CHARACTERIZATION OF SMITHSONIAN INSTITUTION BUILDING STONES USING CONVENTIONAL AND ADVANCED ANALYTICAL METHODS

Emily Aloiz[1], Carol Grissom[1], Jeffrey M. Davis[2] and Richard Livingston[3]

[1] *Museum Conservation Institute, Smithsonian Institution (SI)*
[2] *Surface and Microanalysis Science Division, National Institute of Standards and Technology (NIST)*
[3] *Materials Science & Engineering Department, University of Maryland (UMD)*

Abstract

As part of a project to develop a nondestructive test method for measurement of moisture in stone using prompt gamma neutron activation (PGNA), a systematic characterization was undertaken of the lithology and physical properties of seven building stones used in monumental architecture of the Smithsonian Institution and other important buildings in Washington, DC, from 1847 onward. The building stones make up a representative sample of the American dimension stone industry with respect to style, quarrying techniques and geology: Seneca sandstone, Mankato dolomite, Salem limestone, Holston marble, Vermont mountain white marble, Vermont royal marble and Mt Airy granite. Standard laboratory tests were conducted for physical properties such as porosity, moisture absorption and drying rates. Advanced analytical methods included thermogravimetric analysis (TGA) to quantify the amount of chemically bound water, instrumental neutron activation analysis (INAA) to identify elemental composition and micro-focus X-ray fluorescence with hyperspectral analysis for lithology. Information generated in this study will be essential to defining performance of PGNA for moisture measurement and lead to better understanding of stone deterioration processes in Smithsonian and other buildings throughout North America.

Keywords: hyperspectral analysis, Mt Airy granite, Mankato dolomite, Salem limestone, Holston marble, Vermont marble, thermogravimetric analysis, instrumental neutron activation analysis, Smithsonian Institution

1. Introduction

Quantification of moisture has long been regarded as a necessity in building conservation. Nondestructive methods for measuring moisture within a structure are limited, however, and those that are available, such as electromagnetic techniques, can be inaccurate and lacking in resolution (Hall and Hoff 2012). The University of Maryland (UMD) and Museum Conservation Institute (MCI) of the Smithsonian Institution (SI) are collaborating on the development of a nondestructive test (NDT) system to measure moisture in stone, brick and other porous masonry. To evaluate the performance of the system, specimens of simulated stone with known amounts of hydrogen are being made. Chemical compositions and ranges of moisture content for these specimens are based on systematic characterization of a collection of typical

building stones used in the Smithsonian's monumental architecture and other important buildings in Washington, DC, from 1847 onward.

1.1 Prompt gamma neutron activation analysis of hydrogen

The NDT system uses prompt gamma neutron activation (PGNA) to detect the element hydrogen as an indicator of water *in situ* (Livingston 1992). The basic system consists of a portable neutron-emitting source, a gamma-ray detector and associated electronics. Neutrons penetrate the material under investigation and interact with nuclei of its elements, producing gamma rays in the process. The resulting gamma energy spectrum is then analyzed for the characteristic 2.223 MeV peak of hydrogen. The probe is capable of taking direct moisture measurements at depths of up to 20 cm into the material. The current version of the system includes a second detector that limits the field of view, allowing only those gamma rays traveling in a specific direction to be counted. It then collects the gamma rays' energy spectrum (Livingston *et al.* 2010). Aspects of the performance of the PGNA system that need to be evaluated include sensitivity, dynamic range, minimum level of detection and field of view.

PGNA measures total hydrogen, which includes chemically bound water, adsorbed water and free water in stone. Free or capillary water is found in pores measuring > 5 nm, and it is mobile, migrating through stone by capillary attraction as well as by exchange with the atmosphere as temperature and relative humidity (RH) fluctuate. Chemically bound water includes water of hydration, interstitial water and the OH ion in crystal structures, while adsorbed water is found on surfaces of fine pores measuring < 5 nm in diameter. The three states of water were measured using methods that allowed each to be differentiated.

2. Selected Building Stones

2.1 Seneca sandstone

Seneca red sandstone was chosen for the first Smithsonian building, now known as the Smithsonian Castle. The Castle was designed by James Renwick, Jr., in the free Romanesque style and constructed from 1845-49. The stone was taken from Bull Run quarry located about 23 miles away from Washington, DC; at that time it was the most affordable and durable masonry type available. The color of the stone when quarried was described as lilac pink, but the stone oxidized in air to become the dark red (Munsell® 10R 4/4 weak red) seen today (Owen 1849; Merrill and Mathews 1898).

The current geologic name for Seneca red sandstone is the Poolesville member of the Manassas Formation (Lee and Froelich 1989). It is arkosic micaceous sandstone: in addition to quartz, it contains grains of feldspar and mica. Quarries are no longer in operation, but a small sample of stone from the Castle was obtained for testing. Seneca red sandstone was used in many other buildings in the Washington area including the former District of Columbia Jail (1872; demolished 1976). Salvaged stone from the jail was substituted for Castle sandstone when 5 cm cubes were needed for testing.

2.2 Mankato dolomite

Mankato dolomite was used for the façade of the National Museum of the American Indian (2004). The stone was quarried near Mankato, Minnesota, but its official

geological term is Oneota dolomite (Lathram and Thiel 1946). Test samples, leftover from the recent construction of the museum building, have well graded fine particles that form wavy bedding planes. Large amounts of dolomite as well as calcite compose the stone matrix. The acid insoluble fraction (22.8%) includes quartz, orthoclase and microcline.

2.3. Salem limestone

Salem limestone, found in the Elephant House of the Smithsonian National Zoological Park, is widely used as dimension stone throughout Washington and the US (Patton and Carr 1982). Samples were obtained from the maintenance supply at Washington National Cathedral (1909-1990). Still quarried in Indiana, Salem limestone was well characterized for the National Acid Precipitation Assessment Program (NAPAP) (McGee 1989). It is a fine-grained oolitic biocalcarenite with small voids throughout. Bioclasts include echinoderms, bryozoans and brachiopods. The acid insoluble component measured 7.2%, most likely from fossilized material. Soluble salts account for 1.0% of the samples' weights.

2.4 Holston marble

Holston marble, quarried near Knoxville, Tennessee, features prominently on the National Mall, including the Smithsonian's National Museum of American History (1964) and National Air and Space Museum (1976), as well as the National Gallery of Art (1937, 1971). While referred to as a marble, it is geologically a crystalline limestone formed through sedimentation during the Ordovician age. Holston marble has a distinctive pink color, which turns whitish upon weathering (Dale 1924), and jagged dark lines called styolites. The latter formed when pressure caused dissolution and reorganization of the calcite crystals, and insoluble inclusions congregated along the compaction seam between bedding planes. The test sample had been removed from the National Museum of American History in 2011 as part of an alteration.

2.5 Vermont marble

While Vermont marble (geologically Shelburne marble) is not used at the Smithsonian, it has been widely used in Washington monuments, such as Arlington Cemetery's Memorial Amphitheater (1920) and the Jefferson Memorial (1938). Hilgartner Natural Stone Company in Baltimore supplied two varieties—mountain white and royal. Mountain white displays prominent veins of primarily pyrite, chlorite-serpentine and muscovite, reflected in a high percentage of acid insoluble component (9.5%). Royal marble, well characterized in the NAPAP study (McGee 1989), has muted gray veins through its calcite matrix and 0.2% salt content by weight. It was also found to have a high percentage of acid insoluble component (5.9%) compared to typical marbles.

2.6 Mt Airy granite

Mt Airy granite, the hardest of the test stones, is present on the upper third story of the Smithsonian's National Museum of Natural History (NMNH) (1910). It is a white quartz variety still quarried in North Carolina. Test samples were left over from a 1950s

renovation. Mineral components are primarily quartz, orthoclase, plagioclase and biotite (Councill 1954).

3.   Analytical Methods

3.1 Instrumental neutron activation analysis (INAA)

Instrumental neutron activation analysis is a high precision, high accuracy neutron-based method capable of detecting elements at the parts per million level (Glascock and Neff 2003). Elemental composition is important for the evaluation of PGNA performance, because it affects the transport of neutrons and gamma rays.

3.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted to obtain data on the stones' chemically bound and adsorbed water, setting the minimum detectable limit of the PGNA method for measuring capillary water. Three 15-20 mg powdered samples per stone were heated to 800°C in the TGA instrument's alumina pan at a rate of 20°C per minute in a nitrogen atmosphere. The evolution of water from specific minerals varies depending on factors such as heating rate and particle size. Adsorbed water, which generally evolves before 200°C, can be differentiated from chemically bound water, which generally evolves from 200°C to 700°C. Breakdown of volatiles and carbonates occurs over the same temperature range as chemically bound water, however, creating additional weight loss.

3.3   Porosity and absorption/desorption behavior

Knowledge of how water interacts with the pores of stone is essential to understanding deterioration mechanisms and also indicates where and when hydrogen in free water should be detected by PGNA. Free water is adsorbed into porous material primarily through capillary suction, simulated in the laboratory by placing three 5 cm cubes of each stone on a water tray. During drying, water leaves porous stone only by evaporation at the surface. Free water is transported to the surface by capillarity; only then does adsorbed water in fine pores migrate to the surface through vapor diffusion (Sereda and Feldman 1970). Apparent porosity is important for PGNA, because it determines the maximum amount of free water that can be measured. Saturation was approximated by a total immersion test: 5 cm test cubes were placed in a water bath for 24 hours based on Teutonico (1988: 35).

3.4 Adsorption/desorption isotherms

In addition to liquid transport, hydrogen moves through pores of stone in the form of water vapor. Using ASTM C1498-01, samples (approximately 6 x 6 x 2 cm) were dried in an over at 60°C for 48 hours, then placed stepwise into increasing relative humidities set by 12 saturated salt solutions in individual glass desiccators. This process was repeated until an adsorption curve was generated. Adsorption isotherm testing is ongoing, but once 100% RH is achieved the process will be reversed, measuring desorption by moving the samples from more saturated conditions to drier ones.

4

3.5 Hyperspectral image analysis

Hyperspectral imaging collects a full micro-X-ray flourescence (µXRF) spectrum at every pixel of an image of a sample. This is very similar to EDS mapping commonly done in scanning electron microscopy and electro probe microanalysis. Both methods result in a full x-ray spectrum at each pixel, and methods developed and used to analyze the data work well on both platforms. The resulting three-dimensional data matrix is known as a hyperspectral data cube (Kotula *et al.* 2003). This cube can be interpreted at any location after acquisition allowing for analysis and comparsion of defined regions. It is a powerful imaging tool that can be applied to stone conservation to enhance understanding of the composition of materials. Hyper-spectral analysis was conducted at the National Institute of Standards and Technology (NIST).

4. Results

4.1 Instrumental neutron activation analysis

About 40 elements were detected in two powdered samples of each stone. Major elements are expressed as oxide percentages in Table 1. Magnesium values were corrected for interference from aluminum by fast neutrons. Silicon was calculated by subtracting other elements from the total (Glascock *et al.* 2007). Carbon dioxide (CO_2) content was calculated for carbonate stones based on calcium and magnesium content. Although chemical compositions vary significantly, the effect on neutron transport parameters important for PGNA (macroscopic scattering and capture cross-sections) is relatively minor; parameters are dominated by oxygen content, which does not vary significantly. Extremely high neutron absorbing trace elements were not detected.

Table 1. Chemical composition of a sample of each stone by INAA

	Seneca sandstone		Mankato dolomite	Salem limestone	Holston marble	Vermont marble		Mt Airy granite
	DC Jail	Castle				mountain white	royal	
SiO_2	57.76	56.26	2.60	0.77	0.97	2.88	0.31	47.83
Al_2O_3	23.21	22.94	4.17	0.00	0.00	1.66	0.35	30.61
CaO	0.33	0.58	26.47	54.67	54.75	52.54	54.95	1.69
MgO	0.00	0.16	15.83	0.45	0.29	0.23	0.40	0.00
Fe_2O_3	4.57	6.15	1.09	0.27	0.28	0.37	0.07	2.28
K_2O	3.26	2.83	3.00	0.00	0.00	0.29	0.00	6.91
Na_2O	10.12	10.22	0.07	0.04	0.03	0.16	0.01	10.01
TiO	0.62	0.75	0.26	0.30	0.26	0.29	0.25	0.42
MnO	0.06	0.04	0.10	0.01	0.05	0.00	0.00	0.01

CO_2	0.00	0.00	46.37	43.46	43.35	41.55	43.63	0.00
Other	0.08	0.06	0.02	0.03	0.02	0.03	0.03	0.24

4.2 Thermogravimetric analysis

TGA proved to be a sufficient method to analyze the adsorbed and chemically bound water in the stones: dehydration curves and dehydroxylation curves were present and identifiable. However, organic materials in the Holston marble and Salem limestone complicated results by evolving during the same temperature interval as chemically bound water in minerals such as clays. Organic matter also represents chemically bound

Table 2. TGA percent measured weight loss

Seneca sandstone	Mankato dolomite	Salem limestone	Holston marble	Vermont mountain white marble	Vermont royal marble	Mt Airy granite
0.58 ± 0.25	0.93 ± 0.09	7.23 ± 1.14	12.45 ± 7.58	0.47 ± 0.27	0.14 ± 0.21	0.09 ± 0.13

water, but when it breaks down thermally, measured weight loss is a combination of water vapor and CO_2. Calcite in Vermont royal marble, Holston marble and Salem limestone caused interference above 600ºC because of the evolution of CO_2 from calcium carbonate. Results for weight loss measured by TGA are presented in Table 2.

Two examples of the range in TGA results are given in Figure 1. The first curve represents TGA data obtained for a sample of Vermont mountain white marble. Prior to TGA analysis, the sample was digested in 10% hydrochloric acid to eliminate carbonate content. Weight loss occurs as a distinct step at around 600 ºC, most likely due to chemically bound water in chlorites present within marble veins. For silicate-based Seneca sandstone, weight loss associated with chemically bound water is much more gradual than for the mountain white sample and is likely due to the presence of micas. Vertical steps in the curve reflect the digital limit of the instrument resolution. In addition to loss of weight from chemically bound water, the sample also lost weight from adsorbed water before 200ºC. While adsorbed water on the surface of the powdered sample is relatively significant, it would not be a consideration for PGNA measurements on bulk stone.

Chemically bound water apparently ranges from about 0.1% for Mt Airy granite to more than 12% for Holston marble, nearly two orders of magnitude greater. However, the higher percentage of chemically bound water in the Holston marble may be overestimated, because it includes some unknown mass of carbon in the organic matter.
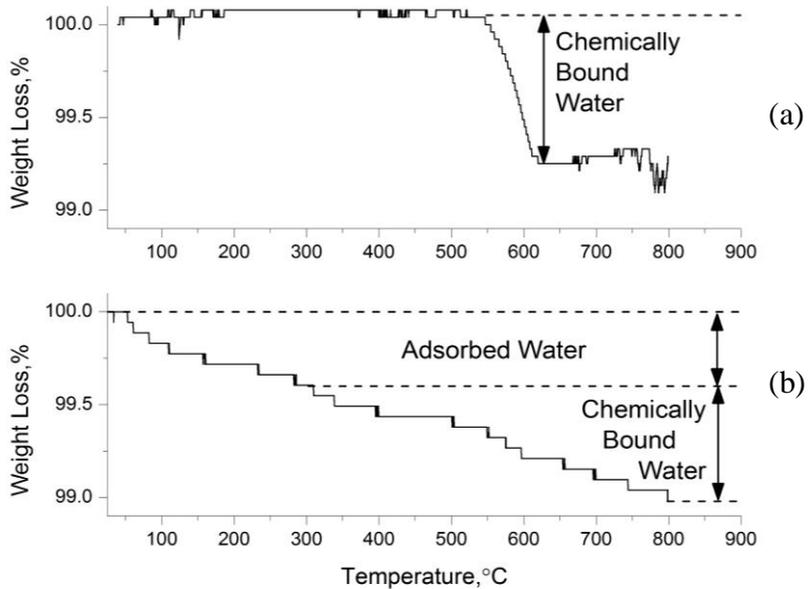
Figure 1: Examples of TGA curves. (a): Vermont mountain white marble; (b): Seneca sandstone.

4.3 Moisture absorption and drying rates

Absorption and desorption behavior follows similar patterns of rapid change in weight as capillary forces drive the uptake or release of free water, followed by a tangential plateau. Among high porosity stones shown in Figure 2, Seneca sandstone absorbed water at a constant rate until saturation, indicating that pores are symmetrical and uniform in size. Variability on the pore structure of Mankato dolomite is evidenced by a less constant rate of absorption as capillary pores filled first and larger pores second. Among low porosity stones shown in Figure 3, Vermont mountain white marble showed the steepest initial absorption rate, indicating that it has the largest most symmetrical pores. Pore size and shape of low porosity stones are very similar; however, the granite continued to absorb water after the others, demonstrating that its total porosity is higher, although pores are smaller and less symmetrical. The jagged slope of low porosity stones' absorption and drying graphs reflects lack of precision in the measuring scale.
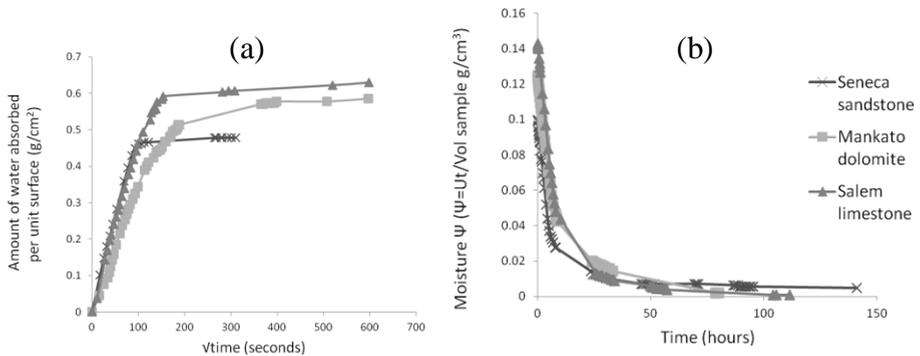
Figure 2. Graphs for one sample each of high porosity stones: Seneca sandstone, Mankato dolomite and Salem limestone. (a) Capillary absorption. (b) Desorption.
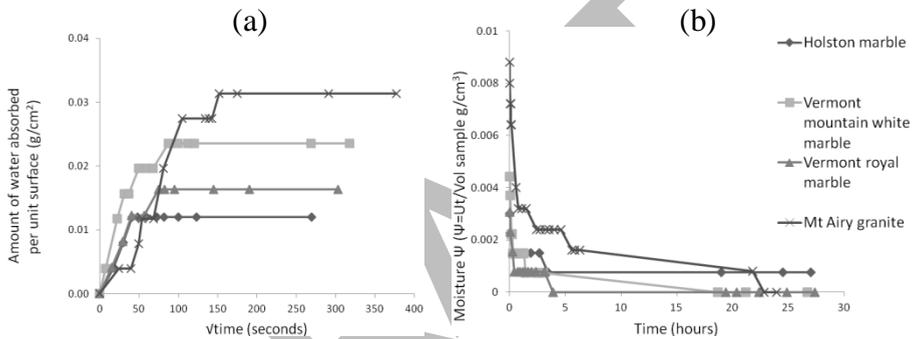

Figure 3. Graphs for one sample each of low porosity stones: Holston marble, Vermont mountain white marble, Vermont royal marble and Mt Airy granite. (a) Capillary absorption. (b) Desorption.

Five moisture related parameters derived from testing are summarized in Table 3. The apparent density $[\rho=W_{dry}(g)/\text{Volume}(cm^3)]$ and volume of open pores $[V_{op}=cm^3 \times 100/125cm^3]$ are important for PGNA performance. Because the density of water is nominally 1 gm/cm^3, porosity by volume was calculated from weight gained. In addition, initial absorption rate and initial drying rate were calculated. The critical moisture content is the amount of water in pores when evaporation from capillary movement ended and evaporation from vapor diffusion began, indicated by a decrease in the drying rate. This volume of water should correlate to the amount of adsorbed water the stones can hold when adsorption isotherm tests are completed.

Table 3: Moisture-related parameters of stones

	Seneca sandstone	Mankato dolomite	Salem limestone	Holston marble	mountain white VT marble	royal VT marble	Mt Airy granite
Apparent density (g/cm^3)	2.35 ±0.03	2.43 ±0.04	2.29 ±0.04	2.78 ±0.04	2.8 ±0.05	2.81 ±0.03	2.76 ±0.04
Apparent porosity	10.11 ±0.12	12.19 ±0.34	13.95± 0.33	0.31 ±0.09	0.45 ±0.01	0.27 ±0.04	0.83 ±0.05

(% vol)							
Initial abs. rate (kg/ m²/√sec)	2.94 ±0.08	1.8 ±0.43	2.89 ±0.22	0.16 ±0.00	0.305 ±0.01	0.18 ±0.01	0.12 ±0.01
Initial drying rate (g/cm³/h)	0.012±0.001	0.012 ±0.001	0.013±0.001	0.005± 0.000	0.013 ±0.003	0.006 ±0.001	0.007±0.001
Critical moisture content (g/cm³)	0.038±0.001	0.084 ±0.016	0.056±0.002	0.002±0.001	0.002 ±0.001	0.001 ±0.000	0.003±0.001

4.4 Hyperspectral image analysis

Each of the seven stones was analyzed through hyperspectral analysis, the final output of which are colored phase images derived by correlating the elemental data obtained from the μXRF data cube at a specific location within the stone surface. As an example of this technique, data obtained from Mt Airy granite are presented here, with images in grayscale. It was imaged in the μXRF at 1 second per analysis spot with 80 μm lateral spacing between analysis spots. An area measuring 29 mm x 24 mm was imaged and a full x-ray spectrum up to 40 keV was saved at each pixel. Data were interrogated using NIST Lispix and ENVI software to derive elemental images and phases. Some elemental images can be seen in Figure 4.
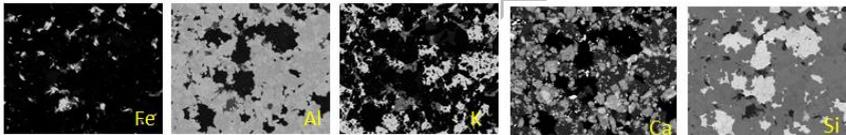

Figure 4: Elemental images for Mt Airy granite from hyperspectral analysis for iron (Fe), aluminum (Al), potassium (K), calcium (Ca) and silicon (Si).

After deriving the elemental images, multivariate statistical algorithms can be applied to identify distinct compositional phases in the data. These derived compositional phases can then be related to mineralogical phases based on average relative abundances for elements such as the ones shown in Figure 4. Results for Mt Airy granite are shown in Figure 5 and summarized in Table 4. It should be noted that such information is on an area fraction basis, which makes it difficult to compare these results with data from TGA and INAA, which are on a mass fraction basis.

Figure 5. Phase masks for Mt Airy granite from hyperspectral analysis. (a) Plagioclase. (b) Quartz. (c) Orthoclase

Table 4. Mineralogical composition of phase masks for Mt Airy granite, including three shown in Figure 5.

Class	plagio-clase	quartz	ortho-clase	Fe-rich quartz	biotite	hema-tite	Fe-rich biotite	illite
area fraction	45.96%	15.57%	23.73%	5.94%	3.86%	2.83%	1.95%	0.17%

4.5 States of water

The maximum concentration of capillary water in the stone can be estimated from the apparent porosity divided by stone density (Winkler 1994). Based on data in Table 3, this ranges from about 0.1% by weight for Vermont marble to 6.1% for Salem limestone. The lower limit of capillary water remains to be determined from adsorption isotherm measurements. However, TGA data in Table 3 indicate that chemically bound water in Salem limestone approaches the same level as maximum capillary water. In the PGNA measurement signals, these two types of water are superimposed to produce measured total hydrogen. Thus, if chemically bound water content in the stone can be estimated, its value can be subtracted from total hydrogen to obtain the capillary water value. Further analysis of this situation depends on direct measurement using PGNA on calibration specimens.

4.6 Durability

Soluble salt content adversely affects durability but is relatively low for stones tested, ranging from 0.0% for the Castle sandstone to 1.0% for Salem limestone. Sulfates and nitrates, which are particularly deleterious, have not been detected. In general, the test stones were known to be relatively durable when selected as building stones. In the case of the Smithsonian Castle, Seneca sandstone was selected after frost damage simulation using a sodium sulfate method developed by Charles G. Page, one of the earliest examples of the use of this kind of durability test (Owen 1849). Results of analyses will be correlated to observations of the stones' weathering on Smithsonian buildings and the 60-year-old NIST test wall of historic commercial building stones, which includes most of the test stones.

5. Conclusions

Investigation of Smithsonian building stones has provided useful information relevant to conditions that may be encountered in application of PGNA to measure moisture in porous masonry and provided insights into durability that can be used in future conservation. Three advanced characterization methods – INAA, TGA and hyperspectral imaging – expand knowledge of the characteristics of the stones.

References

ASTM. 2001. *Standard Test Method for Hygroscopic Sorption Isotherms of Building Materials*. C 1498-01.West Conshohocken, Pennsylvania: ASTM.

Councill, R.J. 1954. *The Commercial Granites of North Carolina,* Bulletin Number 67. North Carolina Deptartment of Conservation and Development.

Dale, T.N. 1924. 'Part ii: Constitution and adaptations of the Holston marble'. In *Marble Deposits of East Tennessee,* Bulletin 28, 87-162. Nashville, Tennessee: Tennessee Division of Geology.

Glascock, M.D. and Neff, H. 2003. 'Neutron activation analysis and provenance research in archaeology'. *Measurement Science and Technology* **14**: 1516.

Glascock, M.D., Speakman, R.J. and Neff, H. 2007. 'Archaeometry at the University of Missouri Research Reactor and the provenance of obsidian artefacts in North America'. *Archaeometry* **49**(2): 343-357.

Hall, C. and Hoff, W.D. 2012. *Water Transport in Brick, Stone and Concrete*. 2nd edn. London: Spon Press.

Kotula, P.G., Keenan, M.R. and Michael, J.R. 2003. 'Automated analysis of SEM X-Ray spectral images: A powerful new microanalysis tool'. *Microscopy and Microanalysis* **9**: 1-17. Available: http://www.geology.wisc.edu/~johnf/g777/MM /Kotula-2003.pdf.

Lathram, E.H. and Thiel, G.A. 1946. 'A comparison of the physical properties and petrographic characteristics of some limestones and dolomites of southeastern Minnesota'. *Journal of Sedimentary Research* **16**(2): 72-85.

Lee, K.Y. and Froelich, A.J. 1989. 'Triassic-Jurassic stratigraphy of the Culpeper and Barboursville basins, Virginia and Maryland'. U.S. Geological Survey Professional Paper 1472. USGS.

Livingston, R.A. 1992. 'Standardization of the neutron probe for the assessment of masonry deterioration'. *Journal of Applied Radiation and Radioisotopes* **4**(10/11): 1285-1300.

Livingston, R.A., Mohamed, A., McComb, J. *et al.* 2010. '2nd generation neutron-based system for measuring chlorides in concrete'. In *Structural Faults & Repair 2010*, Edinburgh.

McGee, E.S. 1989. 'Mineralogical characterization of the Shelburne marble and the Salem limestone test stones used to study the effects of acid rain'. USGS Bulletin 1889. USGS.

Merrill, G.P. and Mathews, E.B. 1898. *The Building and Decorative Stones of Maryland*. Baltimore: Johns Hopkins Press.

Owen, R.D. 1849. *Hints on Public Architecture*. New York: Putnam.

Sereda, P.J. and Feldman, R.F. 1970. 'Wetting and drying of porous materials'. *Canadian Building Digest* (October): 130-134.

Teutonico, J.M. 1988. *A Laboratory Manual for Architectural Conservators*. Rome: ICCROM.

Winkler, E. 1994. *Stone in Architecture: Properties, Durability*. 3rd edn. Berlin: Springer.