046/j.1462-2920.2003.00439.x.

Jaag, O. 1945. Untersuchungen über die Vegetation und Biologie der Algen des nackten Gesteins in den Alpen, im Jura und im schweizerischen Mittelland. *Beiträge zur Kryptogamenflora der Schweiz*, 9:1–560.

Koestler, R. J., P. T. DePriest, and A. E. Charola. 2017 (this volume). "Future Maintenance Plan for the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 59–62. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Koestler, R. J., A. E. Charola, M. Wypyski, and J. J. Lee. 1985. "Microbiologically Induced Deterioration of Dolomitic and Calcitic Stone as Viewed by Scanning Electron Microscopy." In *5th International Congress on Deterioration and Conservation of Stone*, ed. G. Félix, pp. 617–626. Lausanne: Presses Polytechniques Romandes.

Kolo, K., E. Keppens, A. Préat, and P. Claeys. 2007. Experimental Observations on Fungal Diagenesis of Carbonate Substrates. *Journal of Geophysical Research,* 112:G01007. http://dx.doi.org/10.1029/2006JG000203.

Lewin, R. A. 2006. Black Algae. *Journal of Applied Phycology,* 18:699–702. http://dx.doi.org/10.1007/s10811-005-9018-2.

Lombardozzi, V., T. Castrignanò, T., M. D'Antonio, A. Casanova Municchia, and G. Caneva. 2012. An Interactive Database for an Ecological Analysis of Stone Biopitting. *International Biodeterioration and Biodegradation*, 73:8–15. http://doi.org/10.1016/j.ibiod.2012.04.016.

Lüttge, U. 1997. Cyanobacterial Tintenstrich Communities and their Ecology. *Naturwissenschaften*, 84(12):526–534. http://doi.org/10.1007/s001140050439.

May, E., R. Inkpen, and C. Hughes. 2010. Biocolonization of the NMAI Building and Image Analysis Methods for Its Evaluation. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29557.

Miller, A. Z., M. A. Rogerio-Candelera, L. Laiz, J. Wierzchos, C. Ascaso, M. A. Sequeiro Braga, M. Hernández-Mariné, A. Maurício, A. Dionísio, M. F. Macedo, and C. Sáiz-Jimenez. 2010. Laboratory-Induced Endolithic Growth in Calcarenites: Biodeteriorating Potential Assessment. *Microbial Ecology,* 60:55–68. http://dx.doi.org/10.1007/s00248-010-9666-x.

Nienow, J. A., C. P. McKay, and E. I. Friedmann. 1988a. The Cryptoendolithic Microbial Environment in the Ross Desert of Antarctica: Mathematical Models of the Thermal Regime. *Microbial Ecology*, 16:253–270. http://dx.doi.org/10.1007/BF02011699.

———. 1988b. The Cryptoendolithic Microbial Environment in the Ross Desert of Antarctica: Light in the Photosynthetically Active Region. *Microbial Ecology*, 16:271–289. http://dx.doi.org/10.1007/BF02011700.

Pentecost, A. 1992. A Note on the Colonisation of Limestone Rocks by Cyanobacteria. *Archiv für Hydrobiologie,* 124:167–172.

Pentecost, A., and B. A. Whitton. 2000. "Limestones." In *The Ecology of Cyanobacteria: Their Diversity in Time and Space,* ed. B. A. Whitton and M. Potts, pp. 257–279. London: Kluwer.

Sinha, R. P., and D. P. Häder. 2008. UV-Protectants in Cyanobacteria. *Plant Science,* 174:278–289. http://dx.doi.org/10.1016/j.plantsci.2007.12.004.

Viles, H. 1995. Ecological Perspectives on Rock Surface Weathering: Towards a Conceptual Model. *Geomorphology*, 13(1–4):21–35. http://doi.org/10.1016/0169-555X(95)00024-Y.

———. 1987. Blue-Green Algae and Terrestrial Limestone Weathering on Aldabra Atoll: An SEM and Light Microscope Study. *Earth Surface Processes and Landforms*, 12:319–330. http://dx.doi.org/10.1002/esp.3290120310.

Warscheid, T. 2010. Evaluation and Treatment of Microbial Biofilms on the NMAI Building. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29559.

Warscheid, T., and H. Leisen. 2011. "Microbiological Studies on Stone Deterioration and Development of Conservation Measures at Angkor Wat." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series*, ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 1–18. Smithsonian Contributions to Museum Conservation, No. 2. Washington, DC: Smithsonian Scholarly Press.

Keeping the National Museum of the American Indian Building Clean

Carol A. Grissom and A. Elena Charola*

Biocolonization of stone is a natural weathering phenomenon, but the rate at which it occurs depends on the stone and environmental conditions, particularly the availability of light and water. In the case of the National Museum of the American Indian (NMAI) building, rapid biocolonization is favored by the porosity of Kasota limestone (Charola et al., this volume; DePriest and Charola, this volume) and design features that increase the water flow in certain locations (Grissom and Charola, this volume). The present study examined treatments that may control biocolonization on the building. First, several types of biocides were reviewed to select a biocide that was effective and approved for use in the United States. Second, a protocol for cleaning and applying biocide was developed and tested to ensure that it was effective and did not damage the building's stone. Third, installation of metal strips that release metal ions with biocidal effects was tested for long-lasting prevention of recolonization.

BIOCIDES: PROBLEMS AND BENEFITS

Biocides can reduce existing biocolonization, but eliminating it completely is never easy. The effectiveness of a biocide is limited by the depth of its penetration into the stone (Cámara et al., 2011). Moreover, biocides generally do not have long-term residual action, and periodic reapplication is required (see Koestler et al., this volume). In a garden setting such as that of the NMAI building, repeated application of biocides may also be undesirable since surrounding plants may be harmed as well.

Several types of biocide formulations have been used on outdoor stone. Many, such as organotin compounds, have now been banned in most countries. Others based on inorganic compounds, such as the strong oxidant sodium hypochlorite, for example, Clorox, have the disadvantage of leaving behind sodium chloride (common table salt), which can be deleterious to stone. Hydrogen peroxide can be effective without leaving any residue, but it is impractical for large-scale application because it does not have any long-term effect. Furthermore, since both sodium hypochlorite and hydrogen peroxide act by oxidation, they can induce undesirable changes in the color of stone, especially when iron compounds are present as they are in Kasota limestone (Charola et al, this volume).

The most common biocides currently in use on stone are those based on quaternary ammonium salts, often referred to as "quats"; they have been widely used with success on buildings and monuments (Charola et al., 2007; Delgado Rodrigues et al., 2011). Two formulations based on quats have been approved for use on masonry in the United States: D/2 Biological Solution[1] and BioWash (Prosoco). Recent formulations of biocides

Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746, USA.

* Correspondence: C. A. Grissom, grissomc@si.edu

Manuscript received 17 January 2012; accepted 23 May 2016.

containing isothiazolone (Morley et al., 2005) appear to be more effective than quats (Warscheid and Leisen, 2011; Warscheid, 2010) but are not yet available for use on buildings in the United States. Bartolini et al. (2004) have shown that although quat-based biocides have a high extraction capacity for pigments, such as green chlorophyll *a*, orange β-carotene, and the brown scytonemin contained in dark cyanobacteria biofilms, these pigments can remain embedded in stone even after the organisms have been eliminated (Delgado Rodrigues and Valero, 2003).

The effectiveness of quats as a biocide was found to be reduced by more than 90% when mixed with hard water, that is, with concentrations of calcium and magnesium ions greater than about 10 ppm (Ridenour and Armbruster, 1948). As a reference, moderately hard water, such as the tap water in Washington, D.C., contains between 70 and 120 ppm of calcium and magnesium ions, hard water contains between 120 and 180 ppm, and very hard water contains over 180 ppm. The reduction of effectiveness of quats in hard water, however, varies with the chemical structure of the quat as well as the length of the alkyl groups. For example, a blend of C_{12}/C_{14} alkyl groups is still effective even in the presence of over 1,000 ppm calcium and magnesium ions (Merianos, 2001). Similarly, the addition of a nonoxynol-9 nonionic surfactant to commercial formulations allows quats to be more effective in the presence of hard water.

Quats have been observed to be less effective on limestone than on marble but more effective on both these stones than on clay-bearing sandstones (Salvadori and Charola, 2011). They are highly adsorbed onto clays and other siliceous surfaces and require a higher concentration to be effective (Grant and Bravery, 1981; Young et al., 1995). However, because of this adsorption they are slowly released over time, increasing their long-term effectiveness (Salvadori and Charola, 2011). On the basis of this property, formulations have been improved by adding surface bonding agents, such as alkoxysilanes, which allow quats to attach to stone surfaces and resist being washed off (Isquith et al., 1972; Walters et al., 1973). Other improved formulations employ a top layer of silica nanoparticles modified with attached quats over multiple layers of polyacrylic acid and polyallylamine hydrochloride that incorporate silver nanoparticles. The quats in the top layer have a biocidal action on contact with biocolonization, whereas the silver ions in the lower layers are slowly released over time, providing a slower but longer-term biocidal action. This dual approach significantly extends antimicrobial activity (Banerjee et al., 2011). Other approaches are being developed on the basis of antifouling agents that could prevent the formation of biofilms (Cappitelli et al., 2011).

CLEANING: HISTORY AND PROTOCOL DEVELOPMENT

The buff-colored Kasota limestone facade of the National Museum of the American Indian was pristine when the building was inaugurated on September 21, 2004 (see figures 1–3 in Grissom et al., this volume). However, by 2006 black deposits had become noticeable and unsightly enough that the company Clean and Polish Building Solutions (Washington, D.C.) was contracted to surface clean three areas on the Independence Avenue facade of the building. The statement of work required use of an unspecified Hydroclean product, probably the weak acid cleaner HT-626,[2] followed by pressure washing (K. Fleming, Smithsonian Office of Facilities, Engineering and Operations [OFEO], personal communication, 2015). Around the same time, NMAI staff members also began hand scrubbing without cleaners and pressure washing darkened stones accessible at ground level (K. Fogden, NMAI, and D. Grimes, OFEO, personal communication, 2011).

In late 2009, collaboration began between NMAI and Museum Conservation Institute (MCI) staff; the latter consulted with four biodeterioration experts (Charola and Koestler, this volume). A range of cleaning options was discussed at meetings held with the building's stakeholders, including its building manager, Kathleen Fleming; NMAI's associate director for assets and operations, Jane Sledge; the eastern zone manager, John Bixler; associate director for architectural history and historic preservation Sharon Park; and other interested parties. The stakeholders eliminated high-pressure water washing as a possibility because it would likely erode the stone surface, increasing its roughness and exacerbating biocolonization by driving it deeper into the stone. Although pressure washing would make the building look cleaner immediately, recolonization could recur faster (Salvadori, 2010).

The two quat-based biocides approved for use on stone in the United States, Cathedral Stone's D/2 Biological Solution and Prosoco's BioWash, were tested prior to full-scale cleaning. They were applied first in the laboratory to determine whether they would affect the color of stone samples (Bienosek, 2010). Since no effects were observed, the solutions were applied in an outdoor setting at the Smithsonian's Garber facility on blocks of stone left over from construction of the building (Charola et al., 2012) and on an exterior area of the wall surrounding NMAI's loading dock. After test results showed that D/2 was effective in reducing the stone's darkening, this biocide was selected for application on the building, and a scope of work for cleaning was written in the fall of 2010 (Burnett, 2010).

In early 2011, the Smithsonian awarded a contract for cleaning the building with the D/2 biocide to Fresco Cleaning (Arlington, Virginia, at that time and Washington, D.C, currently). Cleaning was limited to darkened areas, which were marked on photographs for the use of the contractor (Figures 1–4). A full set of high-quality images of the building was taken by Kathleen Fogden, NMAI photographer, just prior to cleaning for later comparison.

Cleaning began in the spring of 2011 after danger of frost had passed to avoid freeze-thaw problems (see Charola et al., this volume). Spring is the preferred time to apply biocides in temperate North America since organisms become more active during this period and therefore are more susceptible to biocides. The spring of 2011 was unusually wet due to a La Niña

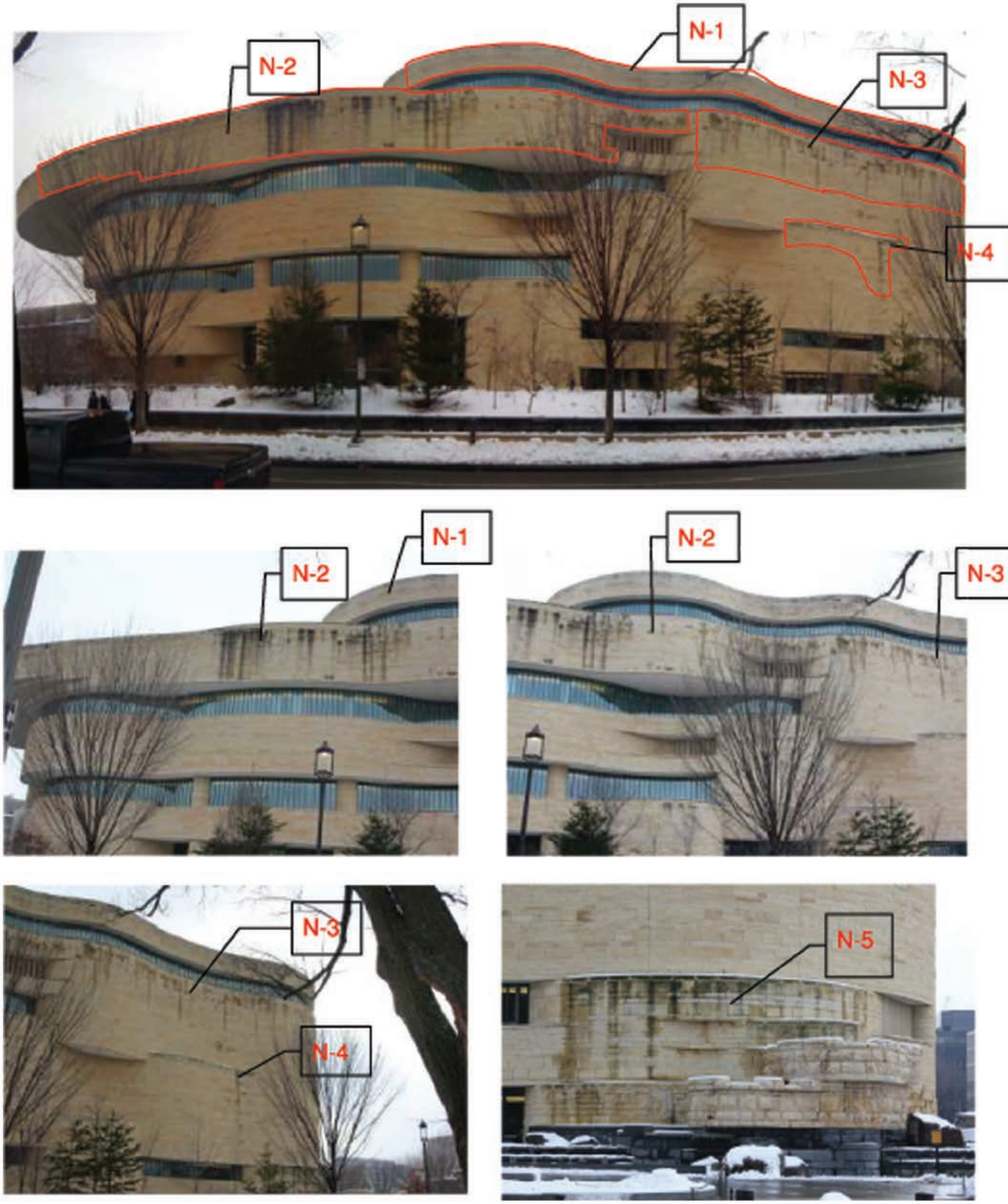

FIGURE 1. Cleaning map for the north facade. Areas N1–N5 to be cleaned are marked. Photos by John Bixler, Smithsonian Institution.

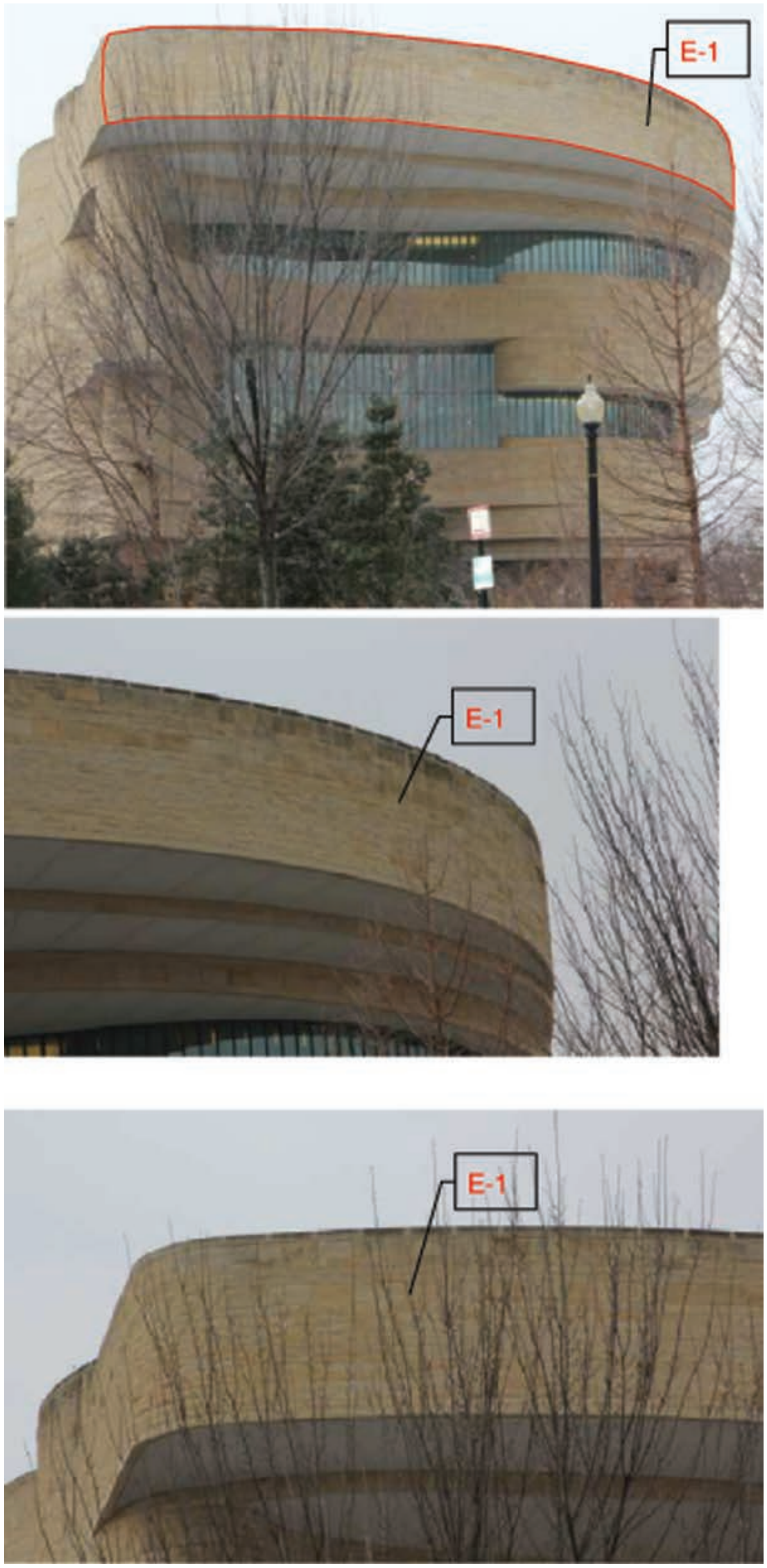

FIGURE 2. Cleaning map for the east facade. Area E1 to be cleaned is marked by outline in the top image. Photos by John Bixler, Smithsonian Institution.

FIGURE 3. Cleaning map for the south facade. Areas S1–S5 to be cleaned are outlined in the top image. Photos by John Bixler, Smithsonian Institution.

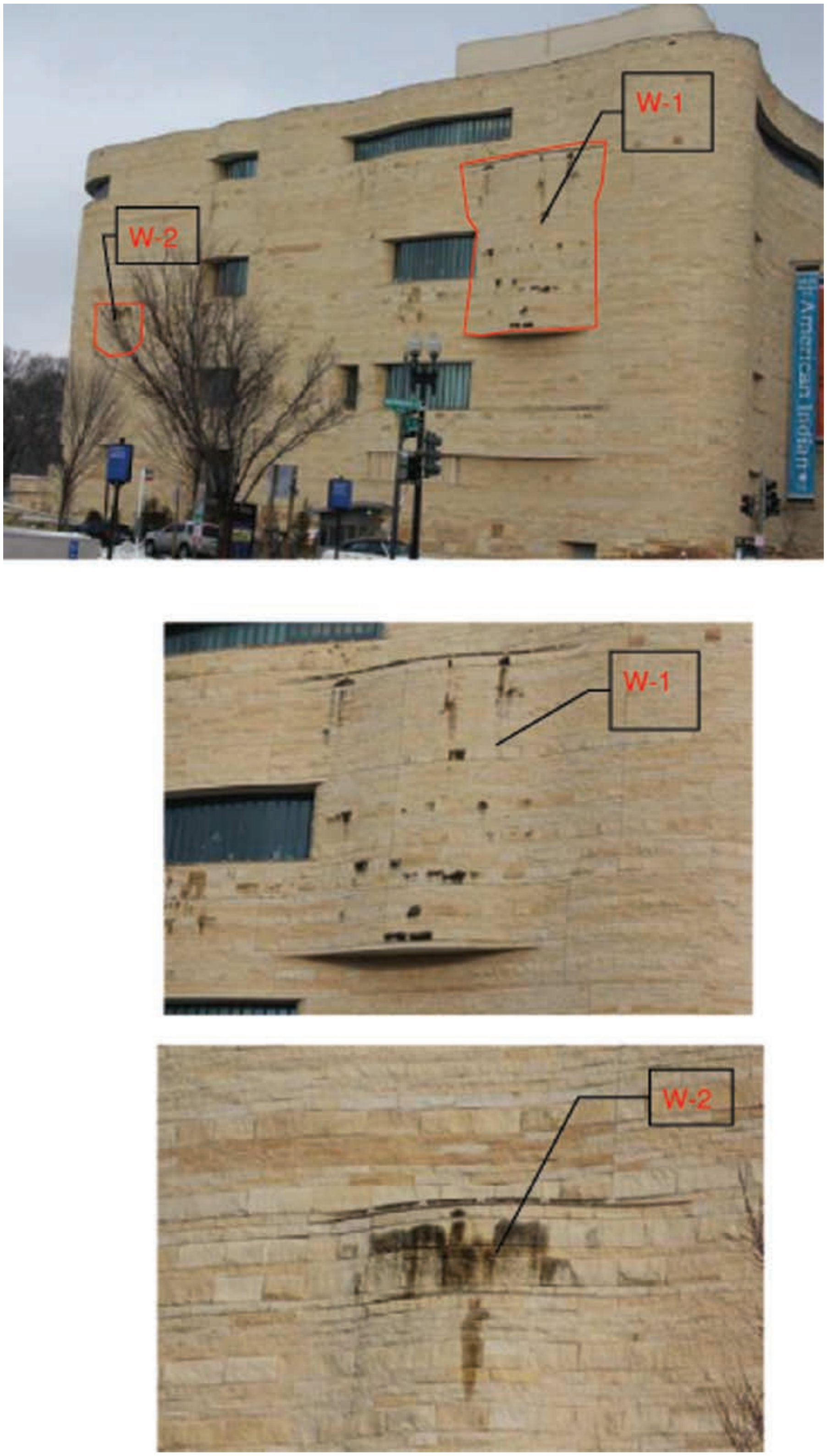

FIGURE 4. Cleaning map for the west facade. Areas W1 and W2 for cleaning are outlined in the top image. Photos by John Bixler, Smithsonian Institution.

FIGURE 5. Application of D/2 on the loading dock wall (left), followed by scrubbing (middle) and rinsing with water (right) on April 6, 2011. Photo by Carol A. Grissom, Smithsonian Institution.

weather pattern, with precipitation for March–April above 19.3 cm, compared with a long-term average of 16.6 cm (National Weather Forecast Office, 2015).

Beginning on April 6, Fresco's workmen cleaned darkened areas accessible from the ground, such as the loading dock wall (Figure 5). Beginning on April 14 and continuing for approximately one week, they cleaned staining on the facade that required use of a lift (Figures 6–7). The cleaning map was generally followed, except that some horizontal surfaces of capstones on the loading dock wall were also cleaned, as were a few horizontal surfaces of capstones near the Senator Daniel K. Inouye Terrace.

Cleaning began with pump-spray application of D/2 onto designated areas (Figure 5, left). In a few cases, such as on the most severe black streaks below the Inouye Terrace, the biocide was applied twice (Figure 7). After waiting at least 10 minutes, the area to which the D/2 had been applied was vigorously scrubbed using long-handled plastic brushes (Figures 5, middle, and 7, right). Finally, the area was rinsed with water from the building's water supply under ordinary pressure (Figure 5, right). After drying, darkened areas were greatly reduced, but areas that had been severely darkened could still be identified by slight shadows (see Figures 8 and 9). Typically, residual biocide effect and loss of dead biological material lead to some further lightening during the first year or more after application, before biocolonization and darkening begin anew. However, since most capstones were not cleaned, their surfaces retained active biocolonization, and any rain water flowing over them would have carried spores and organisms onto the facade, accelerating recolonization there.

A set of high-quality detail images of cleaned areas after the biocide treatment were taken in May 2011 by MCI staff. When compared to images taken just prior to cleaning, the immediate reduction in darkening is remarkable (Figures 8 and 9). Thereafter, areas prone to biocolonization have been photographed annually to record the rate at which microbial recolonization occurs.

In April 2014, in anticipation of dedication of the terrace to Senator Daniel K. Inouye (see figure 7 in Grissom and Charola, this volume), who had introduced the bill in the U.S. Senate to establish the museum, the same treatment method was used by Fresco to clean darkened terrace stonework. This area had not been cleaned in 2011. Prior to cleaning, detailed photographs of eight capstones were taken, and a range of darkened and undarkened areas was measured using a colorimeter to provide baseline data for evaluating subsequent recolonization.

OTHER PREVENTIVE METHODS: ZINC AND OTHER METAL IONS

Since biocides may eliminate biocolonization but do not have enduring residual action, an alternative approach to the problem was tested. As has long been known, some metal ions have biocidal action that prevents development of microorganisms, illustrated by the traditional custom of throwing a silver spoon into a water well to keep the water drinkable (Hernández-Sierra et al., 2008) or spraying Bordeaux mixture[3]—an effective fungicide and bactericide based on an aqueous solution of

FIGURE 6. Working from a lift on the north facade on April 15, 2011. Photo by Carol A. Grissom, Smithsonian Institution.

FIGURE 7. Application of the biocide D/2 to the most severely streaked area below the Inouye Terrace (left), followed by scrubbing the area (right) on April 15, 2011. Photo by Carol A. Grissom, Smithsonian Institution.

FIGURE 8. Area below the Inouye Terrace prior to cleaning in April 2010 (left) and after cleaning in May 2011 (right). Photos by Melvin J. Wachowiak, Smithsonian Institution.

FIGURE 9. Another area on the north facade prior to cleaning in April 2010 (left) and after cleaning in May 2011 (right). Photos by Melvin J. Wachowiak, Smithsonian Institution.

copper sulfate and limewater—on vineyards to prevent mildew (Broome and Donaldson, 2010). On the NMAI building itself the biocidal effect of metal ions can be observed in areas where copper lightning rods have been installed (see the rightmost block in figure 1 in Grissom and Charola, this volume).

The most effective biocidal metals are silver, copper, and zinc, in approximately that order. Silver is too costly to be practical, although silver nanoparticles appear to be a feasible alternative solution (Koestler et al., this volume). Copper compounds have the disadvantage of staining stone blue or green; for example, small green stains can already be seen near the lightning rods on the NMAI building. Zinc compounds are white and not as visible, but colored stones may develop a grayish hue (Salvadori and Charola, 2011). In theory, zinc strips could be installed on the building to release biocidal ions. A uniform flow of water over the strips would be required to achieve maximum effectiveness in preventing biocolonization. Additionally, the broader the zinc strips and the more surface exposed, the more zinc ions would be released, increasing their effectiveness. However, wider strips releasing more zinc ions could ultimately lead to faster discoloration of stonework. Since this method is fundamentally preventive, installation of zinc strips is recommended after surfaces have been cleaned (Wessel, 2003, 2011).

David Wessel provided expertise regarding the installation of zinc strips on the NMAI building at a meeting with NMAI stakeholders in October 2010. The regular shapes of traditional structures on which zinc strips have successfully been installed are far less challenging than the irregularly shaped NMAI building. To test both the installation and the effectiveness of strips in preventing recolonization, zinc strips were installed in two different test locations on the NMAI building in February 2012, about 10 months after cleaning with the biocide.[4] Installation of more strips will be considered after full assessment of results.

The first test location was near the south entrance, where zinc strips measuring 5.5 cm in width and 0.475 cm in thickness were installed on the top ledges of two roughback blocks. These blocks project a few inches from the facade about 2 meters (6 or 7 feet) above ground level. They were badly darkened before cleaning, apparently because of shading by nearby vegetation during the growing season, water collecting on their upper ledges, and slow drying related to air flow around the undulating facade (Figure 10; Grissom and Charola, this volume, figure 13). The width of the zinc strips was dictated by available space, and the strips were attached to the ledges with an adhesive to avoid any splitting of surfaces of the face-bedded roughback stones, which might have occurred with metal fasteners. By April 2014, less than three years after application of the biocide and more than two years after installation of the strips, biocolonization had returned to faces of many adjacent roughback stones but not on stones to which zinc strips were attached (Figure 10, arrows).

The second test location was on the Inouye Terrace, where wider zinc strips measuring 8.9 cm in width and 0.475 cm in thickness were attached with stainless-steel anchors on the top surfaces of parapet capstones about 5 cm from the facade edge. They span the second and third blocks (Figure 11; compare with figure 17 in Grissom and Charola, this volume) and the twelfth and thirteenth blocks, numbered from the junction of the parapet with an adjacent north wall (see figure 7 in Grissom and Charola, this volume) These blocks were selected because they

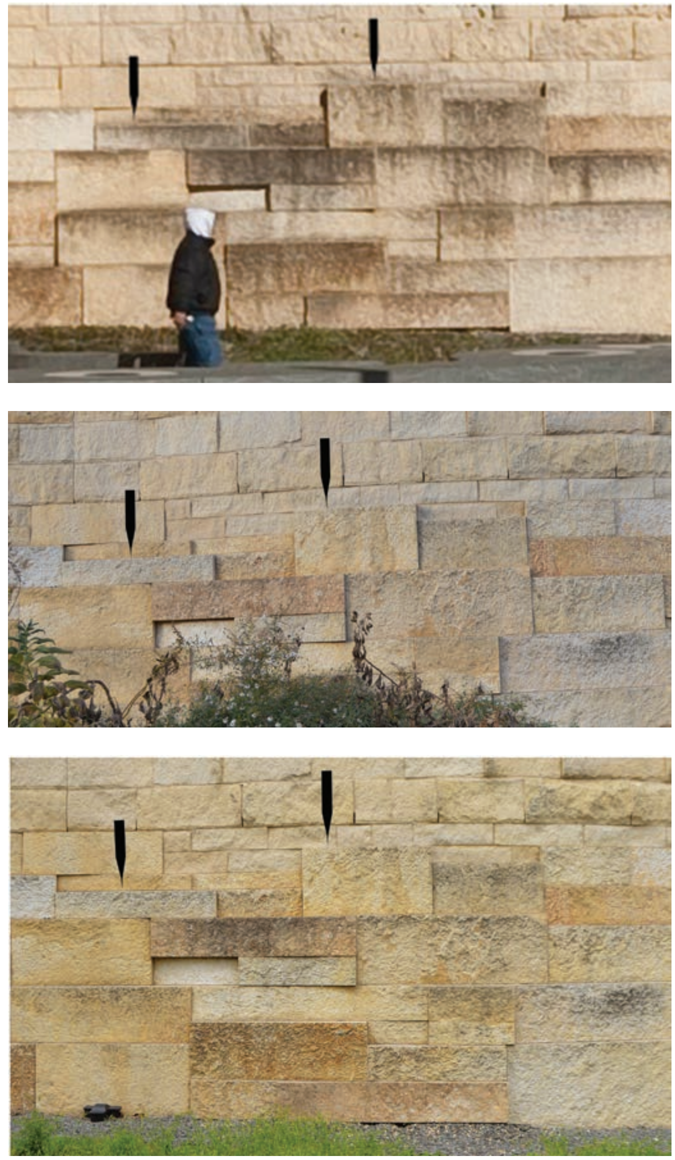

FIGURE 10. Area to the left of the south entrance. Top: before cleaning and installation of zinc strips on roughback blocks indicated by arrows (March 2011). Photo by Katherine Fogden, Smithsonian Institution. Middle: 20 months after cleaning and 10 months after installation of zinc strips (November 2012). Bottom: three years after cleaning and more than two years after installation of strips (April 2014). Middle and right photos by Carol A. Grissom, Smithsonian Institution.

FIGURE 11. Second and third blocks on the Inouye Terrace, to which zinc strips have been attached, shown 18 months after installation on August 14, 2013; see figure 15 of Grissom and Charola (this volume). Photo by Carol A. Grissom, Smithsonian Institution.

were immediately above what had been the most badly streaked areas on the north facade and their recessed joints channeled water down onto these areas. Biocolonization had not been cleaned from the top surfaces of the capstones in 2011, and at the time the zinc strips were installed in early 2012, it almost completely covered these surfaces. By 2014, biocolonization was reduced as clean areas appeared between the zinc strips and the facade and on facade faces of the capstones. Any reduction in the dark streaking on facade stones below them, however, was not yet visible (Figure 12; compare with Figure 8).

Although zinc strips may successfully reduce darkening in many areas, such as on roughback stones and terrace parapets, the occasional stone that protrudes from the facade presents a more difficult and probably insoluble problem because strips cannot be attached inconspicuously above them. Since protruding stones contribute substantially to the building's natural appearance, those that are darkened by biocolonization may have to be accepted as they are—a natural phenomenon.

CONCLUSION

The darkening of the stone surface of the building due to biocolonization can be reduced by the periodic application of biocides and appropriate cleaning. Since biocolonization is part of the natural weathering of porous stone, other approaches are needed to reduce the frequency required to maintain clean surfaces with the use of biocides. The installation of zinc strips has shown that the dark staining due to biocolonization can be reduced, but the unusual design of the NMAI building requires an innovative approach for their installation to be effective. Alternative solutions also need to be explored since no single solution can be found for this distinctive building.

FIGURE 12. Detail of the facade below capstones on which zinc strips shown in Figure 11 were installed (location indicated by the red bar), eight months later (two years and two months after installation). Note that front faces of the blocks were cleaner than surrounding blocks in April 2014. Photo by Carol A. Grissom, Smithsonian Institution.

NOTES

1. D/2 Biological Solution, formerly distributed by Cathedral Stone Products, Inc., was the product tested and used in 2011. Currently, several companies distribute D/2, including Limeworks.us, Telford, Pennsylvania.
2. Hydroclean HT-626 brick, granite, sandstone, and terra-cotta cleaner is based on a mixture of a solvent (2-butoxyethanol) and dilute phosphoric and hydrofluoric acids; see http://www.hydroclean.com/data_sheets/ht-626.htm (accessed July 22, 2016). The solvent serves both as a surfactant to improve surface wetting and as a biocide. On the Kasota limestone, the acids would attack the surface layer of the stone, which might eliminate surface biocolonization in the process. They would also react with released calcium and magnesium ions to form compounds more insoluble than the original stone, such as calcium and magnesium fluoride or calcium and magnesium phosphate. Such acid-based cleaners are unacceptable for limestone, not only because they dissolve the stone surface but also because new compounds that form might trap existing biocolonization and provide nutrients such as phosphates for their further development.
3. In the late nineteenth century, the Bordeaux mixture was developed by P. M. A. Millardet, University of Bordeaux, and tested on Chateau Dauzac vineyards in collaboration with Ernest David, technical director of the Dauzac vineyards.
4. Designs for the test project (OFEO Project 11112101), developed by Architrave P.C., Architects.

REFERENCES

Banerjee, I., R. C. Pangula, and R. S. Kane. 2011. Antifouling Coatings: Recent Developments in the Design of Surfaces That Prevent Fouling by Proteins, Bacteria, and Marine Organisms. *Advanced Materials,* 23:690–718. http://dx.doi.org/10.1002/adma.201001215.

Bartolini, M., S. Ricci, and G. Del Signore. 2004. "Release of Photosynthetic Pigments from Epilithic Biocenosis after Biocide Treatments." In *Proceedings of the 10th International Congress on Deterioration and Conservation of Stone*, ed. D. Kwiatkowski and R. Löfvendahl, pp. 519–526. Stockholm: ICOMOS Sweden.

Bienosek, G. 2010. Stone Discoloration. Suitland, Md.: Museum Conservation Institute.

Broome, D. C., and D. R. Donaldson. 2010. Bordeaux Mixture. Pest Notes Publication 7481. Davis: University of California. http://www.ipm.ucdavis.edu/PMG/PESTNOTES/pn7481.html (accessed July 22, 2016).

Burnett, J. 2010. Scope of Work: Cleaning Building Façade. Washington, D.C.: National Museum of the American Indian.

Cámara, B., A. De los Ríos, M. Urizal, M. Alvarez de Buergo, M. J. Varas, R. Fort, and C. Ascaso. 2011. Characterizing the Microbial Colonization of a Dolostone Quarry: Implications for Stone Biodeterioration and Response to Biocide Treatments. *Microbial Ecology*, 62(2):299–313. http://dx.doi.org/10.1007/s00248-011-9815-x.

Cappitelli, F., F. Villa, and C. Sorlini. 2011. "New Environment-Friendly Approaches against Biodeterioration of Outdoor Cultural Heritage." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series,* ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 51–58. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

Charola, A. E., M. Vale Anjos, J. Delgado Rodrigues, and A. Barreiro. 2007. Developing a Maintenance Plan for the Stone Sculptures and Decorative Elements in the Gardens of the National Palace of Queluz, Portugal. *Restoration of Buildings and Monuments*, 13(6):377–388.

Charola, A. E., M. Wachowiak, E. Keats Webb, C. A. Grissom, E. P. Vicenzi, W. Chong, H. Szczepanowska, and P. DePriest. 2012. "Developing a Methodology to Evaluate the Effectiveness of a Biocide." In *12th International Congress on Deterioration and Conservation of Stone*. New York. ICOMOS-International Scientific Committee for Stone. http://iscs.icomos.org/pdf-files/NewYorkConf/charetal.pdf (accessed July 17, 2016).

Charola, A. E., E. P. Vicenzi, C. A. Grissom, and N. Little. 2017 (this volume). "Composition and Characteristics of Kasota Limestone on the Exterior of the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 17–26. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Charola, A. E., and R. J. Koestler. 2017 (this volume). "The National Museum of the American Indian: An Introduction." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and Robert J. Koestler, pp. 1–4. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Delgado Rodrigues, J., M. Vale Anjos, and A. E. Charola. 2011. "Recolonization of Marble Sculptures in Garden Environment." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series,* ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 71–85. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

Delgado Rodrigues, J., and J. Valero. 2003. A Brief Note on the Elimination of Dark Stains of Biological Origin. *Studies in Conservation,* 48(1):17–22.

DePriest, P., and A. E. Charola. 2017 (this volume). "Biological Colonization and 'Ink Strokes' on Buildings." *In Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 39–44. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Grant, C., and A. F. Bravery, 1981. Laboratory Evaluation of Algicidal Biocides for Use on Constructional Materials. 2. Use of the Vermiculite Bed Technique to Evaluate a Quaternary Ammonium Biocide. *International Biodeterioration Bulletin,* 17(4):125–131.

Grissom, C. A., and A. E. Charola.2017 (this volume). "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 27–38. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Hernández-Sierra, J. F., F. Ruiz, D. C. Cruz Pena, F. Martinez-Gutiérrez, A. E. Martínez, A. J. Pozos Guillén, H. Tapia-Pérez, and G. Martínez Castañón. 2008. The Antimicrobial Sensitivity of *Streptococcus mutans* to Nanoparticles of Silver, Zinc Oxide, and Gold. *Nanomedicine: Nanotechnology, Biology, and Medicine,* 4:237–240.

Isquith, A. J., E. A. Abbott, and P. A. Walters. 1972. Surface-Bonded Antimicrobial Activity of an Organosilicon Quaternary Ammonium Chloride. *Applied Microbiology,* 24(6):859–863.

Koestler, R. J., P. T. DePriest, and A. E. Charola. 2017 (this volume). "Future Maintenance Plan for the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R J. Koestler, pp. 59–62. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Merianos, J. J. 2001. "Surface Active Agents." In *Disinfection, Sterilization, and Preservation,* 5th ed., ed. S. S. Block, pp. 283–320. Malvern, Pa.: Lippincott Williams & Wilkins.

Morley, J. O., A. J. Oliver Kapur, and M. H. Charlton. 2005. Structure–Activity Relationships in 3-Isothiazolones. *Organic and Biomolecular Chemistry,* 3:3713–1319.

National Weather Forecast Office. 2015. Washington D.C. Precipitation. http://www.weather.gov/media/lwx/climate/dcaprecip.pdf (accessed July 22, 2016).

Ridenour, G. M., and E. H. Armbruster. 1948. Some Factors Affecting the Properties of Quaternary Ammonium Compounds as Sanitizers. *American Journal of Public Health,* 38:504–511. http://dx.doi.org/10.2105/AJPH.38.4.504.

Salvadori. O. 2010. Microscopic Characterization of the Biocolonization on the NMAI Building. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29558.

Salvadori, O., and A. E. Charola. 2011. "Methods to Prevent Biocolonization and Recolonization: An Overview of Current Research for Architectural and Archaeological Heritage." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series,* ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 37–50. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

Walters, P. A., E. A. Abbott, and A. J. Isquith. 1973. Algicidal Activity of a Surface-Bonded Organosilicon Quaternary Ammonium Chloride. *Applied Microbiology,* 25(2):253–256.

Warscheid, T. 2010. Evaluation and Treatment of Microbial Biofilms on the NMAI Building. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29559.

Warscheid, T., and H. Leisen. 2011. "Microbiological Studies on Stone Deterioration and Development of Conservation Measures at Angkor Wat." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series*, ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 1–18. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

Wessel, D. P. 2003. "The Use of Metallic Oxides in Control of Biological Growth on Outdoor Monuments." In *Art, Biology and Conservation*, ed. R. J. Koestler, V. Koestler, A. E. Charola, and F. Nieto-Fernandez, pp. 536–551. New York: The Metropolitan Museum of Art.

———. 2011. "Case Study: Field Observations on the Effectiveness of Zinc Strips to Control Biocolonization of Stone." In: *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series,* ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 109–112. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

Young, M. E., B. Wakefield, D. C. M. Urquhart, K. Nicholson, and K. Tonge. 1995. "Assessment in a Field Setting of the Efficacy of Various Biocides on Sandstone." In *Methods of Evaluating Products for the Conservation of Porous Building Materials in Monuments*, pp. 93–99. Rome: ICCROM.

Future Maintenance Plan for the National Museum of the American Indian Building

Robert J. Koestler, Paula T. DePriest, and A. Elena Charola*

The National Museum of the American Indian (NMAI) building is distinctive, not only in the concept that prompted it but in its unusual design. The building's soft curves, along with the surrounding gardens and wilderness, which incorporate running water, make the NMAI building distinctive, increasing its total heritage value and significance.

Weathering of buildings is a natural phenomenon, and soiling or staining is inevitable in urban environments and proportional to the pollution present in the air. Both industrial and natural pollution, such as dust, seeds, spores, and microorganisms, can cause aesthetic and even deterioration problems. The issue of the deterioration induced by air pollution became a critical one more than 50 years ago, and during the past half century people became so accustomed to the resultant soiling patterns that they were accepted as normal.

This type of deterioration is not the case for the staining observed on the NMAI building. First, the building was completed at the time air pollution abatement had significantly reduced this problem. Second, the structure's distinctive design results in a totally different soiling pattern than expected, one that is more noticeable and objectionable. This uncommon pattern has been found to be essentially the result of biocolonization on areas where water flow is increased by design features. It is important to consider that the most unaesthetic staining is concentrated in relatively few areas (Grissom and Charola, "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building," this volume) while the rest of the building is slowly weathering naturally. Therefore, for the preservation and conservation of this building it is important to find a way to limit the staining to that of natural weathering because if biocolonization is not kept at a low level, deterioration of the stone will occur (DePriest and Charola, this volume).

Preliminary solutions to address these problems were proposed and implemented: biocide application and subsequent cleaning of the most soiled areas of the building, followed by installation—in a few test areas—of zinc strips that serve as an inhibitor of biocolonization (Grissom and Charola, "Keeping the National Museum of the American Indian Building Clean," this volume). Testing of the installation method is critical because of the unusual design of the building.

In the first 11 years of the building's life it has already undergone three localized cleaning interventions. Frequent washing can be counterproductive for two reasons. First, since limestone is slightly soluble in water, increased contact with water, especially if brushing or pressure washing is used, may induce both a surface and an inner cohesion

Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746, USA.
* Correspondence: R. J. Koestler, koestlerr@si.edu
Manuscript received 17 January 2012; accepted 23 May 2016.

loss in the stone. Second, although water is rapidly absorbed into the stone, it takes far longer to leave it (Charola et al., this volume), providing an ideal environment for biocolonization since the translucent dolomite and calcite crystals allow sufficient light for microorganism growth down to at least a 1-mm depth (DePriest and Charola, this volume). Both of these issues are almost impossible to halt.

Therefore, the best policy for the NMAI building is prevention, which can only be achieved by a regular maintenance program. The three previous cleaning interventions were not "regular" maintenance but rather "extraordinary" maintenance, and the ideal would be for these to be carried out as infrequently as possible, perhaps every 10 or 20 years, the average time frame for other buildings. Since NMAI is not a typical building because of its flowing curved surfaces, a unique approach for regular maintenance is needed. It is important to note that a single approach may not solve all problems and that it is likely that different areas of the building may require dissimilar approaches.

To develop an appropriate regular maintenance plan for this building, a testing program of selected products was developed and will be implemented on the horizontal capstones on one of the roof terraces. These products can be divided into two groups, those that can be applied directly on the biocolonized surface and those that require the surface to be "clean" before the application. Within each of these groups, two subgroups can be differentiated as a function of the distinct mechanisms for controlling or preventing biocolonization.

The first group of products to be applied to biocolonized surfaces includes biocides. One product, based on a quaternary ammonium formulation, has already been used successfully in the two most recent cleaning interventions and will be retested to compare with other formulations (even though they are not as yet registered for use on architecture in the United States), such as Algalwash, also called mélange d'Angkor, (Warscheid, 2010; Warscheid and Leisen, 2011), and a zinc citrate solution. The latter might replace the installation of zinc strips in areas where they would be visible. An alternative approach is based on the periodic application of limewater. Limewater, a saturated solution of calcium hydroxide, has been used since historic times as a disinfectant. It may also serve to consolidate the stone by taking up carbon dioxide from the air and forming new calcium carbonate compatible with the dolomitic limestone—the so-called lime method traditionally used in the United Kingdom for consolidation and in Mediterranean countries to avoid mold development. Repeated application of limewater may result in whitening because of the deposition of calcium carbonate but a yellow iron oxide pigment could be added to mitigate this effect and achieve a color similar to that of the Kasota limestone. Testing these formulations on site, however, will require time to evaluate their effectiveness. On the positive side, their cost is minimal.

The second group includes products that should be applied to cleaned stone surfaces, such as water repellents as well as formulations conferring superhydrophobicity by use of nanotechnology. Their action is based on preventing the stone surfaces, especially horizontal ones, from absorbing liquid water, thus reducing the biocolonization rate by controlling one of the most important factors required for their growth. Although in principle these products will reduce biocolonization on these surfaces, depending on how water is shed from them, these products might inadvertently enhance colonization on the vertical surfaces below. Furthermore, their long-term behavior may not be satisfactory. As an alternative approach, self-cleaning products based on nanomaterials that are photocatalytically activated, for example, titanium dioxide (TiO_2), may be effective. The preparation of the nanoparticles is critical for their action; therefore, it would be desirable to test different formulations. Since their performance requires sufficient sunlight for activation, their effectiveness will be location dependent as the building does not receive the same amount of light on all sides. Other alternatives to test could be silver or zinc oxide nanoparticle biocidal formulations.

To evaluate the effectiveness of these treatments, it is important to develop a practical monitoring method that takes into account that some of the products may require six months to a year to reach maximum effect (Charola et al., 2007). Zinc solutions will probably require even longer for the cleaning effects to become apparent. The effectiveness of photocatalytic titanium dioxide, silver, or zinc oxide nanoparticle formulations, as well as water repellents, is based on the speed of recolonization, and that cannot be determined a priori.

Although regular monitoring should include normal photography to identify the onset of the changes, it is not a reliable method for quantifying the results. A more sophisticated, but labor-intensive, method was developed (Charola et al., 2012), but a more practical approach, such as colorimetric evaluation, could also be used (Prieto et al., 2004; Pinna et al., 2012). Colorimetric evaluation is already being implemented to monitor changes undergone by the capstones on the Senator Daniel K. Inouye Terrace from pre- to postcleaning and beyond until reinfection. Other methods, such as appropriate hyperspectral imaging techniques (Burud et al., 2014) or fluorometric measurements (Delgado Rodrigues et al., 2004), could also be tested. Furthermore, it would be desirable to evaluate the microorganisms present prior to the application of the various products and to periodically evaluate any changes in the microbial composition.

The maintenance measure(s) eventually selected will need to take into account both the implementation requirements and the desired appearance of the building. It is likely to take a few years to develop appropriate maintenance measures to address the specific issues found in the different areas of the building, but the effort is worthwhile to preserve this unique building.

REFERENCES

Burud, I., L. R. Gobakken, A. Flø, K. Kval, and T. Thiss. 2014. Hyperspectral Imaging of Blue Stain Fungi on Coated and Uncoated Wooden Surfaces. *International Biodeterioration and Biodegradation*, 88:37–43. http://dx.doi.org/10.1016/j.ibiod.2013.12.002.

Charola, A. E., M. Vale Anjos, J. Delgado Rodrigues, and A. Barreiro. 2007. Developing a Maintenance Plan for the Stone Sculptures and Decorative Elements in the Gardens of the National Palace of Queluz. *Restoration of Buildings and Monuments*, 13(6):377–388.

Charola, A. E., M. Wachowiak, E. Keats Webb, C. A. Grissom, E. P. Vicenzi, W. Chong, H. Szczepanowska, and P. DePriest (2012). "Developing a Methodology to Evaluate the Effectiveness of a Biocide." In: *12th International Congress on Deterioration and Conservation of Stone*. New York: ICOMOS-International Scientific Committee for Stone. http://iscs.icomos.org/pdf-files/NewYorkConf/charetal.pdf (accessed July 17, 2016).

Charola, A. E., E. P. Vicenzi, C. A. Grissom, and N. Little. 2017 (this volume). "Composition and Characteristics of Kasota Limestone on the Exterior of the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 17–26. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Delgado Rodrigues, J., J. Valero, R. Wakefield, E. Brechet, and I. Larrañaga. 2004. Monitoraggio della biocolonizzazione e valutazione dell'efficacia di un biocida [Monitoring of biocolonization and evaluation of the effectiveness of a biocide]. *Arkos Scienza e Restauro dell'Archittetura*, 7:52–58.

DePriest, P., and A. E. Charola. 2017 (this volume). "Biological Colonization and 'Ink Strokes' on Buildings." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 39–44. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Grissom, C. A., and A. E. Charola. 2017 (this volume). "Survey and Documentation of Darkening and Streaking on the National Museum of the American Indian Building." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 27–38. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

———. 2017 (this volume). "Keeping the National Museum of the American Indian Building Clean." In *Conservation of the Exterior of the National Museum of the American Indian Building*, ed. J. Sledge, A. E. Charola, P. T. DePriest, and R. J. Koestler, pp. 45–58. Smithsonian Contributions to Museum Conservation, No. 6. Washington, D.C.: Smithsonian Institution Scholarly Press.

Pinna, D., B. Salvadori, and M. Galeotti. 2012. Monitoring the Performance of Innovative and Traditional Biocides Mixed with Consolidants and Water-Repellents for the Prevention of Biological Growth on Stone. *Science of the Total Environment,* 423:132–141. http://dx.doi.org/10.1016/j.scitotenv.2012.02.012.

Prieto, B., B. Silva, and O. Lantes. 2004. Biofilm Quantification on Stone Surfaces: Comparison of Various Methods. *Science of the Total Environment,* 333:1–7. http://dx.doi.org/10.1016/j.scitotenv.2004.05.003.

Warscheid, T. 2010. Evaluation and Treatment of Microbial Biofilms on the NMAI Building. Suitland, Md.: Museum Conservation Institute. http://dx.doi.org/10.5479/10088/29559.

Warscheid, T., and H. Leisen. 2011. "Microbiological Studies on Stone Deterioration and Development of Conservation Measures at Angkor Wat." In *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series*, ed. A. E. Charola, C. McNamara, and R. J. Koestler, pp. 1–18. Smithsonian Contributions to Museum Conservation, No. 2. Washington, D.C.: Smithsonian Institution Scholarly Press.

Index

Page numbers in *italics* indicate figures and tables.

SUMMARY OF REQUIREMENTS FOR SMITHSONIAN CONTRIBUTIONS SERIES

For comprehensive guidelines and specifications, visit www.scholarlypress.si.edu.

ABSTRACTS must not exceed 300 words.

TEXT must be prepared in a recent version of Microsoft Word; use a Times font in 12 point for regular text; be double spaced; and have 1" margins.

REQUIRED ELEMENTS are title page, abstract, table of contents, main text, and references.

FIGURES must be numbered sequentially (1, 2, 3, etc.) in the order called out; have components lettered consistently (in size, font, and style) and described in captions; include a scale bar or scale description, if appropriate; include any legends in or on figures rather than in captions. Figures must be original and must be submitted as individual TIF or EPS files.

FIGURE FILES must meet all required specifications in the Digital Art Preparation Guide. Color images should be requested only if required.

TAXONOMIC KEYS in natural history manuscripts should use the aligned-couplet form for zoology. If cross referencing is required between key and text, do not include page references within the key, but number the keyed-out taxa, using the same numbers with their corresponding heads in the text.

SYNONYMY IN ZOOLOGY must use the short form (taxon, author, year:page), with full reference at the end of the manuscript under "References."

REFERENCES should be in alphabetical order, and in chronological order for same-author entries. Each reference should be cited at least once in main text. Complete bibliographic information must be included in all citations. Examples of the most common types of citations can be found at SISP's website under Resources/Guidelines.