KANSAS GEOLOGICAL SURVEY
OPEN-FILE REPORT 2000-24

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at Steamboat Butte, Montana, Using Ethyl Silicate
Solution Treatments
Project Report

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1930 Constant Avenue
University of Kansas
Lawrence, KS 66047

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David A. Grisafe
Geologic Investigations
Kansas Geological Survey
1930 Constant Avenue
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May, 2000

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INTRODUCTION

Native American rock art sites provide links to our past and should be preserved for future study. Although many sites have been vandalized, the destructive force acting on all rock art is natural weathering. Such sites are attacked by freeze-thaw, wet-dry and heat-cool cycling; wind and water erosion; biological growths; salts; atmospheric pollution; and mineral weathering. Naturally, climatic characteristics, the degree of protection from the elements, and the properties of the stone play important roles in determining which of the agents is detrimental at a given site. The placement of a suitable bonding agent in liquid form into the stone would improve the durability of the stone and retard the effects of such weathering, thus prolonging the life of the petroglyphs.

The Steamboat Butte Site is located in central Montana in Musselshell County. The petroglyphs are carved into the cap rock or the top layer of sandstone of the butte. The petroglyphs have a vertical orientation, meaning they are carved onto the cliff face. The location is exposed to most of the weathering elements mentioned above.

In order to be effective at consolidating the stone and thereby increasing its resistance to weathering, any potential chemical treatment should meet the following criteria:

1) The treatment must penetrate the stone so that the entire zone of weathering is treated.
2) The treatment should improve the compressive strength of the stone, an indication of successful bonding.
3) No discoloration of the stone should occur. This means that no coloring ions should be present and that the solution should have a neutral pH to avoid possible reaction with the mineral components of the stone.
4) The treatment should not completely seal the pore system of the stone; the stone should be able to breathe and rid itself of excess moisture.

At present, one chemical system that meets the above criteria is known commercially as Conservare OH; the chemical solution is primarily composed of ethyl silicate (silicic ethyl ester) dissolved in a methyl ethyl ketone/acetone mixture. The ketone mixture acts as both a solvent and a volatile inert carrier and the low molecular weights of the compounds and low viscosity of the solution promote penetration into the stone. The

solution has a neutral pH. Developed by Wacker Chemie in Germany, this solution in the United States is supplied by ProSoCo, Inc. or Process Solvents Company, Inc., of Lawrence, Kansas, and they have successfully used this solution for consolidation purposes on many historic buildings. Treatments have produced increased strength of the stone and no appreciable discoloration has occurred. Based on improvements in the compressive strengths of different types of stone treated with Conservare OH, the stone consolidation is particularly effective when used on sandstones. An example of the effect on the properties of sandstone has been reported by Zinsmeister et al. (1988). Perhaps most important is the fact that with proper application, the pore system of the stone is not sealed, and the stone can rid itself of any excess moisture. The basic mechanism of the chemical treatment is quite simple; the ethyl silicate hydrolyzes upon exposure to moisture within the stone to form a siliceous cement and the volatile by-product, ethyl alcohol.

Conservare OH was used for the first time on Native American petroglyphs at the Faris Cave Site, Ellsworth County, Kansas, as reported in Grisafe (1996) and produced outstanding results. Core samples treated in the laboratory showed large increases in strength and resistance to freeze-thaw cycles, no discoloration occurred in either lab samples or on-site test panels, and the stone retained some of its permeability, thus allowing the stone to breathe and eliminate excess moisture. A recent laboratory study on the Hell Creek Sandstone collected from Pompeys Pillar National Historic Landmark in Montana, where the explorer William Clark carved his signature in 1806, yielded similar results (Grisafe, 1999). Another successful laboratory examination and subsequent treatment, that of the carved name of W.F. Cody (Buffalo Bill) in Ellsworth County, Kansas, is reported by Grisafe (2000).

The primary objective of this laboratory study was to determine the chemistry and mineralogy of the stone and then measure the absorption, compressive strength, and freeze-thaw resistance of both untreated and treated stone. These measurements will determine the suitability of treating the stone at the Steamboat Butte Site with the ethyl silicate solution consolidating agent in order to increase the resistance of the stone to weathering and thereby preserve the petroglyphs.

PROCEDURE

During the visit to the site, numerous small blocks of stone were collected and transported to the testing laboratory of the Kansas Geological Survey. Several of the samples were examined by x-ray diffraction to determine the mineralogy of the test specimens. In addition, samples were also examined under a reflected-light microscope and whole-rock chemical analyses of major components were obtained from some of the samples using atomic absorption spectroscopy.

Key physical properties were determined, including the capillary and immersion absorption, compressive strength, and freeze-thaw resistance. All physical properties

were measured on core samples cut from blocks of stone collected at the site, such cores being approximately 1.5 inches in diameter and 1.5 to 1.75 inches in height, using a trim saw to insure the bases were parallel. Capillary absorption as a function of time was determined by placing the cores (base side down) on a water-saturated sponge and measuring their weight gain at periodic intervals. For comparison, cores were immersed in water for 24 hours or longer and their weight gain measured.

The capillary absorption characteristics (amount and rate of water uptake) of the stone were determined; these served as a guide to the treatment times to be used on the test cores. Each treated set consisted of 12 cores. All cores were placed in a stainless steel pan containing a thin layer of the ethyl silicate solution, allowing the chemical solution to be absorbed through their bases. This method more closely simulates field treatment, where the solution would be absorbed from the surface inward, than completely immersing the cores in the solution. Because sufficient permeability and porosity existed after one treatment, two sets of cores were given a second treatment. Finally, one set was given a third treatment. Based on recommendations by the supplier, a curing period of at least one month was allowed between treatments or before property measurements were undertaken to insure the reaction was at least 95% complete.

Initial weights before treatment and final treated weights were used to determine the amount of solids precipitated within the stone cores. Absorption, compressive strength, and freeze-thaw resistance were also measured on both treated and untreated cores in order to evaluate the effectiveness of the treatments. In summary, the test results indicated whether future treatment by this solution is warranted. Such future work would involve selection and treatment of a small test panel at the site, followed by actual treatment of the petroglyphs.

Compressive strength was measured on a Riehl Dynamometer located at the Materials Testing Laboratory of the Kansas Department of Transportation (located at 2300 N. VanBuren in Topeka, Kansas). The diameter and height of each core was measured to the nearest hundreth of an inch. The height measurement was done to insure the height to diameter ratio of the sample fell within the range of values specified in compressive strength test ASTM C-170. The load required to break each core was recorded and the compressive strength of each core was calculated by dividing the load at failure by the cross-sectional area of the core. Values were calculated in both pounds per square inch (lb/in^2) and kilograms per square centimeter (kg/cm^2). An average of nine cores was used to determine each compressive strength value.

To evaluate freeze-thaw resistance the cores were subjected to a cycle of about 16 hours at -20° C followed by about 8 hours of immersion in room temperature water. Weight loss of the cores was determined after 25, 50, 75, 100, and 150 cycles. An average of three cores from each set of cores was used to determine the absorption characteristics and freeze-thaw resistance. In this study we used a total of 150 freeze-thaw cycles, and several days were required to obtain cores of constant weight (at 50° C) after every 25 cycles. As a result, this test required more time than the other property measurements.

RESULTS

Coring, trimming, and grinding samples for mineralogical and chemical analysis all indicated the sandstone at Steamboat Butte is not well bonded.

Mineralogy

Field examination (hand lens and 10% hydrochloric acid) suggested medium- to fine grained sandstone that contained little matrix and not much calcium carbonate. The tan color of the stone suggested the presence of iron-bearing material. Reflected light microscopy indicated the stone consisted largely of quartz grains imbedded in a relatively small amount of light, fine-grained matrix. The matrix varies in color from white to tan. Most quartz grains are clear, but many have some coloration or coating on them. A small number of other non-quartz grains are quite dark, some with red coloration on the surface or into the surrounding matrix, presumably iron-rich mineral(s). Other minerals present include feldspars.

X-ray diffraction patterns were obtained from samples ground in a corundum mortar and pestle to -200 mesh and dispersed on glass slides using acetone. The resulting diffraction patterns indicated a rather poorly carbonate-cemented sandstone, primarily quartz with small amounts of both calcite and dolomite. As expected from microscopic examination, little feldspar is present. Also present in small amounts are kaolinite and mica-illite. Since there is little or perhaps no mica present by optical examination, the mica-illite diffraction pattern is dominantly from illite-type clay. Examples of the diffraction patterns obtained from three samples are shown in Figure 1. The patterns are nearly identical. Figure 2 shows one of the samples complete with the computer generated matching phases.

Chemical Analyses

Representative chemical analyses in weight percent of major oxides are shown in Table 1. The chemistry of the samples is obviously similar, but this is not surprising considering the similarity of optical and x-ray diffraction examinations.

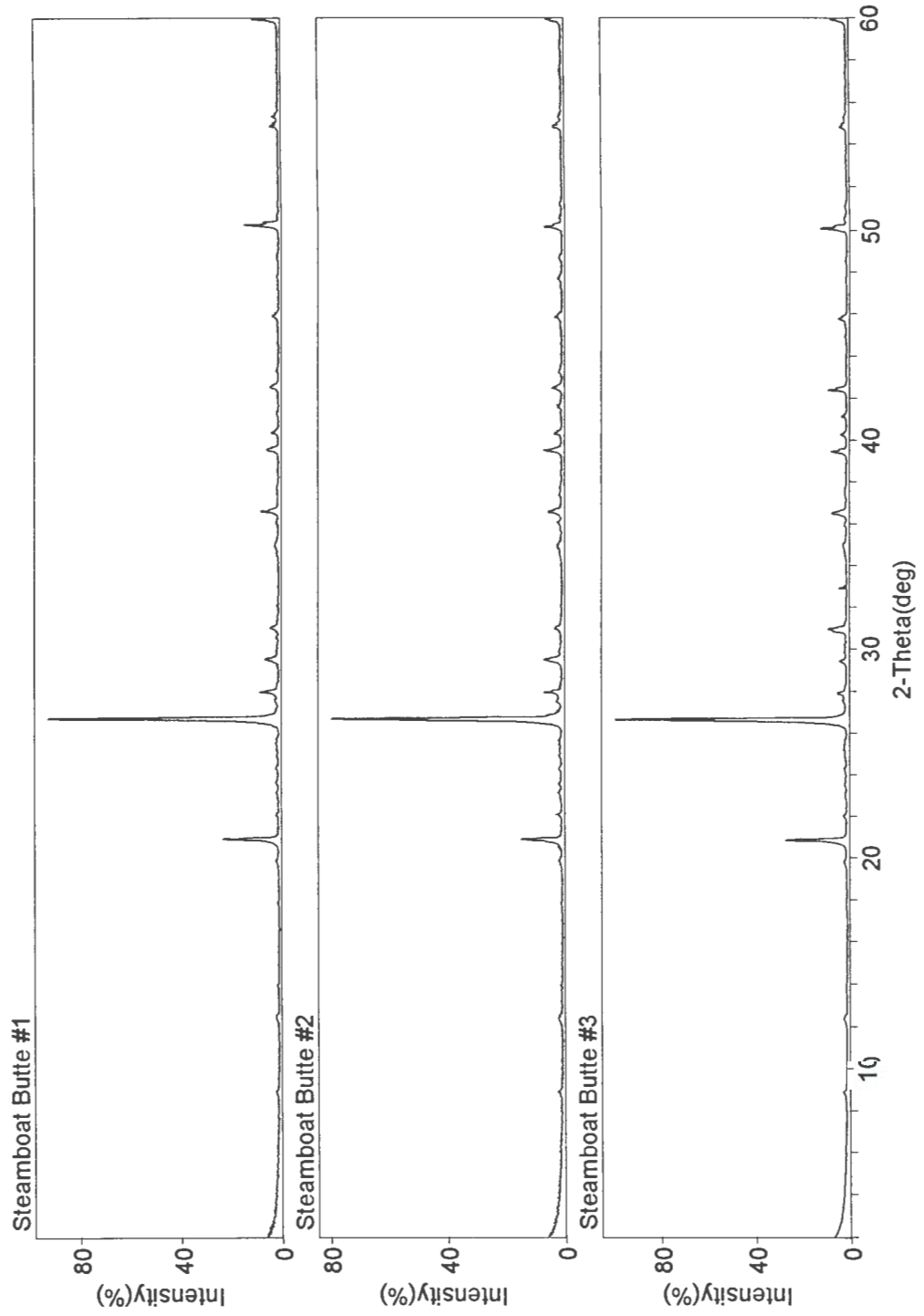
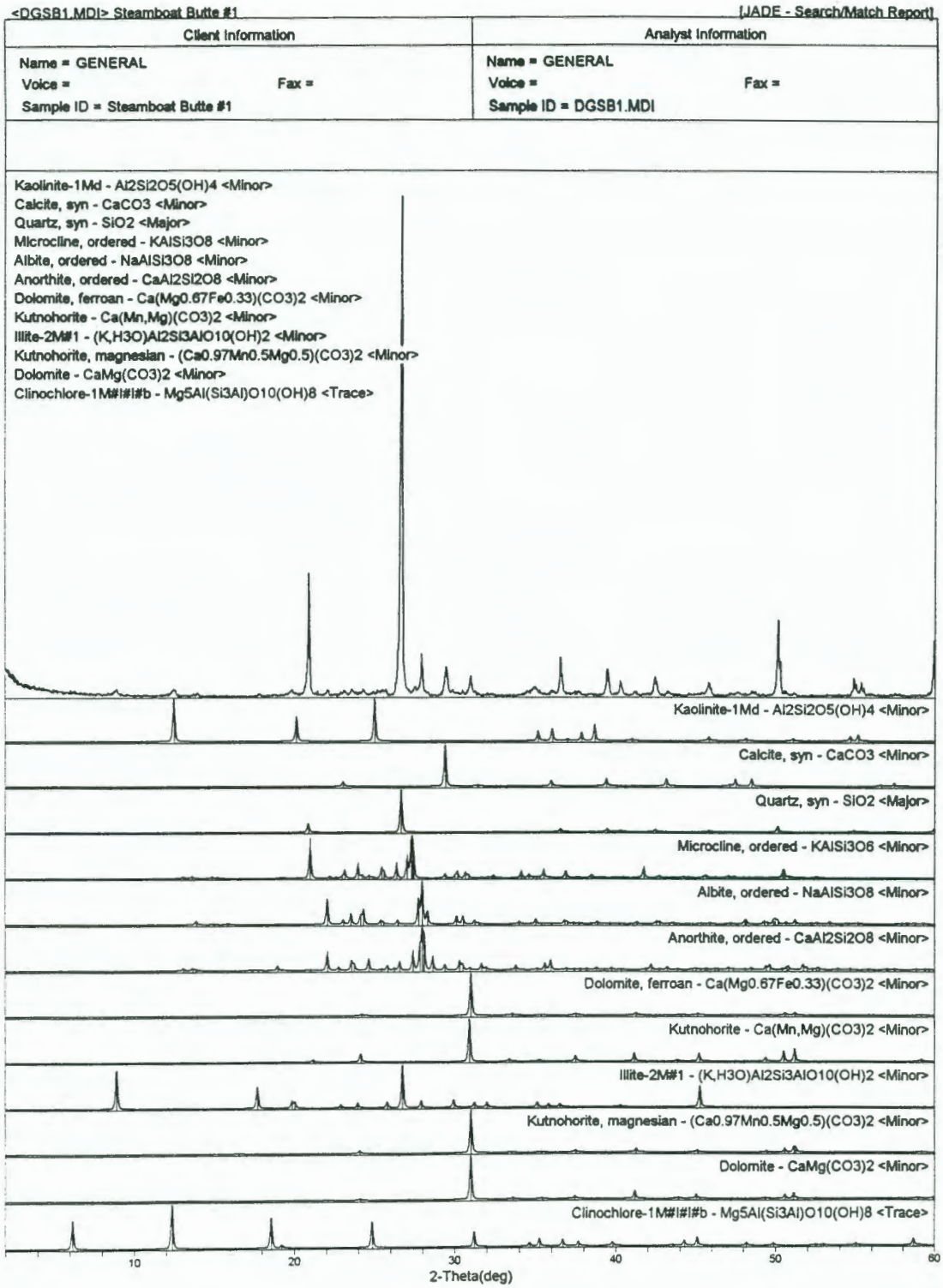


Figure 1. X-ray Diffraction Patterns for Samples at the Castle Butte Site.



KGS

Figure 2. X-ray Diffraction Pattern of a Castle Butte Sample with the Accompanying Computerized Search-Match Report.

Table 1

Chemical Analyses of the Tongue River Sandstone by Atomic Absorption at the Steamboat Butte Site (Weight Percent Composition)

	Sample Core		
Oxide	1	2	3
SiO_2	69.14	70.68	72.53
Al_2O_3	7.75	8.14	7.68
Fe_2O_3	3.18	3.21	2.59
TiO_2	0.40	0.37	0.46
MnO	0.05	0.04	0.02
CaO	6.14	5.42	4.48
MgO	2.03	1.70	2.23
K_2O	2.05	2.16	2.04
Na_2O	0.81	0.88	0.80
Loss on ignition (1000° C)	9.98	7.42	7.18
Total	99.98	100.02	100.01

Capillary and Immersion Absorption

The capillary absorptions of cores were determined by placing the base of each core on a saturated sponge and measuring the weight gain of the core over time. Such information is useful to obtain an idea of how rapidly the stone would absorb liquid. Finally, immersion absorption of the cores was done to compare the total weight gain of the stone to that obtained by capillary absorption. Using an average of three cores, the untreated sandstone showed a capillary absorption weight gain of 11.2% after only 15 minutes, a clear indication of the high porosity and permeability of the stone. The 24 hour capillary absorption weight gain was 12.1% (versus an immersion weight gain of 12.8%). The

capillary absorption figures indicate the stone absorbed 92.5% of its 24 hour absorption in the first 15 minutes. It was decided that the initial treatment of ethyl silicate solution should be about 20 minutes in duration. This assured all of the cores were wet on the top surface. The second and third treatments were 20 and 30 minutes respectively.

Table 2

Percentage Weight Gain of Untreated and Treated Cores from the Steamboat Butte Site by Capillary Absorption
(all times in hours)

Treatment	0.5	1.0	4.0	24	48
Untreated	11.6	11.6	11.7	12.1	12.9
1 OH	8.3	9.2	9.6	9.8	10.1
2 OH	4.7	5.6	6.4	6.8	7.1
3 OH	1.6	1.8	2.2	2.8	3.1

Partial results of these tests are summarized in Table 2 with each value being the average of three cores. As expected, successive treatments with the ethyl silicate solution cause a decrease in the absorption rate of the stone for a given time interval as well as the long term absorption. However, even with three treatments, there is still a degree of permeability remaining so the stone is able to breathe and eliminate moisture.

Compressive Strength

The average values for the compressive strengths of the treated and untreated cores are presented in Table 3. Each figure represents the average of nine cores. It is apparent that the ethyl silicate treatment greatly improves the compressive strength of the sandstone with additional treatments producing even greater strengths.

Table 3

Compressive Strength of Treated and Untreated Cores of Sandstone from the Steamboat Butte Petroglyph Site

Treatment		Compressive Strength		
	% Solids	lb/in^2	kg/cm^2	% Increase
Untreated	---	700	49	---
1 OH	5.1	1,935	136	175
2 OH	7.7	3,350	235	380
3 OH	9.3	5,290	372	655

The % solids figure refers to the percent weight gain of the final cured weight compared to the original, untreated, dry weight. This is a relative value rather than absolute since the amount of solids deposited will vary depending upon the length of the treatment time, length of curing time and curing conditions (temperature and humidity). This is why each treated set of cores for a given treatment cycle were given identical times of treatment and curing before weighing or measuring properties.

Freeze-Thaw Resistance

The weight loss for each core was measured after every 25 freeze-thaw cycles. Table 4 summarizes the average weight loss of cores after every 25 cycles with each value representing the average of three cores. Figure 3 shows the cores after 25 and 100 cycles. The front row of the 25 cycle photograph are untreated cores that completely disintegrated during the next 25 cycles.

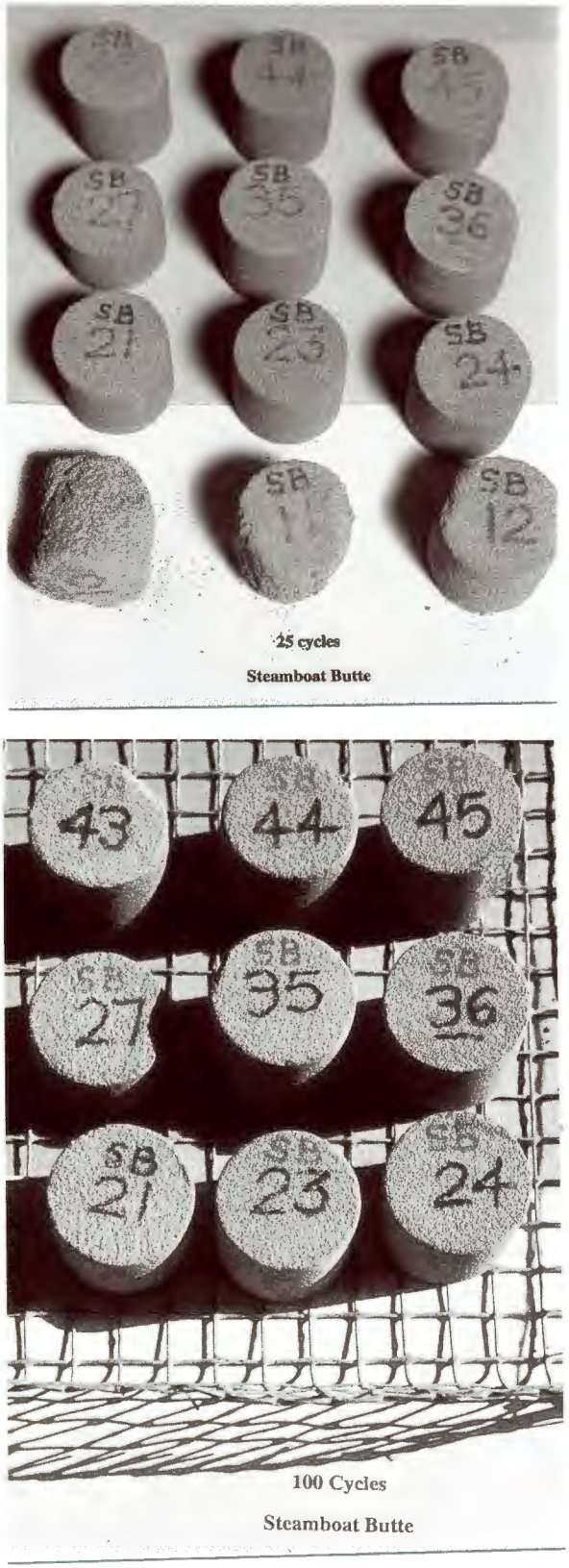


Figure 3. Cores from Steamboat Butte after 25 and 100 Freeze-Thaw Cycles.

Table 4

Freeze-Thaw Resistance of Treated and Untreated Cores of the Tongue River Sandstone from the Steamboat Butte Site

	Percent Weight Loss After Cycle				
Treatment	25	50	75	100	150
Untreated	14.0	100	---	---	---
1 OH	0.1	0.1	0.1	0.1	0.2
2 OH	0.1	0.1	0.1	0.1	0.1
3 OH	0.1	0.1	0.1	0.1	0.1

The values in Table 4 clearly show a vast improvement in the freeze-thaw resistance of the porous sandstone that was treated with the Conservare OH stone consolidant. The small weight percent loss (0.1%) after 25 cycles can be attributed to loosely bonded surface grains that are dislodged after a few freeze-thaw cycles. To determine whether the additional OH treatments produce long term benefits, it would be necessary to continue freeze-thaw cycling; perhaps several hundred cycles would be required before significant differences could be detected.

SUMMARY

The results of this study show the core samples collected from Steamboat Butte have similar mineralogical, chemical, and physical properties. The sandstone is poorly bonded and very porous and permeable. Small amounts of calcium carbonate, dolomite, and clay minerals comprise the matrix with the grains being largely quartz with a small amount of feldspar.

The high porosity and permeability allowed substantial amounts of the ethyl silicate to penetrate the stone and subsequently lead to pronounced consolidation. The treatments produced very large increases in both the compressive strength and freeze-thaw resistance while preserving a portion of the porosity and permeability. The laboratory results certainly suggest that ethyl silicate treatment(s) would prolong the life of the Native American petroglyphs at Steamboat Butte.

ACKNOWLEDGMENTS

Appreciation is expressed to the U.S. Bureau of Land Management, Billings Resource Area, Billings, Montana, whose financial support made this study possible.

REFERENCES

ASTM C-170, Compressive Strength of Natural Building Stone, American Society for Testing and Materials.

Grisafe, David A. (1996). Preserving Native American petroglyphs on porous sandstone. Plains Anthropologist 41, Number 158, p. 373-382.

Grisafe, David A. (1999). Improvement of Sandstone Durability: Evaluating a Treatment's Suitability for Preserving Historic Inscriptions. Technology and Conservation 13, Number 1, p. 20-26.

Grisafe, David A. (2000). Preservation of Historic Graffiti Using Ethyl Silicate: the Signature of W.F. Cody in Ellsworth County, Kansas. Transactions of the Kansas Academy of Science 103, Numbers 3-4,

Zinsmeister, K.J.H., N.R. Weiss, and F.R. Gale (1988). Consolidation Treatment: Massillon (Ohio) Sandstone. J. Preservation Technology 20: p. 35-39.