

WESTERN ARCHEOLOGICAL CENTER  
Tucson, Arizona

GEOLOGICAL ANALYSIS OF ROCK DETERIORATION  
AT SELECTED NATIONAL PARK SERVICE  
ARCHEOLOGICAL SITES

GEOLOGICAL DETERIORATION OF STONE MASONRY

Drawn from work at:

Aztec  
Bandelier  
Canyon de Chelly  
El Morro  
Montezuma Castle  
Navajo  
Tonto  
Walnut Canyon  
Wupatki National Monuments  
Mesa Verde National Park

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GEOLOGICAL DETERIORATION OF  
STONE MASONRY

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- I. Introduction. The purpose of this contract was to provide a geological perspective to the problem of stone-masonry deterioration in the arid Southwestern U. S. The outline of the investigative method follows.
  - A. Identification of problem sites from the following:
    1. Experience of Western Archeological Center staff.
    2. Phone contacts with site staffs.
  - B. Field investigations.
    1. Personal visits to several dozen ruins at 11 National Park Service jurisdictions.
    2. On-site discussion with Monument or Park staffs.
    3. Sampling of fresh and deteriorated stone masonry and natural rock for laboratory analysis.
  - C. Laboratory investigations.
    1. Infrared absorption spectrophotometry.
      - a. Bulk mineral determinations of mineral types, quantities and changes in fresh and deteriorated materials.
      - b. Analysis of salts for identification and determination of changes of salt species and quantities in deteriorating zones.
      - c. Analysis of fine sieve portions of selected samples for further characterization of subtle clay-salt mixtures.
    2. Microscopic (thin section) examination as back-up to IR work.
    3. Chemical analysis of soluble salt fractions.
  - D. Interpretation of field and lab. results.
    1. Application to preventative measures.
    2. Recommended future investigations.
- II. Sites Considered. Several of the sites visited showed severe general problems while others showed localized problems, less severe general deterioration or essentially no conditions of immediate concern. In order of apparent concern:
  - A. Chaco Canyon and Mesa Verde - Severe deterioration is evident at exposed sites on mesa tops and at Chaco, on the valley floor. Cliff sites at Mesa Verde show localized deterioration only.
  - B. Aztec and Bandelier - General and localized deterioration of somewhat less severe nature than for "A".
  - C. El Morro - Special conditions of natural deterioration of the cliff face which threaten the surface inscriptions.
  - D. Canyon de Chelly - Localized deterioration was moderate to severe at Antelope House but not a general problem at other sites visited.

E. Wupatki and Navajo - Minor localized problems.

Other sites showed miscellaneous problems of lesser concern and will be excluded from discussion in this report.

III. Rock Deterioration. As treated here "rock deterioration" includes physical and chemical geologic processes called weathering, generally similar to the processes of soil formation.

While previous reports (Rock Motion Hazard Reports A & B) dealt with mechanical deterioration of rock in masse resulting in motion, this report deals with subtle alteration of the building stones, foundation rock or associated cliff faces. These alterations are internal chemical-mineral changes or grain-by-grain motion resulting in loss of strength, color change, and erosion of the archeological materials.

At the sites considered here, the resource materials are rock (rock being an aggregate of minerals) and in all sites except Bandelier, the rock is sandstone. The fragmental volcanic rocks of Bandelier, when deteriorating, behave somewhat like sandstones so the processes of deterioration can be generalized. Possible geologic processes of granular-rock deterioration:

- A. Alteration of mineral grains.  
e.g. Feldspars change, in part, to clays; carbonate grains dissolve out or are replaced by other minerals. Magnetite oxidizes and hydrolizes to soft, bulky iron compounds.
- B. Cementing agents removed or replaced.  
e.g. Carbonates dissolved out leaving voids, or replaced by low strength materials. Stable cementing agents replaced by mobile (soluble) materials or expanding-contracting species.
- C. Existing clay minerals shrink and swell.  
e.g. Smectite (montmorillonite-type) clays change volume drastically during wet-dry weather cycles pushing adjacent mineral grains out of place.
- D. Salt crystals grow in voids cyclically (relative to water saturation).  
e.g. Salt crystals grow between mineral grains, push them out of place, salts dissolve and precipitate elsewhere.
- E. Salts change volume in place.  
e.g. A given salt changes its character and volume by taking water into its structure during wet or humid periods and desiccating during dry periods.
- F. Freeze-thaw.  
e.g. Ice crystal damage is proportional to intensity of temperature changes, degree of moisture saturation, and the number of freeze-thaw cycles experienced yearly on a given rock face exposure.

- G. Organic action.  
e.g. Root growth in cracks and micro-fractures shatters rock.  
Organic acids from lichen growth or organic residues attack rock minerals. Organic residues affect salt activity, Eh and Ph.
- H. Complex salt solutions alter the chemical stability of masonry mineralogy.

It is likely that freeze-thaw has a deteriorating effect at sites considered. Intensity and cycling will vary according to the moisture within rocks and the thermal variations. At some sites maximum effect would be on north wall or cliff faces. Other sites may show maximum effects on south faces. In any case the problem is more climatological-meteorological than geological and cannot be analyzed here.

Organic deterioration is obviously related to lichen growth at El Morrow and it is suspected that organic compounds contribute to rock deterioration in most of the ruins. A unique rock deterioration environment is likely due to long-time accumulation of human and animal excrement, refuse and organic remains in the ruin sites. Salt, pH (acid-alkaline) and Eh (oxidation-reduction) effects are likely.

- IV. Water-Salt Cycles in Archeological Sites. Each of the deterioration processes take place only in the presence of water. Moisture is the ultimate control variable to be dealt with in the prevention of deterioration.

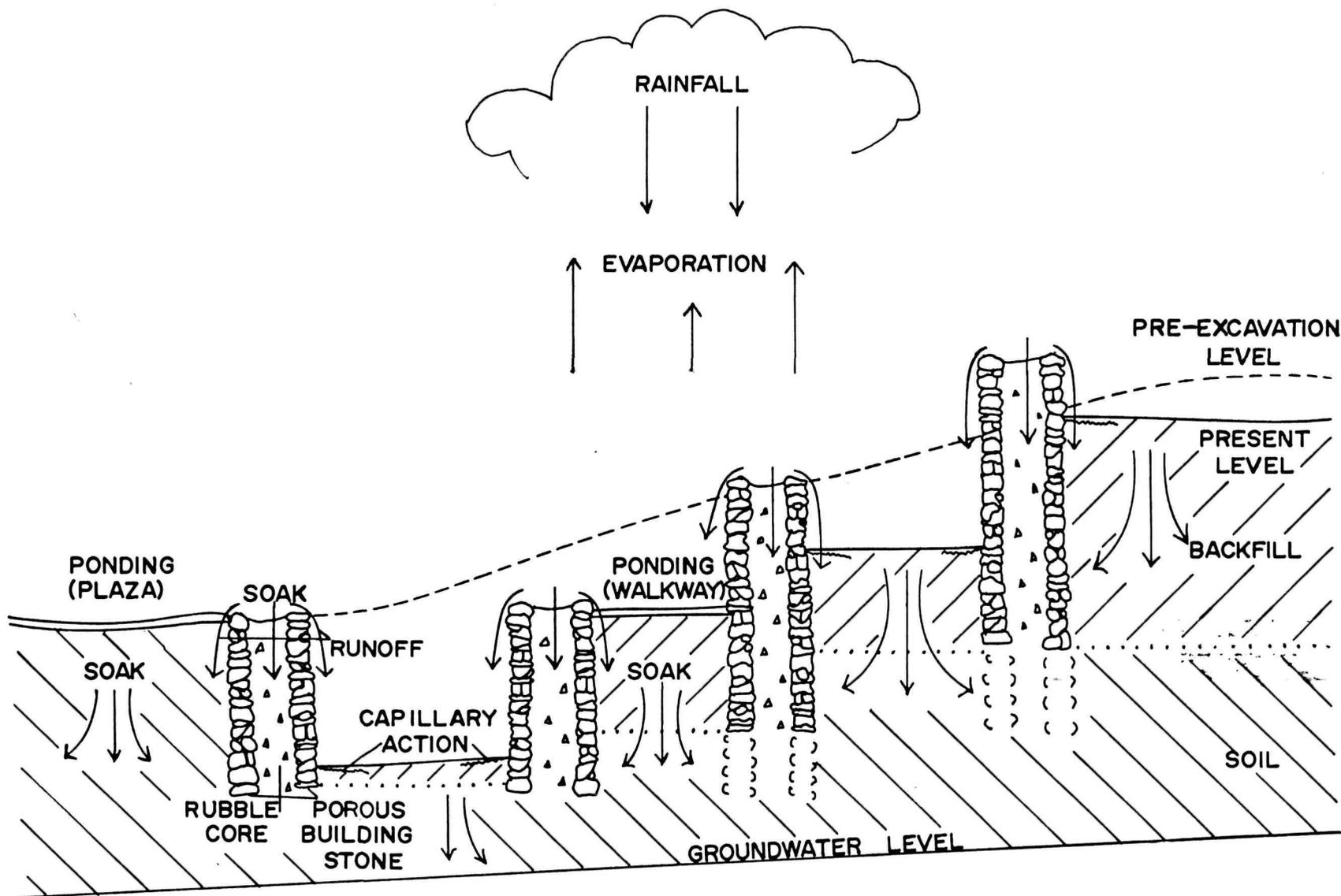
The addition of soluble salts to the system then increases the potential deterioration effects of:

- A. Crystal growth -- physical disruption.
- B. Hygroscopic action -- physical disruption.
- C. Changes in the weathering environment in terms of Eh and pH.

This alters any balance that has been achieved within the rocks in their natural state. The rocks now present in archeological masonry may be affected by simple ionic solutions or combinations of simple and complex ions or replacement of one species by another.

The unique environment of the ruins has already created unique chemical systems including many possible salt, Eh, pH, temperature, and moisture combinations. This unique environment may approach a new equilibrium through time, burial and chemical activity. This approach to new, equilibrium, (different from the natural environment of the rocks), certainly involves the processes we term "deterioration." This third adjustment could be more or less damaging depending on the individual situation, but is a consideration in management of the ruins.

Observed field conditions tie in with the likely water-salt interactions shown in Figures 1 and 2.



NOTE: SOME WALLS HAVE NO CAPS OR ARE PERMEABLE TO WATER

Figure 1: The Water Cycle, Chaco-Mesa Verde Type Sites



Note that airborne particulate salts are abundant in the arid environment and that the ruins provide for complex organic inputs and unusual salt concentrations relative to habitation. Post-habitation use of ruins by bats, birds, and pack rats provides significant organic input.

Observed conditions:

- A. The most general wall deterioration is at or near ground level, particularly when fill is higher on the opposite side of the wall.
- B. The most severe deterioration is where walls long-buried in moist soil are now exposed by excavation and still chronically moist.
- C. Kivas and base portions of wall adjoining deeply back-filled rooms best satisfy condition "B".
- D. Thick rubble-core walls may retain salts and moisture sufficient to satisfy condition "B".
- E. Surface salt blooms may or may not appear in the deteriorated zones (and often appear in non-deteriorated zones).
- F. Oxidation, noted as color changes toward reds, yellows and oranges may or may not be evident in deteriorated zones (though oxidation generally accompanies the most severe examples).
- G. In attacked zones, highly to moderately permeable masonry stones show roughly equal deterioration. Very low permeability materials survive even in severe deterioration zones.
- H. Recently excavated wall sections may immediately show intense deterioration. Such walls disintegrate quickly if chronic moisture conditions prevail.
- I. Poor drainage of wall tops, rooms and plazas adjoining kivas is generally associated with the most severe deteriorations. Simple passage of water, such as down a wall face even beneath a drain point, does not necessarily promote severe deterioration.
- J. Deterioration can be quite random on a given wall depending on susceptibility of various rock types present and the degree of deterioration of the particular stones prior to construction.

V. Examples of Deterioration.

- A. Aztec. Rock types vary considerably so deterioration can be quite random. The near-surface water table has been noted as a cause of deterioration in kivas. A present kivas show generalized deterioration related to surface water accumulations in backfill, rubble-core walls and on plazas or walkways.

Random deterioration exists within enclosed rooms at the base of rubble-core walls. High salt concentrations (mainly nitrates) exist in such areas though salt bloom is not always visible (Figures 3 through 6).

- B. Bandelier. The rock used in masonry at Bandelier is tuff; composed of geologically unstable volcanic glass particles partially welded together by originally contained heat. Glass instability does not appear to play a role in deterioration of the masonry stones. Minor oxidation and dissociation of the particles are the only processes generally evident. The effects are focused at and below ground level. Visible surface salts and non-visible salts within the rock mass were detected in such zones at Longhouse and Frijolito. Intense oxidation and deterioration of tuff-masonry is evident in the masonry of Rainbow House kiva walls (Figures 7 and 8).
- C. Chaco Canyon. The most severe deterioration noted during this study exists in the kiva at Pueblo del Arroyo. Oxidation, salt crusting and physical disintegration of sandstone masonry is carried to a visible extreme. Slump failure of the kiva wall has taken place on occasion, revealing deterioration within the rubble core as well. Groundwater may have risen to ruin level periodically since habitation, though ponding and soaking by surface water is probably a sufficient moisture source for initial deterioration. Processes are accelerated by continued chronic moistening and exposure of the wall face.

Similar but less severe conditions exist in many Pueblo Bonito kivas. Unusually thick rubble core walls accept rainwater, and some ponding on nearby plazas and walkways was evident. Random deterioration occurs throughout the Chaco Canyon ruins where backfill levels vary from room to room (Figures 9 through 12).

- D. Mesa Verde. Deterioration tends to be minor within cliff ruins visited at Mesa Verde (Spruce Tree, Balcony House, Cliff Palace), though at Cliff Palace some moderate deterioration is evident. Moisture has left notable salt bloom on some kiva walls, though it is not necessarily accompanied by significant deterioration.

The mesa-top sites, particularly Far View and Site 820, show intense general deterioration rivalling that of Pueblo del Arroyo at Chaco Canyon. Even recently excavated kivas (Site 820) show advance oxidation and deterioration due to long-term underground wetness. Chronic moisture conditions prevail after excavation as shown by mosses growing along kiva wall bases. Surface salt bloom is minor to moderate.

Sun Temple, despite its exposure, was amazingly free of deterioration apparently due to effective but unsightly concrete wall caps (that act as drain gutters) and relatively low-level, contoured backfill profiles (Figures 13 and 15).



Figure 3. Aztec. General deterioration accompanied by moderate oxidation on wall of Kiva "N". Water ponds somewhat on walkway above. Rubble core wall may absorb some surface water directly.



Figure 4. Aztec. Localized intense deterioration culminating in partial failure shows intense oxidation within the wall. Some such zones carry very high nitrate contents and the normally stable green impermeable rocks there deteriorate more rapidly than the generally susceptible sandstones. Kiva "V".



Figure 5. Aztec. Dense green siltstone generally does not deteriorate (see Figure 4). Here on the west wall, it shows beginning deterioration but much less than the permeable sandstones. This zone is in a drain water-course.



Figure 6. Drain water-courses are moist and bordered by salts following snow melt. White surface salts parallel the wall-top also. Sources are: (a) water, soil, and cement added as soil-cement caps; (b) more likely, airborne particulate salts. In any regard, deterioration is minor.

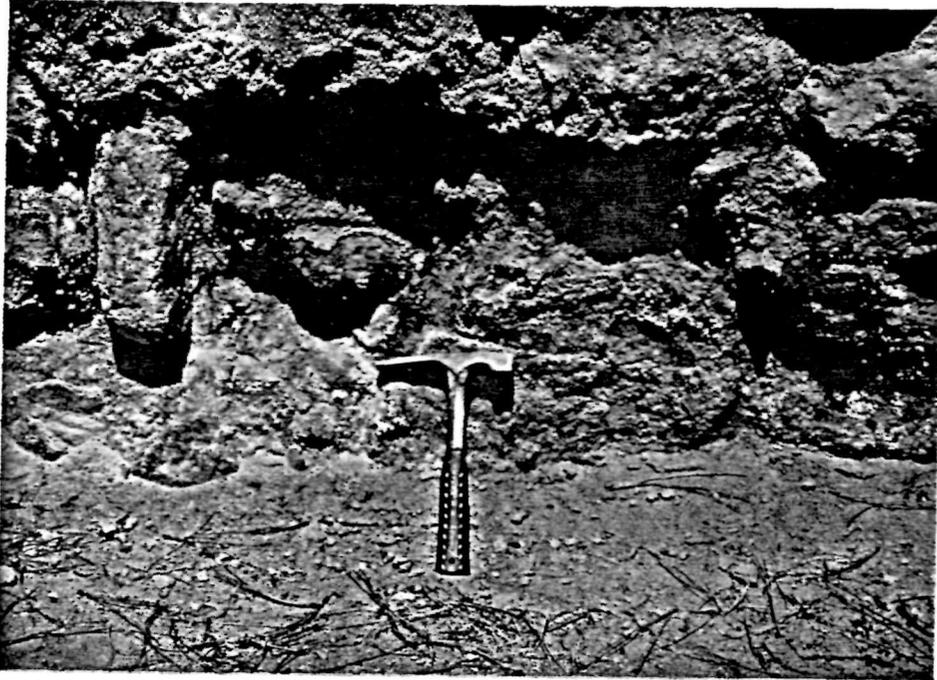


Figure 7. Bandelier. General deterioration at and below ground affecting tuff masonry, Longhouse. Though the volcanic glass fragments are geologically-chemically unstable, salt-moisture effects are physical dissociation of grains and minor oxidation rather than gross devitrification of the glass itself as might be expected.



Figure 8. Rainbow House Kiva. Intense oxidation accompanies severe deterioration and obvious surface salt bloom in moist zones. Here some devitrification of the glass may be promoted. The glass fragments themselves are still sound, however, and intergrain dissociation is the deteriorating effect.



Figure 9. Chaco Canyon. Extreme chronic moist zone showing intense oxidation and surface salt bloom in kiva wall, Pueblo del Arroyo. The rock has been softened and is deteriorating physically.



Figure 10. South wall, opposite view of Figure 9. Similar deterioration resultant in slump of wall materials. The apparently loose slump debris has dried and solidified due to its salt content, though surface salt bloom is minor here.

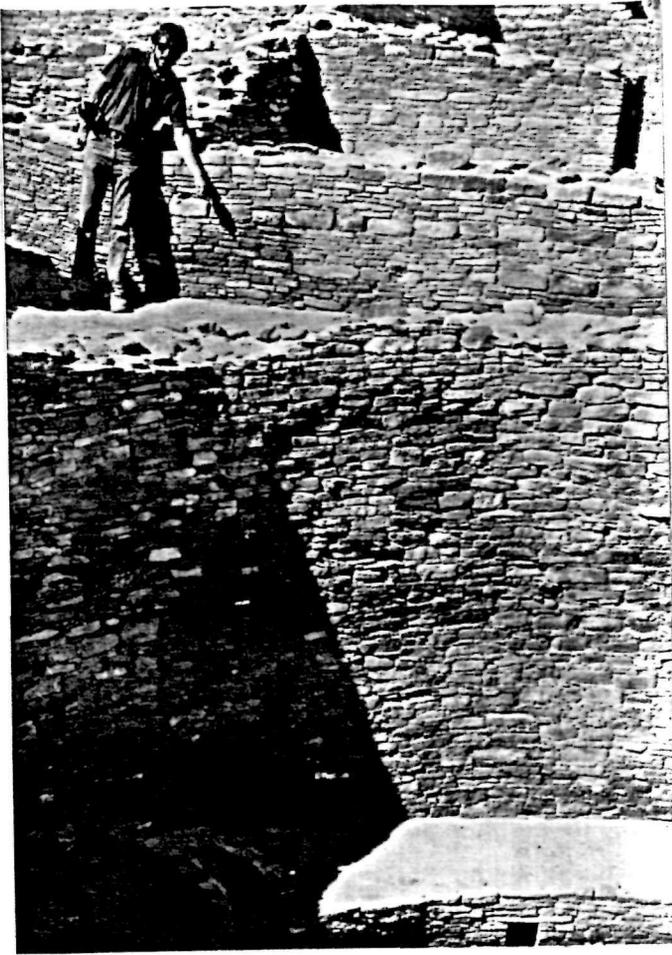


Figure 11. Pueblo Bonito. General deterioration of moderate to severe nature seen in several kivas. Ponding in the area pointed out by Jay and in the room behind contribute to chronic moistness.

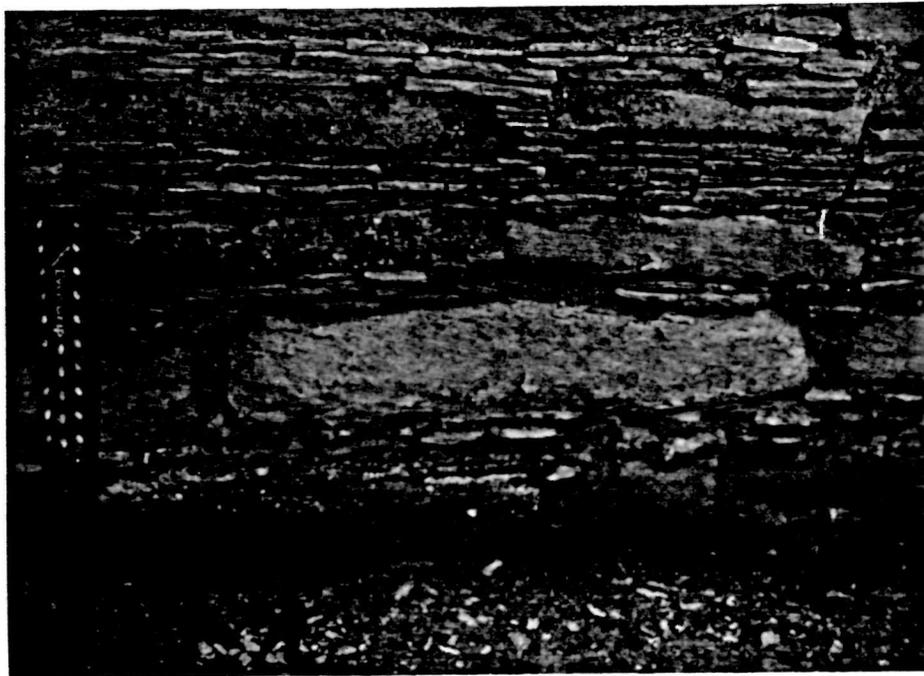


Figure 12. Pueblo Bonito. Random deterioration of susceptible stones near ground level. Rooms behind this wall, rear, are back-filled to a level higher than outside grade.

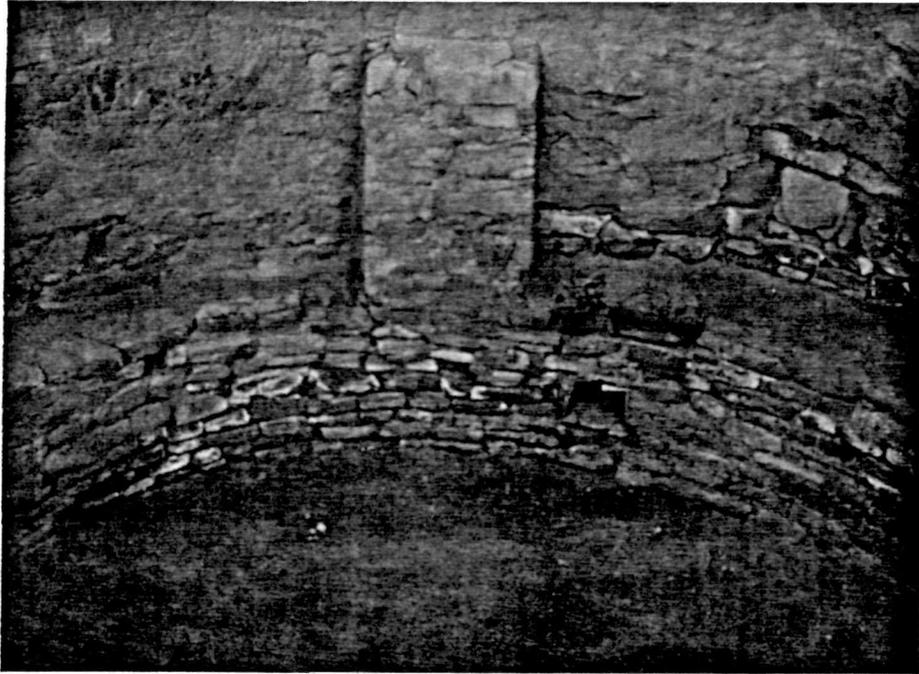


Figure 13. Mesa Verde. Noticeable salt bloom not accompanied by advanced deterioration. Kiva "C," Cliff Palace.



Figure 14. Mesa Verde. General deterioration typical of that seen in kivas of poorly drained mesa-top ruins at Mesa Verde. East wall, central kiva, Farview.



Figure 15. Mesa Verde. Extreme case, oxidation and physical deterioration. South wall, central kiva, Farview.



Figure 16. El Morro. The general condition for deterioration is base-caving at and above soil line in susceptible soft sandstone, due to long-term, low-level moisture activity. Upward slabbing threatens historic inscriptions and prehistoric petroglyphs.

- E. El Morro. The area is a special case in the context of this study in that the deterioration is an endemic geologic process functioning naturally on exposed cliff faces. There is little effect on natural processes due to human input.

The immediate threat to resources is greater here than at the many ruin-centered Park and Monument sites. Unfortunately, few clues as to the nature of the deterioration emerged from study of El Morro materials.

Again water is the prime agent. Salts are present, but in low concentrations. Carbonate mobility is apparent but patterns are not clear. A reddish surface crust clearly has formed over the George Ziska Inscription since its carving and is now flaking away. However, the mineralogy of the crust is not discernably different from that of uncrusted rock.

Rock deterioration due to lichen growth is obvious at El Morro and freeze-thaw damage is likely to be important in the few chronic moist zones (Figures 16 through 20).

- F. Wupatki. Deterioration of masonry is not a significant problem at any of several ruins visited in Wupatki National Monument, but the rock pedestals on which ruins are built are subject to deterioration similar to that affecting masonry at other sites.

High carbonate sandstones show both mobility of carbonates and their replacement by low strength iron oxides. Nitrates are fairly abundant so the deteriorations may be accelerating since habitation (accumulation of organic salts). Ruins and visitors are threatened by rock fall from ledges overhanging the deterioration coves. (See Rock Motion Hazard, Report A.)

- G. Navajo. Deterioration of masonry is quite minor. A photo of the Betatakin alcove wall is included to document the potential of advanced salt action relative to the deterioration of sandstone (Figure 21).

- H. Canyon de Chelly. Locally intense deterioration exists in small room remnants below moist fill in Sliding Rock Ruin. At Antelope House excavated rooms and kivas show intense effects of pre-excavation deterioration. Though partially backfilled, physical deterioration is rapid near new grade levels (Figure 22).

- VI. Though water is the prime variable in systems effecting rock deterioration, water in itself is limited in its activity to:

- solution effects
- minor erosion in rivulets and by raindrop impact
- freeze-thaw
- slight changes in wet vs. dry-strength of materials

In the geologic perspective, water is mainly a medium affecting changes in mineral species, quantity or strength, which in turn affect deterioration.

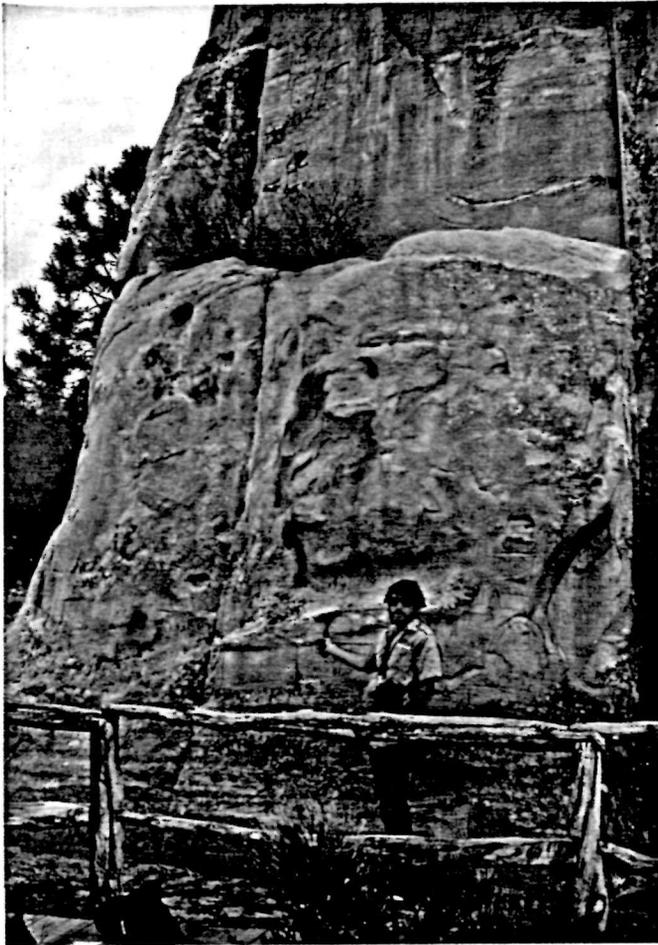


Figure 17. El Morro. More intense local deterioration in the chronic moist zone above the hammer. Rapid erosion of this face is evidenced by rivulet tracks and piles of eroded sand. The moisture reservoir could be eliminated by sealing the obvious crack where shrubs grow. Northeast point of Inscription Rock.

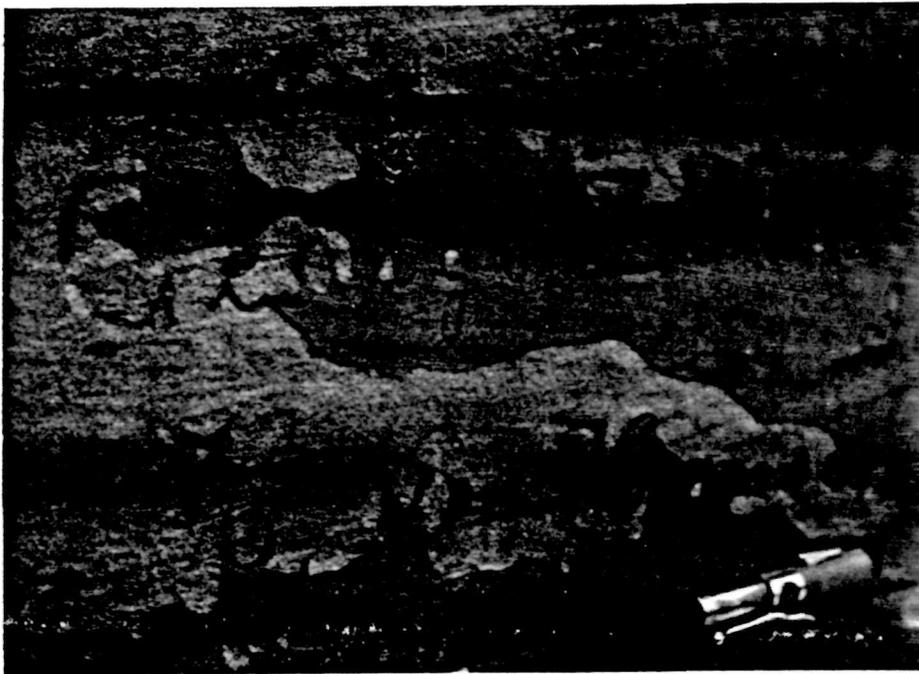


Figure 18. El Morro. Red crust formed since inscription now flakes off, removing detail of the resource. Mineralogical differences between crust and uncrusted rock are not evident in spite of obvious visual differences.



Figure 19. El Morro. Blistering and flaking of rock associated with lichen growth, north face, Inscription Rock. Deterioration rates in lichen-covered areas are at least double that for simple weathering-erosion of a "clean" exposed face.



Figure 20. El Morro. Chronic moisture evident in concentric slabbing zones; freeze-thaw is a likely contributing agent of deterioration in this case of "incipient alcove formation." North face, Inscription Rock.

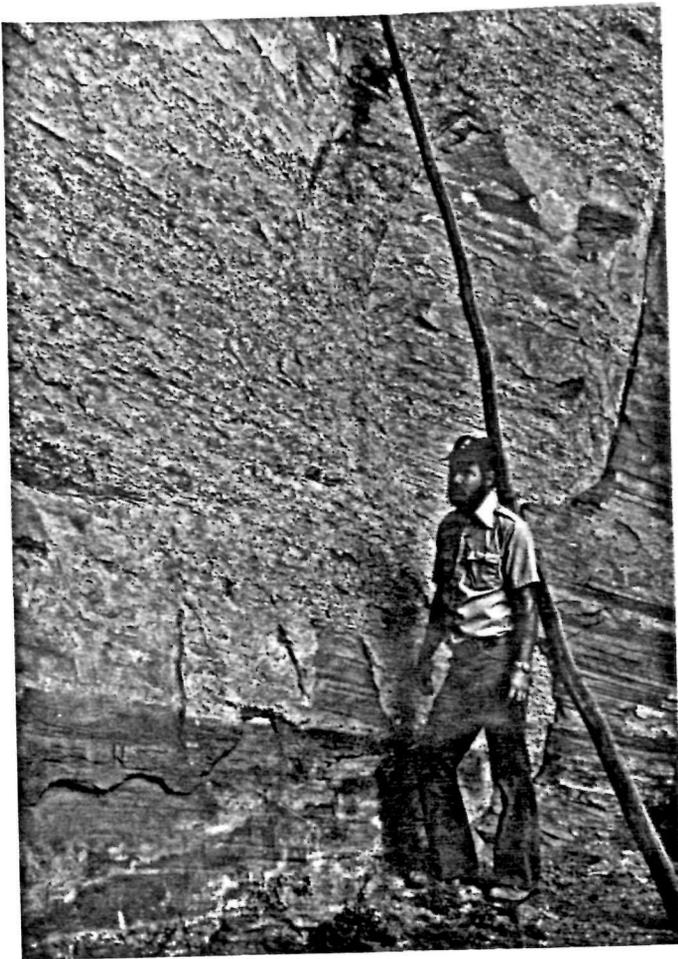


Figure 21. Navajo. Long-term effects of salt action shown as flaking of salt-impregnated chips from the face of Betatakin Alcove.

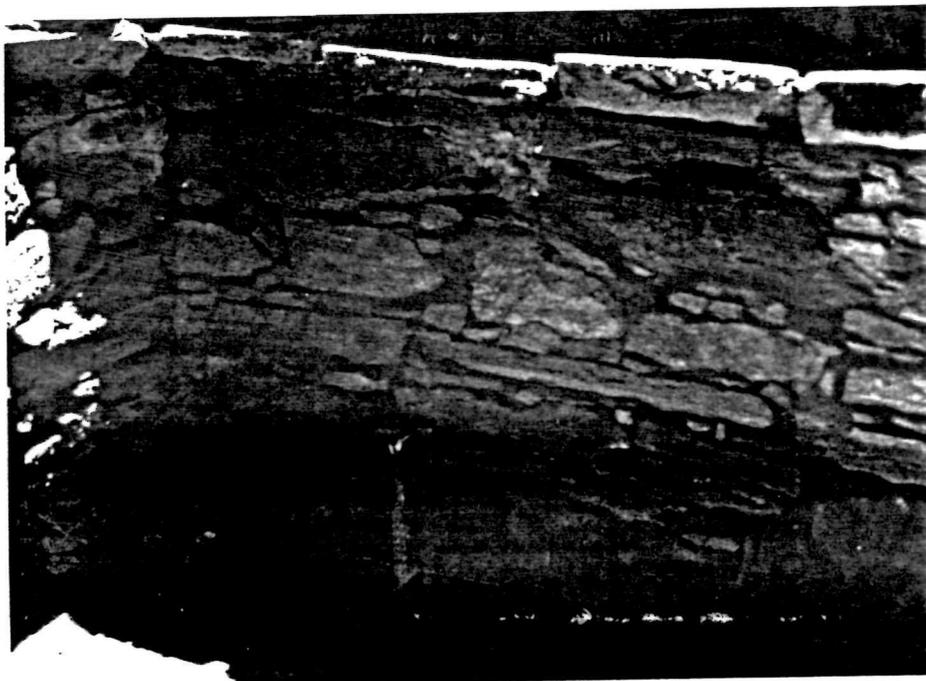


Figure 22. Canyon de Chelly. Oxidation and chemical deterioration is exposed by recent excavation in Antelope House. Physical deterioration continues rapidly due to moisture concentration near the back-fill surface.

The obvious geologic approach then is to identify deteriorated and non-deteriorated rock materials from the archeological environment and determine the type and quantity of mineral change.

Such mineral change may be subtle and is generally affective over time spans of  $10^3$ - $10^6$  years. (The geologic processes most resembling the archeological problems are those of rock weathering and soil development). It was felt that relatively new techniques of Infrared Absorption Spectrophotometry would be appropriately versatile, accurate and inexpensive for application to the subtle and varied mineral changes expected in the short-term (102-103) years archeological setting.

Routine bulk IR (infrared) analyses were combined with follow-up specialized analyses on selected problem samples. These consisted of analysis of fine sieve fractions for characterization of subtle clay-salt mixtures present in the masonry samples in small quantities, and analysis of hand-picked surface salts for identification of salt species.

Further follow-up work included microscopic analysis to verify subtle or low volume mineral species and identify important textural relationships.

Soluble salt analyses were done by soaking one part rock or soil from the archeological sites in 20 parts distilled water and analyzing for cation-anion content to further characterize salt components in the deteriorated zones.

Tables 1 through 7 define the samples site by site and list the IR results from the bulk analyses along with results of microscopic analysis. The "Notes" section at the end of each table summarizes the significant mineralogical changes for that site.

Table 8 summarizes the clay-salt characterization from IR analysis of fine-sieved sample fractions.

Table 9 summarizes hand-picked surface salt analyses by IR.

Table 10 lists results of the soluble salt analyses.

## VII. Interpretation--Results.

Deterioration is extreme when masonry is buried for long time periods in moist ground. Chemical deterioration of the rock and oxidation is well-advanced by the time of excavation. Exposure then allows physical deterioration (crumbling and removal of mineral grains).

Probably the two processes can proceed simultaneously where a wall face is chronically moist due to percolation from cliff seeps or wet debris-fill behind the wall.

Salts are important, but not necessarily as the visible white salt crusts and blooms. The role of these white salts is uncertain, but they are likely effective in the final stage, namely physical deterioration.  $\text{NaSO}_4$  species, well-known for their physically destructive capabilities are present but nitrate species appear to be more closely correlated with intensely deteriorated zones. The nitrates are often invisible even in weight concentrations of over 20 percent of the rock mass.

Certain salt solutions likely affect the solubility of carbonate grains and natural cementing agents. They also affect oxidation and precipitation of low strength iron compounds apparently during or after solution of original carbonates. The nitrates in organic or solution-complex form are highly suspect in the actual mineralogical alterations noted.

Salts added from the atmosphere are abundant as are organic inputs from human habitation and animal occupation since abandonment of the ruins. Salts added in the water, cement and soils used for ruin repair probably are not of concern.

Clays which have particularly destructive potential through shrink-swell activity, namely smectite (montmorillonite) types, are not abundant in either the deteriorated or non-deteriorated rocks. Minor quantities of shrink-swell clays formed at sandstone or tuff grain boundaries could have destructive effect, but this is nowhere demonstrated in the materials analyzed. No strong indication or significant clay formation exists through minor exceptions were noted.

Lithic fragments (shale and volcanic) are present in most of the sandstones examined and are possible foci of deterioration. This does not appear to be significant, however. (Some sericite illite formation is possible in these fragments during deterioration.) Volcanic glass, as in the tuffs of Bandelier, is a chemically unstable material, tending to alter quickly to clays under weathering. No significant clays are evident. Some tuff recrystallization (devitrification) is possible, but mainly to the stable minerals, quartz and feldspar.

The major process of chemical-mineralogical deterioration is the solution and transition of carbonate grains and cements from the natural rock of building stones. The dolomite and calcite rock materials are dissolved, likely by complex salt solution in rain and runoff waters. Transition by precipitation is to lower strength calcite, dolomite, and miscellaneous carbonate and bicarbonate salts dominated by Na-rich types in hydrated form. Precipitation may be in, on, or more likely removed from, the stone in which solution was effective.

Removal of original carbonate is nearly always accompanied by addition of red, brown, yellow or orange oxide masses mainly composed of i.e. goethite. Intense deterioration tends toward reds, and oxide concentrations may approach 10 percent by weight (more by volume).

Distribution of the soft, low strength oxide along grain boundaries greatly decreases rock strength.

Nitrate salts appear to participate in the replacement of carbonate by iron oxide. Several samples show microscopic aggregates of probable nitrate salts dispersed in the oxide replacement masses--even though solution and removal of these salts would seem likely during preparation of the micro-slides (thin sections). Eh and ph effects are probable. Also replacement of dense carbonate by porous oxides may provide or at least maintain openings for later salt mobility, crystal growth, and hygroscopic activity.

Salt mobility in terms of crystal growth, re-solution, re-precipitation and new expansive crystal growth is a certain effect of physical deterioration. Also certain complex salt species present in wet exterior zones were found to be chemically similar to different species existing on the dry interior of roofed rooms. The difference is in hydration state (the incorporation of water into crystal structure, resulting in volume change). This effect could take place in many variations and by many salt species as humidity or wall moisture changes daily, seasonally, or cyclically as moisture moves through walls after storms. The volume changes could effect physical deterioration.

#### VIII. Prevention - Application.

- A. Increased efforts may be made to keep water out of the masonry, fill and soils in the ruins sites.
- (1) Very simple improvements are still wanting at many ruins e.g. sloping, channeling or fill and soil surfaces to direct excess water out of rooms.
  - (2) Constructed drainways, tiles and pipes are the next step in sophistication and are working well in some parts of some sites. Maintenance and improvements are necessary to ensure that such systems originate at levels that in fact intercept water, that they are sloped so to actually transport the water and that they terminate out of rooms, beyond plazas and away from the ruins so not to deliver the water to a new problem area.
  - (3) Capping of walls, particularly rubble-core Chaco Canyon or Mesa Verde types will keep much moisture out of the rubble. Wall caps at Sun Temple, Mesa Verde are impermeable to water and are concave upward acting as drainways to deliver water to drain pipes. Sun Temple is a model for the effect of good wall capping, but is unsightly due to the obvious concrete work. More aesthetic capping-drain systems should be developed.
- B. Long-term subsurface and visible surface deterioration can be slowed drastically by decreasing moisture content of fills,

soils, and masonry. However, buried rock in many cases has already reached a high state of deterioration in balance with the subsurface environment.

- (1) Exposure of long-buried masonry to the atmosphere initiates a new phase of physical deterioration. Prevent unnecessary exposure.
- (2) Particularly rapid deterioration is affective on such exposed walls when backfill is higher behind the exposed surface than in front of the surface. Attempts should be made to contour backfill surfaces to avoid change in the backfill levels on walls. Perhaps backfill levels could be designed to approximate pre-excavation levels in some sites.

C. Salt Action. Salts are endemic. The accumulations already exist and because the prime sources of salts are likely the intra-ruin debris and particulates from the air, little can be done to prevent or eliminate accumulations.

- (1) Elimination of moisture will greatly decrease the effect of salt action.
- (2) Buffers might be used to limit effects of chemical (salt) solutions on carbonate cements in the natural rock of masonry (Eh, pH control).
- (3) Complexing agents or added ionic mixes to form less soluble species with the most harmful substances might be possible. Such agents must be chosen carefully to avoid intense discolorations or other unsuspected effects. Masonry strengths could be increased by added insoluble salt. Permeability of backfill and plaza surfaces could be decreased if appropriate salts are found.
- (4) The addition of salt to ruins through cements, soil cements, or soil plasters used in repairs does not appear to be a serious source of damaging accumulations. Some white surface blooms may result, however. This could be moderated by testing water and soils to obtain supplies with the lowest possible salt content. Inexpensive tests can be made on a standard mix of soil in the water to be used (1 part solid to 10 parts water by weight). The analysis can be made as if it were a well-water test at any service organization such as the Soil and Water Testing Lab, University of Arizona (approximately \$5/sample).

#### IV. Further Investigative Work Relative to the Deterioration of Masonry.

A. The next logical steps to tie geological perceptions to possible engineering-chemical treatments are:

- (1) Initiate a detailed analysis of the most seriously deteriorating sites at Chaco Canyon and Mesa Verde. This analysis

would verify the salt species present, including halides; determine in field and lab the Eh, pH environments effective in deterioration at these sites; verify the lack of significant clay activity; and identify organic or other complexes that may complicate the environments.

- (2) The detailed geologic work should be coordinated with some basic geochemical considerations relating to possible work with salt control chemistry. This would involve some re-searching (through literature) of Eh, pH relationships between: carbonates-salts, carbonates-iron oxides, and iron oxides-salts. Also a survey of possible effects relative to nitrate complexes, organics, clay-salt relationships and the behavior of salt species in a changing temperature-moisture environment should be conducted.
- B. The above work could lead to possible tests with buffers, complexing agents, and insoluble compounds involving consultation with chemists/chemical engineers.
  - C. Immediate steps to improve drain design, wall capping and back-fill contours could be begun by NPS staff. This could well include immediate consideration of the water coursing that threatens several inscriptions on the point of Inscription Rock, El Morro.
  - D. A soil-water test program or individual efforts on the part of site staffs to choose the best possible (low salt) repair materials could begin. A dual purpose could be served by finding low shrink-swell clay content materials to avoid the cracking and scaling of repair mortar/plasters observed at several sites.

TABLE 1 - AZTEC MINERALOGY

<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
A-1A West Wall Room 218 (salts altered)	High permeability, very weak fizz-HCl (except on surface crusts). Gray-green coarse sandstone with white surface stains.	Qtz:53% + chalced factor (~55%) Fsp:32% Carbs:3/4% Kaol:<1% Epid:probable NO <sub>3</sub> ~1%, SO <sub>4</sub> present	Qtz:chalced 5:1 FeOs:minor Clays:minor Seric:present Lithic frags abundant Chlor-Epid:moderate
A-1B Room 218 (altered)	Similar to A-1A. Altered but no white salts visible.	Qtz:44% + chalced factor (~48%) Fsp:29% Carbs: 1/2% Kaol: ~2% Epid:probable NO <sub>3</sub> ~1%, SO <sub>4</sub> minor	Same as A-1A
A-1C Rubble pile (fresher equi- valent of above)	Similar to A-1A. No salts	Qtz:48% + chalced factor (~50%) Fsp:36% Carbs:1/2% Kaol:~1% Epid:probable NO <sub>3</sub> ~2%, SO <sub>4</sub> present	Same as above except lower FeOs and less Chlor-Epid
A-3 Just above floor in deteriorated covered Room #197	Low permeability, green siltstone. Dark-stained, deteriorated. No salts visible.	Qtz:41% + chalced (~45%) Fsp:20% Carbs: ~5% Epid:present Chlor:? NO <sub>3</sub> ~30%, SO <sub>4</sub> present	Qtz:chalced 4:1 FeOs:moderate Carbs:local remnants Lithic frags abundant Salt aggregates Chlor-Epid: abundant
A-4 Soil pile imported for repairs	Red silty clay	Carbs: 2.5% (mixed species) NO <sub>3</sub> minor ~1%, SO <sub>4</sub> notable	None

TABLE 1 - AZTEC MINERALOGY (Continued)

<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
A-5 Highly deteriorated zone in Kiva "V"	Moderate-low permeability. No fizz - HCl. Medium-grained green fissile sandstone. Crumbly, no salts visible.	Qtz:54% + chalced (~58%) Fsp:19% Carbs:1% Montm-type clay present Epid:present Chlor:probable NO <sub>3</sub> ~8%, SO <sub>4</sub> present	Qtz:chalced 4:1 Feos:minor-moderate Carbs:minor Green (Montm-Chlor) most abundant Lithic frags abundant
A-7 Soil from plaza - 6" below surface	Buff silty clay	Carbs: 3% NO <sub>3</sub> absent, SO <sub>4</sub> ~2%	None
A-D Soil-cement mortar	3/1 soil-cement	Carbs: 13% (dolo) NO <sub>3</sub> ~1%, SO <sub>4</sub> Minor	None
A-G "Fresh" rock from rubble stockpile	Low permeability. No fizz-HCl, green fissile siltstone.	Qtz: 58% + chalced Fsp: 15% Carbs: 3/4% Kaol:present Chlor:abundant Epid:probable NO <sub>3</sub> ~1%, SO <sub>4</sub> absent	Qtz:chalced (masked) Carbs:very low FeOs:low Very high green (Montm-Chlor) Epid:minor

NOTES: Nitrate activity probably important. Clay-chlorites, probably developed prior to construction, may participate in deterioration. Nitrates not necessarily visible as bloom. Total carbonate mobility not important at Aztec. FeOs may increase slightly in deteriorated zones. Gross differences in permeability, plus moisture and salts, are more important than Carb/FeO interaction.

TABLE 2 - BANDELIER MINERALOGY

<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
B-1 Soil from stockpile for mortar repairs.	Buff silty clay.	Carbs:1% NO <sub>3</sub> absent, SO <sub>4</sub> minor	None
B-2 Tuff from cliff above west end room Longhouse.	Soft gray welded tuff. High permeability. Low fizz HCl.	Qtz:(+chalced + devit glass) 28% + factor (~40%) Fsp:19% + devit glass Carbs:1/2% NO <sub>3</sub> minor, SO <sub>4</sub> absent	Glass with ~20% Qtz and Fsp phenos
B-3 Hardened face of cliff.	Case hardened reddish surface on tuff. Moderate permeability. No fizz HCl.	Qtz:(+ opalline SiO <sub>2</sub> ) 34% + factor (~50%) Fsp:47% Carbs:3/4% NO <sub>3</sub> absent, SO <sub>4</sub> absent	Same as B-2. Glass is reddish, somewhat clouded. Small spots of SiO <sub>2</sub> .
B-4 Altered tuff from beneath ground level Longhouse.	Soft, crumbly light gray tuff, white caliche coating. Moderate permeability. Moderate fizz HCl.	Qtz:(+ opalline SiO <sub>2</sub> ± devit glass) 30% + factor (~40%) Fsp:55% Carbs:1/2% NO <sub>3</sub> absent, SO <sub>4</sub> absent	None
B-5 Boulder, central Longhouse, below ground.	Soft, coved material, pinkish tuff. Moderate-high permeability. Moderate fizz, HCl, some caliche.	Qtz:(+ opalline SiO <sub>2</sub> ± devit glass) 18% + factor (~30%) Fsp:19% + devit glass Carbs:10% calc + dolo NO <sub>3</sub> ~30%, SO <sub>4</sub> absent	None
B-6 Rainbow House Kiva. Altered tuff with salts.	Hard dark gray tuff with white coatings. Low fizz, HCl. Low permeability.	Qtz:(+ opal-chalced) 32% + factor (~40%) Fsp:54% Carbs:1/2% NO <sub>3</sub> minor, SO <sub>4</sub> absent	Glass with 30% phenos. Glass is significantly clouded (largely devitrified) but very finely so.

TABLE 2 - BANDELIER MINERALOGY (Continued)

<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
B-8 Rainbow House. Altered tuff below soil.	White altered tuff. Moderate permeability. Low fizz, HCl.	Qtz:(+ opal-chalced + devit glass) 30% + factor (~40%) Fsp:39% Carbs:3/4% NO <sub>3</sub> ~2%, SO <sub>4</sub> minor	Glass with 25% phenos, somewhat clouded, reddish.

NOTES: Clays are minor. Devitrification produces Qtz + Fsp where effective. Carbonate mobility not important; may add strength to underground materials. Case hardening combines total devitrification with addition of opaline SiO<sub>2</sub> for impermeability and stability. Deterioration is apparently physical dissociation of larger glass and pumice fragments. The glass itself is still sound. Nitrate activity probably important.

TABLE 3 - CHACO CANYON MINERALOGY

	<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
C-1	Outcrop. Cliff above Pueblo del Arroyo.  — Outcrop	Moderate permeability strong fizz, HCl, buff-pink to red dish, medium-grained, soft sandstone.	None	Qtz + chalced predom no carb fragments. Feldspars and devit glass show seric + kaol; chlor-epid present. FeOs very heavy in reddish section. Lithic frags (volc and shale)
C-2(2)	Partially buried masonry block, Pueblo Alto. Dry-exposed tip of block.	High permeability, strong fizz, HCl, buff yellow, medium-grained sandstone, soft.	Qtz:50% chalced factor (~60%) Fsp:10% Carb:19% (dolo:calc 1:1) Kaol:~2% Seric:~2% NO <sub>3</sub> trace, SO <sub>4</sub> trace	Qtz:chalced 1:1 Carb as frags + some cement FeOs:moderate Chlor-Epid:minor Not all carbs rimmed by FeOs.
C-2(3)	Buried-moist portion of above.	Same as C-2(2). Softer exterior but harder in mass.	Qtz:50% + chalced factor (~60%) Fsp:10% Carb:26% (dolo:calc 2:1) Kaol:~3% Seric:~2% Epid:present NO <sub>3</sub> absent, SO <sub>4</sub> trace	Qtz:(same) New carbs not rimmed by FeOs. FeOs:moderate Chlor-Epid:minor
C-2(4)	Similar rock, completely buried.	Similar, yellow-green softest.	Qtz:52% + chalced factor (~65%) Fsp:13% Carb:9% (dolo:calc 4:1) Kaol:~2% Seric:~8% NO <sub>3</sub> trace, SO <sub>4</sub> trace	Qtz:(same) Chlor-Epid:very minor Sericitization evident. Less original carb than (2) and (3) above. FeOs:moderate (rim all carbs)

TABLE 3- CHACO CANYON MINERALOGY (Continued)

<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
C-3 Outcrop, cliff above Pueblo Bonito.	High permeability. Moderate fizz. Medium-grained soft sandstone, buff-pink.	Qtz:59% + chalced factor (~65%) Fsp:13% Carb:7% (dolo) Kaol:~4% Seric:~6% NO <sub>3</sub> absent, SO <sub>4</sub> present	Chalced:qtz 2:1 Shales and volc frags present FeOs:moderate Seric:present Chlor-Epid:present
C-4 South wall of large kiva, Pueblo del Arroyo.	Moderate-low permeability. Strong fizz, medium-grained moderately hard buff sandstone. Reddish plus white salts.	Qtz:26% + chalced factor (~35%) Fsp:23% Carb:36% (calc) Kaol:~2% Seric:~2% Epid:trace Chlor:trace NO <sub>3</sub> trace, SO <sub>4</sub> absent	Chalced:qtz 3:2 Carbonate as grains and matrix. Shale and volc frags abundant. FeOs:moderate-high Chlor-Epid:present
C-5 Deteriorated area, north wall, large kiva, Pueblo del Arroyo.	Low permeability, dense gray sandstone-limestone, hard. Strong fizz, HCl. Calcite crystals visible.	Qtz:45% + chalced factor (~55%) Fsp:11% Carb:40% (calc:dolo 6:1) Kaol:~5% Seric:? Epid:present NO <sub>3</sub> trace, SO <sub>4</sub> present	Carb present as grains and matrix. Chalced:qtz 1:2 Seric:present Chlor-Epid: significant FeOs:very minor
C-6 Deteriorated zone, Room 209, Pueblo Bonito.	High permeability, buff-orange medium-grained soft sandstone, strong fizz, HCl.	Qtz:69% + chalced factor (~75%) Fsp:12% Carb:3% Kaol:~3% NO <sub>3</sub> trace, SO <sub>4</sub> trace	Original carb low, that present is deteriorated, replaced by FeOs. Chalced:qtz 2:3 FeOs prominent on grain edges. Chlor-Epid:minor

TABLE 3 - CHACO CANYON MINERALOGY

	<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
C-7	Fresh equivalent of C-6 type deterioration, unnumbered room north of 116. Outside.	High permeability, buff, medium-grained soft sandstone, strong fizz, HCl.	Qtz:52% + chalced factor (~65%) Fsp:11% Carb:18% (dolo) Kaol:~2% Epid:trace NO <sub>3</sub> absent, SO <sub>4</sub> trace	Very similar to C-6 in texture. Less FeO. Carbonate grains fresh and coherent with moderate FeO edges. Chalced:qtz 2:3 Seric:very minor Chlor-Epid:minor
C-A	Soil cement taken from Pueblo Bonito	Soil cement clod at mixer.	Carb:~10% Mixed carb other than dolo-calc (dolo predom) NO <sub>3</sub> ~1%, SO <sub>4</sub> trace	None
C-B	Soil fill from plaza Pueblo Bonito.		Carb:~2% NO <sub>3</sub> ~1%, SO <sub>4</sub> trace	None

NOTES: Nitrates are generally in low concentration at Chaco Canyon. Carbs can be added in subsurface. FeOs replace and rim existing carbs; lower strength results. Dolomite-calcite transition not always in same direction. Clays, chlorite, epidote increases probably insignificant. Sericite (illite?) may form during deterioration. Transitions from high to low strength carbonates and iron-oxide interactions are critical.

TABLE 4 - MESA VERDE MINERALOGY

<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
M-2 Fresh float near Spruce Tree House.	High permeability, very low fizz, HCl. Fine sandstone.	Qtz:79% + chalced factor (~83%) Fsp:5% Carb:6% calc + dolo 1:1 Kaol:absent (Clays very minor) NO <sub>3</sub> absent, SO <sub>4</sub> present	Qtz:chalced 4:1 Carbs as frags, some as cement. FeOs:moderate (yellow) Green clays present Seric:present Lithic fragments
M-4 Farview House. Fairly fresh rock from Central. Kiva 9' above floor, east wall.	High permeability. Very low fizz, HCl. Buff to red, medium-grained sandstone (one end oxidized, other end fresh).	<u>Buff</u> Qtz:71% + chalced factor Fsp:6% Carb:2.5% (calc) Kaol:~2% Goethite:minor NO <sub>3</sub> absent, SO <sub>4</sub> present	None
		<u>Red (oxidized)</u> Qtz:~71% + chalced factor Fsp:5% Carb:1.5% Kaol:~2% Goethite:notable NO <sub>3</sub> absent, SO <sub>4</sub> present	None
M-5 Farview House, central kiva. Deteriorated zone south wall 3' above floor.	Moderately-low permeability. Strong fizz, HCl. Buff-pink fine sandstone, moderately hard.	Qtz:62% + chalced factor (~75%) Fsp:7% Carb: 1 1/2% dolo + calc Kaol:~3% Seric:probable Goethite:notable NO <sub>3</sub> ~3%, SO <sub>4</sub> present	Qtz:chalced 3:1 Carbs:none large FeOs:heavier than M-2 (reddish) Chlor:present + green clays Seric:more than M-2 Salts mixed with FeOs as intergrain fibrous aggregates

TABLE 4 - MESA VERDE MINERALOGY (Continued)

	<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
M-6	Same as M-5 Deteriorated	Low permeability. Weak fizz, HCl. Orange to dark red fine sandstone. Very soft, crumbly.	Qtz:74% + chalced factor (~78%) Fsp:7% Carb:1/2% Kaol:~2% Goethite:prominent NO <sub>3</sub> ~15%, SO <sub>4</sub> poss	Qtz:chalced 4:1 Carbs:very minor FeOs:mod-heavy (red) Seric:very minor Lithics minor Crystals in FeO masses, probably nitrates.
M-7	Rubble pile. Masonry excavated from site 820.	Low permeability. No fizz, HCl. Red, fine moderately hard sandstone.	Qtz:90% + chalced (~93%) Fsp:6% Carb:<1/2% Kaol:~2% NO <sub>3</sub> ~1%, SO <sub>4</sub> absent	Qtz:chalced 3:1 Carbs:not visible FeOs:moderate Seric:minor Lithics:minor Few xls in Feo masses.
M-8	Deteriorated zone in main kiva site 820.	(not determined) Red-orange fine sandstone, soft.	Qtz:90% + chalced (~91%) Carb:<1/2% Kaol:~1% Goethite:present NO <sub>3</sub> ~2%, SO <sub>4</sub> poss	Qtz:chalced 5:1 Carbs:not visible FeOs:moderate Green clays present Few xls in FeOs.
M-9	Fresh rock from out-crop near Sun Temple.	High permeability, strong fizz, HCl. Buff-orange fine	Qtz:85% + chalced (~87%) Fsp:5% Carb:7% dolo:calc 2:1 Kaol:~2% NO <sub>3</sub> ~1%, SO <sub>4</sub> poss	Qtz:chalced 4:1 Carbs:prominent grains and cement. FeOs:minor-mod (yellow) Chlor:minor Xls present in FeOs.

NOTES: Carbonates move out of fresh rock replaced by FeOs and salts. FeOs form intergrain masses with salts. (Red FeOs replace CO<sub>3</sub>.) Nitrate activity may be important. Clays not important. No sign of sericite increase with advanced deterioration.

TABLE 5 - EL MORRO MINERALOGY

	<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
EM-1A	Slabbing rock from moist covered zone at trail mark 1.	Moderate-high permeability, high fizz, buff fine-grained sandstone. Soft-crumbly. Altered.	Qtz:61% + chalced factor (~65%) Fsp:13% Carb:10% Kaol:minor Seric:minor NO <sub>3</sub> absent, SO <sub>4</sub> minor	Qtz:chalced 5:1 Lithic frags present FeOs:minor
EM-1B	Similar	Same as EM-1A. Fresher.	Qtz:60% + chalced factor (~63%) Fsp:8% Carb:1% Kaol:~4% Seric:~10%(?) + chlorite NO <sub>3</sub> absent, SO <sub>4</sub> minor	Qtz:chalced 5:1 Lithic frags present (contain the only visible sericite) Chlor:moderate FeOs:minor
EM-2	Similar	Same as EM-1A. Freshest.	Qtz:73% + chalced factor (~75%) Fsp:11% Carb:1% Kaol:2% Seric:minor NO <sub>3</sub> absent, SO <sub>4</sub> minor	Qtz:chalced 4:1 Less sericite than EM-1B Chlorite content similar Sericitization along grain boundaries FeOs:minor
EM-5	Below G. Ziska inscription.	Reddish harder crust forming within sandstone.	Qtz:80% + chalced factor (~85%) Fsp:10% Carb:1/2% Kaol:~3% Seric:minor NO <sub>3</sub> absent, SO <sub>4</sub> ~2%	No discernible difference from EM-2 No sericite on grain boundaries FeOs:minor

TABLE 5 - EL MORRO MINERALOGY

<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
EM-7 Intense deterioration below E. Pen Long.	Soft white crumbly medium-grained sandstone. Moderate permeability, no fizz.	Qtz:79% + chalced factor (~83%) Fsp:7% Carb:1/2% Kaol:~1% Seric:present NO <sub>3</sub> 1%, SO <sub>4</sub> ~4%	Little difference from above. Sericitization along grain boundaries.

NOTES: Trends not apparent for El Morro. Nitrates are minor. Carbonate mobility is not clear cut. Total cement is minor; rock susceptible to physical deterioration. (Percentages well under 100 percent for EM-1 and 2 suggests original opalline cement subject to alteration.)

TABLE 6 - WUPATKI MINERALOGY

<u>Location</u>	<u>Description</u>	<u>IR Mineral Analysis</u>	<u>Microscopic</u>
W-1A Altered base outcrop, Wupatki.	Moderate permeability, strong fizz. Red-buff fine sandstone.	Qtz:52% + chalced (~55%) Fsp:8% Carb:13% (dolo) Kaol:8% Seric:present NO <sub>3</sub> ~3%, SO <sub>4</sub> ~2%	Qtz:chalced 5:1 Lithic frags present Carb as cement is replaced in part by FeOs Qtz grains cloudy.
W-1B Same as W-1A; fresher.	Same as W-1A.	Qtz:60% + chalced (~63%) Fsp:7% Carb:13% (dolo + calc) Kaol:11% Seric:present NO <sub>3</sub> ~2%, SO <sub>4</sub> trace	Similar to above. Qtz grains clearer.
W-2A Soft. Masonry. Float.	Moderate permeability strong fizz, soft red-buff fine sandstone.	Qtz:66% + chalced (~68%) Fsp:7% Carb:15% (dolo + calc) Kaol:12% Seric:present NO <sub>3</sub> trace, SO <sub>4</sub> trace	Similar to above
W-2B Hard masonry float.	Low permeability. Same as above.	Qtz:37% + chalced (~40%) Fsp:7% Carb:40% (calc) Kaol:trace Epid:present NO <sub>3</sub> ~2%, SO <sub>4</sub> ~2%	Qtz replaced by calcite. Very little FeO. Chlor-Epid abundant.

NOTES: Dolomite increases during deterioration due to removal of more soluble calcite (except where calcite is added in subsurface as caliche). Removal of carbonate is major deterioration process possibly assisted by addition of FeOs at grain boundaries. Nitrates are fairly abundant.

TABLE 7 - CANYON de CHELLY MINERALOGY

Altered masonry sequence from  
to be high oxidation (color) and low moist strength.

room

"Alteration" considered

<u>Sample</u>	<u>Least Altered</u>		<u>Most Altered</u>
CDC-1	(A)	(B)	(C)
quartz	87%	77%	67%
feldspar	8%	9%	10%
clays	least	moderate	most (kaolinite present)
carbonates	absent	trace	3/4%
nitrates	trace	14%	12%
sulfates	2%	1%	trace
iron oxides	least	moderate	most

NOTES: Meaning is speculative due to lack of knowledge of original rock mineralogies. Quartz contents probably are pre-masonry. Feldspars could have been successively higher in original A to C, thus contributing clays. FeOs likely replacing higher original carbonates in C and B. Sulfate trend is likely coincidental. Deterioration mainly increase in FeOs at expense of carbs.

TABLE 8 - IR ANALYSES OF CONCENTRATED FINE-SIEVED PORTION OF SELECTED SAMPLES FOR CLAY-SALT CHARACTERIZATION

<u>Sample</u>	<u>Location</u>	<u>IR Analysis</u>
A-1A	West wall, Room 218 Aztec sandstone.	Clays minor. Kaolinite definitely present. Epidote, chlorite and goethite concentrate in fines. Carbonate increases somewhat. Unidentified hydrous salt concentrates (perhaps similar to hydromagnesite in structure). Bicarbonate present.
A-5	Highly deteriorated zone, Kiva "V", Aztec, sandstone.	Clays minor. Kaolinite, epidote, chlorite present. Carbs decrease in fines. Nitrates greatly increase. Unidentified hydrous salt increased as in A-1A. Some bicarbonate present.
B-2	Tuff from cliff, west end Longhouse Bandelier.	Clays very minor. Trace kaolinite, no smectites evident. Nitrates concentrate - apparently in hydrated form. Carbonates slightly concentrated, trace sulfate appears. Mainly siliceous glass. Probable bicarbonate.
B-6	Rainbow House Kiva, altered tuff with surface salts, Bandelier.	Clays very minor. Some kaolinite, no smectites. Nitrates and carbonates greatly concentrated. Carbonates are mixed species. Different hydrated species than in those samples above is predominant (strong IR absorption at 3300 band). Many possible hydrous sulfates (Boehmite possible; AlOOH).
C-2(2)	Exposed tip of partially buried sandstone block Pueblo Alto, Chaco Canyon.	Kaolinite and sericite concentrate x5. Smectites possible. Epidote, chlorite, goethite present. Carbonates very high as calcite-dolomite mix. NO <sub>3</sub> very minor. SO <sub>4</sub> minor.
C-2(3)	Buried portion.	Higher kaolinite, less sericite. Otherwise same as above.
C-2(4)	Deeper, similar rock.	More sericite, otherwise same as above.
C-4	South wall large kiva, deteriorated zone, hard rock. Pueblo del Arroyo, Chaco Canyon.	Kaolinite sericite minor. Calcite very high. Epidote present, minor smectite possible. SO <sub>4</sub> , NO <sub>3</sub> minor.
M-2	Fresh float, Mesa Verde	Clays significant. Kaolinite dominates, sericite present, smectite possible. Epidote-chlorite present. Goethite minor. Dolomite very high, trace NO <sub>3</sub> and SO <sub>4</sub> (bulk analysis suggests smectite).

TABLE 8 - (Continued)

<u>Sample</u>	<u>Location</u>	<u>IR Analysis</u>
M-6	Orange crumbly rock, Farview House, central kiva.	Clays minor to significant, kaolinite, sericite, and possible smectite. Nitrate very high. Smectite not suggested in bulk analysis. $SO_4$ minor.
EM-1	Altered cliff base, El Morro.	Clay significant, kaolinite with possible sericite and smectite. Unidentified hydrous phase (chlorite or hydrous salt, band at 3590). Carbonate (calcite + Na-carb) very concentrated. $NO_3$ absent, $SO_4$ minor.
EM-9	Shiny alteration surface on cliff, El Morro.	Higher kaolinite, low carbonate. $NO_3$ very minor, $SO_4$ minor.
W-2B	Hard masonry float, Wupatki.	Clay minor-moderate. Kaolinite sericite mix. Minor smectite likely. Chlorite-epidote present $NO_3$ and $SO_4$ minor. Calcite very high.
CDC-1A	Least altered of deteriorated rock sequence, Canyon de Chelly.	Clays very minor, carbonates minor, trace of $NO_3$ and $SO_4$ . Goethite present, epidote and chlorite minor.
CDC-1C	Most altered.	Kaolinite and sericite plus epidote-chlorite. Bicarbonate, goethite present. $NO_3$ quite high, $SO_4$ present.
NOTES:	Clays are generally minor in the bulk rock of masonry and likely do not participate significantly in or form during deterioration. Smectites and other expansive clays are lacking or present in very small quantity. Possible exceptions: Chaco Canyon (slight possibility) Mesa Verde (possibly present, pre-masonry) Wupatki (present, pre-masonry) Canyon de Chelly (kaolinite and sericite may increase during masonry deterioration)	

Nitrates tend to be present within the masonry while sulfates tend to form surface bloom. Carbonates and bicarbonates are present within and as blooms on the rock masonry. Glasses (Bandelier) devitrify under alteration to quartz and feldspar. Clays do not form significantly at Bandelier.

TABLE 9 - IR ANALYSES OF SELECTED SURFACE SALTS

<u>Sample</u>	<u>Location</u>	<u>IR Analysis</u>
A-1A	East-facing wall, open Room 218, Aztec. White salt bloom on sandstone.	<p>Complex hydrous salts showing high <math>\text{SO}_4</math>, high to moderate <math>\text{NO}_3</math> and moderate to unidentifiable species with high hydration levels.</p> <p>Upon drying <math>\text{SO}_4</math>s approach syngenite (<math>\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}</math> or mirabilite, <math>\text{Na}_2(\text{SO}_4) \cdot 10\text{H}_2\text{O}</math> type structures. <math>\text{NO}_3</math> reverts to simple <math>\text{KNO}_3</math> or <math>\text{NaNO}_3</math> type structure. <math>\text{CO}_3</math> are likely calcite plus <math>\text{NaCO}_3</math>. (Possible darapskite <math>\text{Na}_3(\text{NO}_3)\text{SO}_4 \cdot \text{H}_2\text{O}</math>).</p> <p>Bulk sandstone A-1A showed 3/4T carbonates, approximately 1% nitrates and &lt;1% sulfates.</p> <p>Soluble salt analysis shows abundant Ca, Na, <math>\text{SO}_4</math>, <math>\text{HCO}_3</math>, <math>\text{NO}_3</math> is low indicating loss to analysis due to organic nature or complexing. <sup>3</sup> K not run.</p>
A-2	Enclosed, buried Room 12. Fibrous-furry white salt bloom.	<p>Highly hydrous mix again high <math>\text{SO}_4</math> with lower complex <math>\text{NO}_3</math> and <math>\text{CO}_3</math>.</p> <p>Upon drying <math>\text{SO}_4</math> does not change significantly. Nitrates apparently dehydrate to simple <math>\text{KNO}_3</math> or <math>\text{NaNO}_3</math> structure. <math>\text{CO}_3</math> present mainly as <math>\text{NaCO}_3</math>. Sulfates remain a complex mineralogy or mixture.</p> <p>Bulk sample of salts plus clay contamination showed moderate <math>\text{CO}_3</math> but minor <math>\text{NO}_3</math> and <math>\text{SO}_4</math>. Minerals were apparently complex and poorly developed in spite of fibrous form.</p> <p>Soluble salt analysis shows abundant Ca, Na, <math>\text{SO}_4</math>, <math>\text{HCO}_3</math>. Moderate Cl, <math>\text{NO}_3</math> with minor mg K not run.</p>
C-4	North-facing wall of large kiva, Pueblo del Arroyo, Chaco Canyon. White powdery salt bloom.	<p>Very similar to A-1A except higher <math>\text{NO}_3</math> and carbonate relative to <math>\text{SO}_4</math> mineralogy.</p> <p>Upon drying - same as A-1A - <math>\text{CO}_3</math> as calcite and <math>\text{NaCO}_3</math>.</p> <p>Bulk sandstone C-4 shows very high carbonate as calcite but undetectable <math>\text{SO}_4</math> or <math>\text{NO}_3</math> mineralogy.</p> <p>Soluble salt analysis.</p>

TABLE 9 - IR ANALYSES OF SELECTED SURFACE SALTS (Continued)

<u>Sample</u>	<u>Location</u>	<u>IR Analysis</u>
B-5	Partially buried boulder, central Longhouse area, Bandelier. White crusts and powdery bloom.	Essentially calcium carbonate with moderate $\text{NaCO}_3\text{s}$ in hydrated states. Also minor $\text{SO}_4$ mineralogy is present.  Upon drying hydration levels greatly reduced, possibly in hydrated glasses as well as salts.  Bulk tuff sample B-5 showed extremely high nitrate (not appearing as surface salt bloom). Carbonates were very high and $\text{SO}_4$ undetected.  Soluble salt analysis.
B-6	Large kiva, Rainbow House. Salt bloom from deteriorated tuff.	Again, salt mix similar to A-1A and C-4, with higher $\text{SO}_4$ relative to $\text{CO}_3$ and $\text{NO}_3$ . Nitrate partially complex, partially present as simple $\text{KNO}_3$ - $\text{NaNO}_3$ structure. High levels of hydration exist.  Upon drying. More $\text{NO}_3$ reverts to simple structure, $\text{SO}_4\text{s}$ revert as in A-1A. Possible hydrous $\text{NO}_3$ - $\text{SO}_4$ salt such as Darapskite.  Bulk tuff Sample B-6. Low salt content. $\text{CO}_3$ 3/4%, $\text{NO}_3$ <1%, $\text{SO}_4$ undetectable.

NOTES: Nitrates less abundant as surface salts, likely to appear within mass of rock. Often in most deteriorated rocks. Sulfates, nitrates, and carbonates present as hydrated forms which change with drying either naturally (different species in covered rooms) or in lab (48 hours at  $110^\circ$  in vacuum). Volume changes with hydration-dehydration should be an effective tool for deterioration in seasonally moist zones. Various hydration states of similar salts are apparent. Salts from different sites are remarkably similar, suggesting common mineralogy perhaps as complex K-Na-Ca-Mg sulfate\_nitrate-carbonate minerals in various hydration states. Changing ratios of constituents more strongly suggest mixtures of simple or complex salts. Salts are likely to be of organic origin to some degree. (Human animal excrement and remains). Nitrate-rich samples showed lowest pHs (though still slightly alkaline).  $\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  type species (associated with high expansions) are present.

TABLE 10 - SOLUBLE SALT ANALYSES (1 part rock or soil in 20 parts H<sub>2</sub>O by weight)

<u>Sample</u>	<u>Description</u>	ppm <u>(Analyzed)</u>	ppm <u>(From EC)</u>	<u>pH<sub>a</sub></u>	<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>	<u>Cl</u>	<u>SO<sub>4</sub></u>	<u>HCO<sub>3</sub></u>	<u>NO<sub>3</sub></u>	<u>NOTE</u>
(AZTEC)													
A-1A	S. Stone + Salts	100	150	7.7	15	0	16	X	3	26	37	1	*(N)
A-1B	S. Stone No Salts	300	500	7.5	15	2	103	X	84	60	32	7	*(N)
A-2	Fibrous Salts	1000	1200	7.9	8	2	300	X	240	600	34	7	*(N)
A-3	Green Siltstone	530	1300	7.6	120	27	160	X	130	48	27	18	** (N+)
A-4	Repair Soil	90	80	7.9	21	2	4	X	8	9	49	1	*(N)
A-7	Plaza Soil	90	50	7.9	19	0	4	X	3	9	59	1	*
(BANDELIER)													
B-1	Repair Soil	75	40	7.4	7	1	4	13	12	14	27	0.1	*
B-2	Tuff, Cliff	270	370	7.2	57	2	42	13	13	92	54	4	
B-5	Below Ground	300	530	7.4	67	13	28	35	40	23	49	40	(N+)
B-6	Altered Salts	1700	2300	7.7	79	4	230	360	120	790	39	41	*
(CHACO CANYON)													
C-A	Soil Cement	350	410	9.1 <sup>b</sup>	83	0	87	20	28	87	49 <sup>c</sup>	0.2	*
C-B	Plaza Soil	110	110	7.9	18	1	3	16	12	23	49	0.2	*(N)
C-3	Outcrop, Cliff	75	100	8.0	12	1	2	15	12	15	54	1	*
C-4	Red + Salts	1900	1900	7.9	44	4	450	18	96	780	44	28	*(N)
(MESA VERDE)													
M-8	Red (Site 820)	560	1050	7.4	140	51	58	X	92	190	24	15	(N)
M-9	Outcrop (Sun T.)	70	80	7.8	16	0	2	X	4	11	39	1	*(N)

NOTES: (Table 10 - Continued)

- (a) Recall that this table is for 1:20 dilutions pH figures are not comparable even proportionately to those expected in the ruins.
- (b) Unusually high pH was for soil portland cement mix.
- (c) Significant  $\text{CO}_3$  also present in this soil-cement mix.
- X "K" analysis not run for these samples.
- \* Ion imbalance in analysis - cations deficient. (K analysis will correct this for some samples.)
- \*\* Ion imbalance - anions deficient.
- (N) Notable nitrate present in IR-mineral analysis, not shown here.
- (N+) Very high nitrate in mineral analysis, (<10%  $\text{NO}_3$ ) not showing here.

Note especially gross imbalances in analyzed ppm as compared  $\text{EC} \times 10^3$  (x750) which is an approximate check.

Soluble Fe and  $\text{PO}_4$  are generally low.

Halides (represented by Cl which may be present in complex salts rather than as halide) are nowhere the prominent salt but could be present in significant quantities in deteriorated zones. Halides are not detectable by IR analysis.

Nitrates are not responding to soluble salt analysis and nitrate complexing may account for some of the analytic discrepancies.

Low pH may correspond with certain nitrate chemistries.

$\text{CO}_3$  is generally absent and  $\text{HCO}_3$  is quite consistent suggesting some buffering.

Visible salt blooms are predominantly  $\text{SO}_4$ .

Sulfates are not showing in soluble salt analysis in quantities indicated in IR mineral analyses, but discrepancies are less than for nitrates.