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# EFFECTS OF FREEZING ON COLLOIDAL HALLOYSITE: IMPLICATIONS FOR TEMPERATE SOILS

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**Abstract**—The literature reports that freezing of aqueous aluminosilicate clay suspensions can produce clay aggregates that disperse with agitation. Our experiments indicate that colloidal suspensions extracted from north Idaho loess soils (Boralfs), when frozen, form silt- and sand-sized agglomerates that resist dispersion with agitation. XRD and TEM analyses showed that colloids are dominantly halloysite between 0.10 to 0.30 $\mu$m in diameter. The colloidal halloysite has anomalously high mole ratios of Si/Al and a high Fe content. Freeze-produced agglomerates are light yellow to yellowish-brown in color, occur in the form of plates, wedges, cuspates, or laths, and often exhibit uniform optical properties, suggesting a crystalline product. Selected area electron diffraction, however, indicates that the agglomerates are polycrystalline. With proper orientation, agglomerates produce acute bisectrix interference figures that are optically negative with variable 2V, generally <30°. XRD analyses and IR spectra imply that the agglomerates are halloysite. Measured optical properties, however, are different than those reported for halloysite and may be affected by the high Fe content and polycrystalline nature of the agglomerates. Grains, exhibiting similar optical properties as laboratory-produced agglomerates, are a minor proportion of the very-fine sand fraction in some horizons of the soils studied. Freeze-aided agglomeration of colloidal material may be an important process in temperate climates. It may be overlooked because of particle destruction by soil pretreatments or morphological order and/or optical similarity to some micaceous minerals.

**Key Words**—Fragipan, Idaho, Loess, Tephra, Transmission electron microscopy, X-ray diffraction.

## INTRODUCTION

Freezing of clays has been reported to produce rapid changes in the physical appearance and physiochemical properties of clay. Results have varied depending on the rate of freezing, the clay : water ratio, the type of clay mineral, and the electrolyte chemistry and concentration. Generally, freezing leads to aggregation of clay, removal of some interlayer water of expanding-lattice clays, and particular microstructural rearrangements of clays (Ahlrichs and White, 1962; Lincoln and Tettenhorst, 1971; Rowell and Dillon, 1972; Saunders *et al.*, 1986). Freeze-aided changes in clays appear nonpermanent and can be reversed by agitation (Lincoln and Tettenhorst, 1971).

In the course of investigations into the causes of strength and brittleness of north Idaho fragipan soils, clay colloid suspensions were stored in a refrigerator prior to analyses. Some colloid suspensions were inadvertently frozen. Thawed suspensions contained large agglomerates. In contrast to literature reports of freeze-produced aggregates, our agglomerates resisted dispersion and appeared as distinct "crystals" with measurable optical properties. This paper reports on the results of controlled experimentation of this phenomenon and speculates on its potential importance in the pedogenesis of temperate soils.

## MATERIALS AND METHODS

### *The study area and soils*

Soils used in this study were collected in north Idaho along the western foot slopes of the Bitteroot Mountains near the Clearwater Valley. At present, the soils have a mesic to udic moisture regime and a frigid temperature regime. The native vegetation is forest, dominated by Douglas fir (*Pseudotsuga menziesii*) and Grand fir (*Abies grandis*). A portion of the forest has been converted to pasture and cropland. Parent material consists of a veneer of Mazama tephra (6800 ± 100 y.b.p.) overlying loess. The loess ranges in age from Holocene to mid-Wisconsinan, and possibly older (Busacca, 1989)—many soil profiles show a sequence of loess paleosols. Residual soils, developed chiefly in schist or granite, underlie the loess. A total of 8 soil pedons were described and sampled (Tables 1, 2).

### *Laboratory procedures*

Field-collected soil material was air-dried in the laboratory. No pretreatment, such as organic matter removal or dispersant, was used before extraction of colloidal clays. Two methods were used to extract colloidal material from all horizons of all pedons: 1) immiscible displacement (Mubarek and Olsen, 1976), and 2) cen-

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Table 1. Classification and horizonation of the sampled pedons.

| Soil series | Classification | Horizonation[1] |
|---|---|---|
| Helmer Taxadjunct | Fine-silty, mixed, Andic Fragiboralf | Oi–Oe–A–Bs1–Bs2–2BE–2E/Btx–2Btx–2Bt1–2Bt2<br>+4 +3 5 13 25 38 58 91 140 170 |
| Kauder #1 | Fine-silty, mixed, Andic Fragiboralf | A–Bs1–Bs2–2E–2BE–3BEx–3Btx–4Btx1–4Btx2–4Btx3<br>3 10 30 51 79 99 117 152 188 234 |
| Kauder #2 | | Oi–A–Bsc–2EB–2BE–2Btx1–2Btx2–3Cr1–3Cr2<br>+5 4 38 64 86 124 160 191 236 |
| Tank Creek Variant | Fine-loamy, mixed, Andic Glossoboralf | Oi–Oe–A–Bs1–Bs2–2Ab–2Eb–2Btb–2BCb–3Eb–3Btb–3BC<br>+4 +3 3 13 33 51 59 86 105 127 150 175 |
| Grangemont | Fine-silty, mixed, Andix Fragiboralf | Oi–A–Bs–2BE–2BEx–2Beb–2Btxb–3BEb–3Btb<br>+7 10 28 48 69 89 145 173 234 |
| Grangemont Variant | Fine-silty, mixed, Andic Fragiboralf | Oi–A–Bs–2EB–2BE–2BEx–3Btx–3Btb1–3Btb2<br>+5 13 33 64 114 130 163 218 254 |
| Reggear #1 | Fine-silty, mixed, Typic Fragiboralf | Oi–A–Bw–2E–2BE–2Btx1–2Btx2–3Btx<br>+1315 28 51 74 99 147 213 |
| Reggear #2 | | Oi–A–2Bw–2BE–2E/B–2B/E–2Btcx–3Btxb–3Btb1–3Btb2–3C<br>+5 8 23 41 51 81 117 135 175 185 201 |

[1] Numbers beneath horizons correspond to depth in cm; for O horizons, the upper boundaries are given; for mineral horizons, the lower boundary is given. The Helmer taxadjunct, Kauder, Tank Creek Variant, Grangemont Variant, and Grangemont Variant soils all have surface additions of Mazama tephra which make up a large proportion of the A and Bs horizons. The Reggear soils have only a minor proportion of Mazama tephra in surface horizons. Horizons below tephra veneer formed predominantly in loess. For definitions of horizon nomenclature see Soil Survey Staff (1990).

trifugation of a water-soil slurry. These methods were chosen to separate colloids without any soil pretreatment, and each would tend to separate selectively those colloids with a strong affinity for water (small, non-aggregated colloids). For immiscible displacement, 20–25 g of soil material was placed in 50 ml polypropylene centrifuge tubes. Deionized water was added, with mixing, until the soil was slightly undersaturated. After an equilibration period of two days, 5 ml of $CCl_4$ was placed on the wet soil. The tubes were then centrifuged at approximately 1500 g for 30 min. The displaced water was carefully removed with a micropipette and saved for later analyses. Four to 8 replicates were needed to obtain enough sample for analyses. In the second method, a 1:2 soil/deionized water slurry was mixed, allowed to equilibrate for several hours, and then placed in 50 ml polypropylene centrifuge tubes. The tubes were centrifuged at approximately 1500 g for 10 min. The liquid was decanted into a second tube and centrifuged at 1500 g for another 10 min. These steps were continued until the coloration and optical density of the solutions were similar to those obtained by immiscible displacement. This usually required 3–4 separate centrifugations.

The elemental composition of the immiscibly-displaced extracts was evaluated by atomic absorption spectroscopy. Nitrous oxide was used as the oxidant for Si and Al determinations. The absorbed light was read high in the flame to assure as complete an atomization of colloidal material as possible.

Table 2. General characteristics of typical fragipan-containing pedons from north Idaho; Helmer taxadjunct series (fine-silty, mixed, Andic Fragiboralf).[1]

| Horizon | Texture | Moist color | Clay mineralogy[2] | Clay | Organic carbon | Dithionite Fe | Dithionite Al |
|---|---|---|---|---|---|---|---|
| | | | | g kg$^{-1}$ | | | |
| A | SiL | 10YR 3/4 | Vermiculite/halloysite/mica | 90 | 42 | 16 | 6 |
| Bs1 | SiL | 10YR 4/3 | Vermiculite/halloysite/mica | 72 | 17 | 16 | 5 |
| Bs2 | SiL | 10YR 4/4 | Vermiculite/halloysite/mica | 54 | 13 | 17 | 5 |
| 2BE | SiL | 10YR 5/4 | Halloysite/mica/verm-mica[3] | 132 | 3 | 14 | 1 |
| 2E/B | SiL | 10YR 5/3 & 5/4 | | 219 | 2 | 18 | 2 |
| 2Btx | SiCL | 7.5YR 4/4 | Halloysite/mica/verm-mica | 311 | 2 | 23 | 2 |
| 2Bt1 | SiCL | 7.5YR 4/4 | | 354 | 2 | 27 | 3 |
| 2Bt2 | SiCL | 7.5YR 4/4 | Halloysite/mica/verm-mica | 384 | 2 | 29 | 3 |

[1] The A, Bs1, and Bs2 horizons formed in Mazama tephra; the lower horizons formed in loess. Analyses performed at National Soil Survey Laboratory, Lincoln, Nebraska.

[2] Less than 2-$\mu$m fraction of long-range ordered minerals in descending order of abundance.

[3] Interstratified vermiculite-mica.

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Colloids were examined with the transmission electron microscope (TEM) and by X-ray diffraction (XRD). For TEM analysis, a drop of the immiscibly-displaced extract was placed on a carbon-coated, Formvar-covered grid and examined with a Zeiss EM-10 electron microscope at an accelerating voltage of 80 kV. An anticontamination device filled with liquid $N_2$ was used at all times. Instrument brightness was kept at a minimum and was increased only to take photomicrographs. Photomicrographs were taken as quickly as possible to avoid surface contamination or distortion of the colloids. Electron diffraction of the colloids was also undertaken. Colloids were flocculated with a $MgCl_2$ solution for X-ray analysis. Separate subsamples were treated with $Mg^{2+}$ and $K^+$ to saturate the exchange complex (Whittig and Allardice, 1986). Another subsample was left untreated. The treatments were oriented by sedimention on glass slides. We also experimented with filtration to concentrate the samples for XRD. Samples were filtered through 0.22 $\mu$m membrane filters until clogged (only fair orientation), allowed to dry, and then taped to glass slides for XRD (no solvating cations were used). The prepared material was examined with a Philips diffractometer using CuK$\alpha$ radiation. Instrument conditions were: automatic divergence slit, graphite monochromator, 0.2 mm receiving slit, scintillation counting, $2°2\theta$ $min^{-1}$ scan rate.

One subsample set of the colloidal extracts was placed in a 2°C refrigerator, the other was placed in a freezer at −10°C. Both sets were examined periodically for the formation of clay agglomerates. Additional subsamples were subjected to several freezing and thawing cycles and the products examined.

Products formed under freezing conditions were characterized using several methods. Standard optical mineralogy procedures were used to study the agglomerates (Stoiber and Morse, 1981; Phillips and Griffen, 1981). For XRD, agglomerates were ground as a propanol slurry for approximately 1 min in an agate crucible. The slurry was either sedimented on a glass slide and dried before XRD (oriented), or dried and the dried powder was sprinkled on a NaF internal standard in a sample template (random orientation). X-ray conditions were as stated above. For infrared spectroscopy, agglomerates were mixed with KBr, pelletized, and examined with an FT-IR. The resultant spectra were corrected for background with a pure KBr pellet.

Elemental composition of the agglomerates was determined by two methods: 1) A HF digestion method and atomic absorption spectroscopy (Buckley and Cranston, 1970) were used to determine elemental content of bulk samples of the agglomerates, and 2) specific agglomerates that exhibited optical continuity across the entire grain were mounted on aluminum stubs and examined with a scanning electron microscope equipped with an energy-dispersive wavelength X-ray analyzer. Elements in the agglomerates were quantified by comparison to mineral standards. Freeze-produced agglomerates were examined with a Philips CM-10 electron microscope with electron diffraction capabilities. Specimens were placed on a carbon-coated, Formvar-covered grid. The accelerating voltage was 100 kV.

To determine if freeze-produced agglomerates occurred in the pedons studied, untreated material from selected loess horizons (assumed to be periodically frozen) was wet-sieved. The very-fine sand fraction was examined with a petrographic microscope using optical methods as detailed above. Heavy liquid separation techniques (Jackson, 1956) were used to concentrate suspected freeze-produced agglomerates for XRD. The very fine sand fraction was placed in nitrobenzene (s.g. = 1.20) and incremental additions of tetrabromoethane (s.g. = 2.97) were added until particles began to float. Floating particles were examined with a petrographic microscope to determine if they matched optically the agglomerates formed in the laboratory. Density separates, in which suspected freeze-produced agglomerates were concentrated, were ground as an ethanol slurry, sedimented on a glass slide, and examined by XRD under the conditions stated above.

## RESULTS

### *The colloidal starting materials*

Colloidal solutions extracted by either immiscible displacement or centrifugation of soil-water slurries were generally yellow in color. The Tyndall effect was minimal in most extracts, which first suggested that the coloration was due to some organic chromophore instead of a colloidal substance. Variation in the levels of immiscibly-displaced Si, Al, Fe, and K, among horizons was evident (Table 3). Tephra-rich horizons had lower levels of Si, Al, Fe, higher levels of K, and higher Si/Al and Si/Fe mole ratios than loess-rich horizons. Coloration of the colloidal extracts varied among horizons. The tephra-rich horizons were very light yellow to clear, eluvial and mixed eluvial-illuvial horizons were mostly deep yellow in color with a minimal Tyndall effect, and lower argillic horizons were either very light yellow or strong yellow with a distinct Tyndall effect. The intensity of coloration manifested itself in solution levels of Si and Al and the mole ratio of Si/Al (Table 3).

Transmission electron microscope observation of immiscibly-displaced extracts showed differences in colloid morphology among parent materials. Colloids extracted from tephra-rich horizons consisted of linked spheroids that shrank when instrument brightness was increased (Figure 1A). Initially, we believed the material was a contaminant, but it was only seen in extracts of the tephra horizons. The morphology of the material is similar to that of allophane (Henmi and Wada, 1976). However, large groups of the material produced an electron diffraction pattern that displayed

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Table 3. Relationship of immiscibly-displaced mean levels of Si, Al, Fe, and K and mole ratios of Si/Al and Si/Fe to horizon classification and colloidal solution color.

| Category | Number of samples | Si | Al | Fe | K | Mole ratio Si/Al | Mole ratio Si/Fe |
|---|---|---|---|---|---|---|---|
| | mM $m^{-3}$ | | | | | | |
| | Horizon classification[1] | | | | | | |
| Tephra | 3 | 230 | 52 | 14 | 150 | 4.4 | 16.4 |
| Eluvial/illuvial | 9 | 1487 | 852 | 230 | 90 | 1.7 | 6.5 |
| Underlying | 11 | 1963 | 1093 | 288 | 60 | 1.8 | 6.8 |
| | Soil solution color | | | | | | |
| Clear | 10 | 1540 | 710 | 190 | 80 | 2.2 | 8.1 |
| Slightly yellow | 5 | 810 | 540 | 150 | 70 | 1.5 | 5.4 |
| Yellow | 8 | 2370 | 1460 | 250 | 100 | 1.6 | 9.5 |

[1] Eluvial/illuvial horizons refer to E horizons or mixed E/Bt horizons. Underlying horizons are those illuvial horizons beneath the E/Bt horizons.

more rings than have been reported for allophane (Wada and Yoshinaga, 1969). Colloids extracted from loess horizons were comprised of subhedral tabular forms and spheroids that ranged in diameter from 0.10 to 0.30 μm (Figure 1B). Both tabular (Kunze and Bradley, 1964) and spherical forms (Sudo and Takahashi, 1956) of halloysite have been reported.

X-ray diffraction of air-dried colloidal material displayed broad reflections at approximately 7.5, 4.45, and 3.75 Å (Figure 2A) that did not change appreciably with different solvating cations (data not shown). Heating the colloids to 150°C for 30 min caused a decrease in the spacings to 7.3 and 3.57 Å (Figures 2A,B). Heating also reduced the intensity of the 4.45 Å reflection and intensified the 7.3 and 3.57 Å refections (Figure 2B). The equality in intensity of the 4.45 and 7.5 Å reflections in air-dried samples, the fact that heating decreased the 4.45 Å reflection, and the morphology of the colloids all indicate that the dominant mineral in the colloid extracts is dehydrated halloysite or metahalloysite (Dixon, 1989). Minute levels of vermiculite were found in some samples (data not shown).

*The end products of freezing*

Colloidal material kept at 2°C did not form agglomerates or products that could be resolved with the light microscope, even after two months. Frozen colloidal solutions, however, reacted to produce agglomerates. Agglomerates formed as quickly as it took the samples to freeze (about 2 hours), and occurred in a central core within the 50 ml centrifuge tubes. Observed with a binocular microscope, the agglomerates formed a dendritic pattern radiating from the cylindrical core, with air bubbles often defining the path. Lincoln and Tettenhorst (1971) have described a similar phenomenon.

When the aggregated products were thawed, a disjunct property was noticed. Tephra-rich horizons did not produce agglomerates large enough to be resolved with the light microscope. Indeed, with agitation, the agglomerates dispersed and the solution resembled the original unfrozen starting mixture. The frozen loess-rich colloidal solutions, on the other hand, all produced large agglomerates. Moreover, with repeated freezing and thawing, agglomerate size generally increased. The largest agglomerates were silt- and sand-sized and were stable. They resisted dispersion during intense agitation, a characteristic that has not, to our knowledge, been reported in the literature. Although we did not quantify them, it was apparent that frozen extracts from mixed eluvial and illuvial horizons produced the greatest aggregate yields.

When observed with a petrographic microscope, many agglomerates had uniform optical properties over the entire grain boundary. For this reason, they were suspected as being single crystals. Agglomerates occurred in wedge, lath-like, cuspate, and platy forms that were yellow, yellowish-brown or reddish-brown in color, or colorless (Figures 3A,B). Size was variable. The largest agglomerates were over 100 μm in diameter, and the smallest were at the limits of resolution of the light microscope. Platy forms, because of their orientation, showed low birefringence (first-order gray) and generally remained extinct during complete rotation of the microscope stage. Lath-like forms had a birefringence corresponding to first-order gray-to-yellow. Wedge-shaped and cuspate forms, however, exhibited second- and third-order interference colors. Most forms displayed an undulose to wavy extinction. Many agglomerates consisted of smaller optically-uniform units fused together, akin to polycrystalline quartz (Figure 3C). In randomly-oriented specimens, the lowest refractive index was between 1.568 and 1.570, and the highest refractive index was between 1.592 and 1.594. Lath-like forms were length-slow. Platy forms and wedge-like forms displayed an acute bisectrix figure that was biaxial negative with a small and variable 2V, always less than 30°.

Agglomerates slowly degraded when treated with 30%

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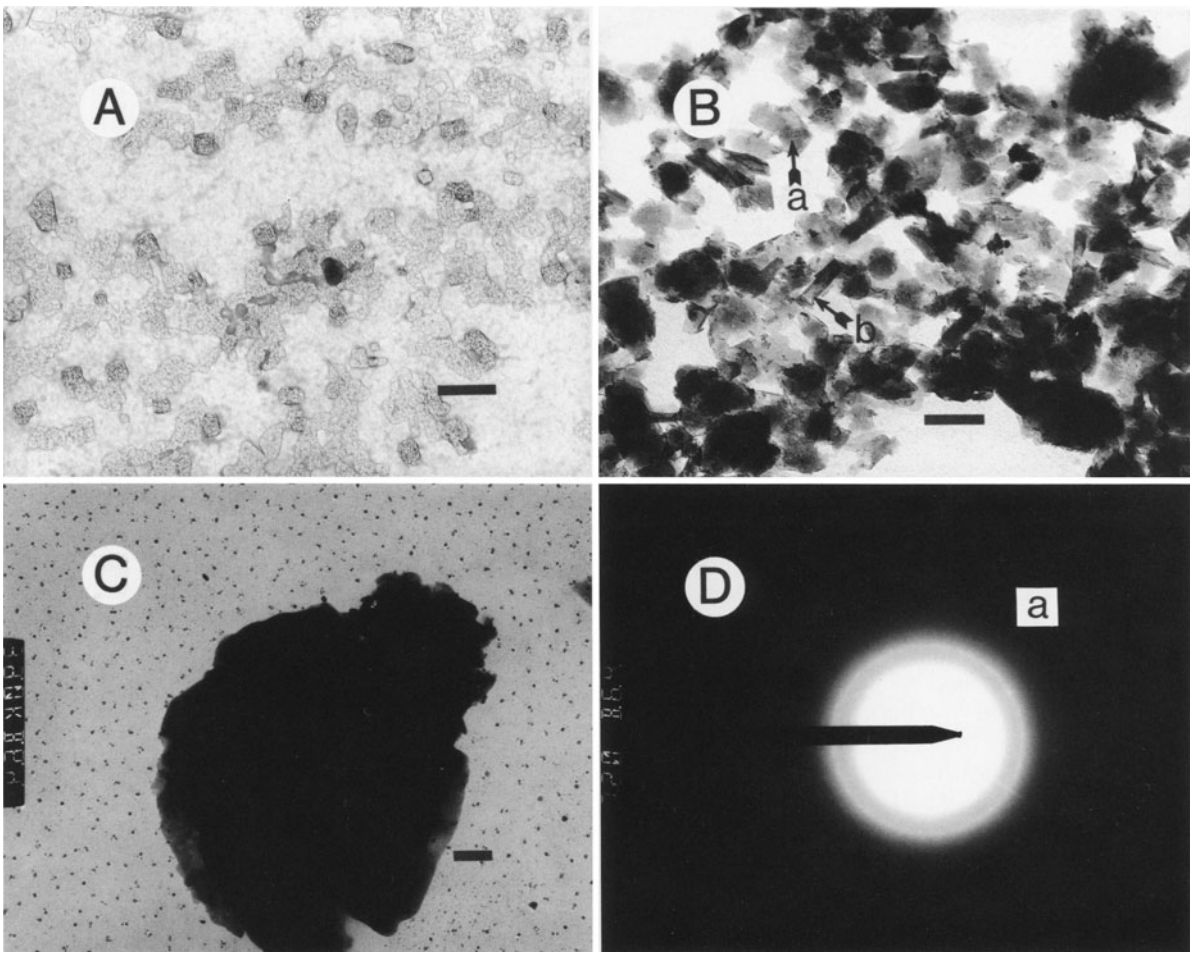



Figure 1. Electron micrographs of colloids and freeze-produced agglomerates. (A) shows typical morphology of colloids extracted from tephra-rich horizons—possibly allophane. (B) displays colloids extracted from loess horizons. Most colloids are subhedral tabular forms (a) and lath-like forms (b). Other micrographs indicate a small proportion of colloids are spheroidal and platy with pseudohexagonal symmetry. (C) shows bright field image of a small freeze-produced agglomerate. (D) is an electron diffraction pattern of the preceding agglomerate. All electron diffraction patterns displayed two rings; the diffuse ring with a diameter marked (a) is too faint to be seen in this reproduction. Line scale for all photomicrographs = 0.2 $\mu$m.

$H_2O_2$. Citrate-dithionite treatment (Jackson, 1956) caused the crystals to become uncolored in a matter of 10 minutes, and the crystals degraded over a period of several hours.

Combined samples of freeze-produced agglomerates displayed X-ray patterns similar to published values for dehydrated halloysite (Figure 2C). Unlike the colloid precursor, the (001) spacing was lower (7.3 vs 7.5 Å), and heating the crystals to 150°C did not diminish the reflection at 4.45 Å (Figure 2D). The combined sample IR pattern (Figure 4) is similar to those that have been reported for kaolinite and halloysite (Farmer, 1974). However, kaolinites show absorption bands near 3668 and 3651 $cm^{-1}$ (OH stretching vibrations) that are absent in dehydrated halloysites (van der Marel and Krohmer, 1969). Our agglomerates also lacked these IR absorption bands, which is supportive of a halloysitic mineralogy.

The Si/Al mole ratios of the freeze-produced products are atypically high for halloysite (Table 4). Ideally, halloysite has a Si/Al mole ratio of 1 (Newman and Brown, 1987), but some Fe-rich halloysites have high Si/Al ratios (Wada and Mizota, 1982). The Si/Al and Si/Fe mole ratios of the agglomerates are grossly similar to the starting colloid mixture. However, euhedral forms have lower Si/Al and Si/Fe mole ratios than either the starting colloid mixture or the bulk aggregate products (Table 4).

J. B. Dixon (personal communication) has suggested that the agglomerates formed by freezing could be crystal aggregates and that an electron diffraction pattern should display a ring-type pattern. Electron diffraction

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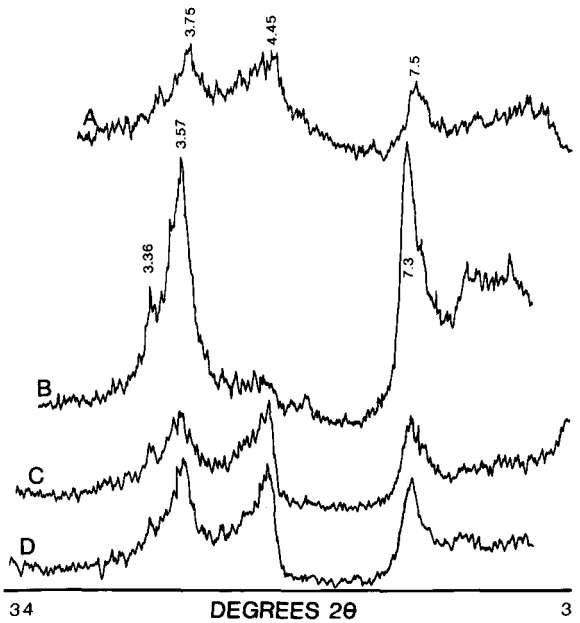



Figure 2. X-ray diffractographs of the colloid starting material and the freeze-produced agglomerates. (A) is a typical pattern of air-dried colloidal clay minerals extracted from loess horizons—the mother liquor. (B) is the pattern of the prior sample heated to 150°C for 30 min. (C) is the pattern of a bulk sample of the agglomerated products. (D) is the pattern of the prior sample heated to 150°C for 30 min.

from sizeable agglomerates was impossible as they became charged and blew off the grid. Fortunately, we were able to image very small agglomerates and obtain an electron diffraction pattern (Figures 1, C,D). Indeed, the freeze-produced agglomerates appear to be made up of minute halloysite crystals.

*Presence in soil*

The fact that freeze-produced agglomerates form so readily in the laboratory suggests that they may occur in temperate soils with an appropriate colloidal mineralogy. We examined selected surface and subsurface soil horizons of the collected pedons that would likely be subjected to freezing temperatures during the winter. In the very-fine sand fraction of some loess soil horizons, a minor proportion of grains were similar in appearance to those formed by the freezing of colloidal halloysite (Figure 3D). However, some differences were noted. Suspected freeze-produced soil agglomerates: 1) had a slightly higher refractive index than laboratory-produced agglomerates, 2) had acute bisectrix interference figures with a 2V always near 0°, and 3) contained inclusions not found in laboratory-produced agglomerates. Similar to laboratory agglomerates, many suspected freeze-produced agglomerates in soil were aggregations of uniformly optically-active regions.

Conjectured freeze-produced soil grains did not react as readily to 30% $H_2O_2$ as did the laboratory-produced agglomerates. However, with heating, they did degrade completely, if slowly. Citrate-dithionite treatment completely bleached and degraded these grains in a short period.

Heavy liquid separation was used to concentrate suspected freeze-produced soil agglomerates from the very-fine sand fraction. Grains similar in appearance to laboratory-produced agglomerates occurred in a wide range of specific gravities—1.9 to 2.4. Although optical microscopy indicated that these suspected freeze-produced agglomerates were only a minor proportion of the heavy liquid separates, XRD of these separates suggests the presence of halloysite as indicated by reflections at 7.1 and 4.4 Å, and by the similar peak intensity of the 4.4 Å reflection in relation to the 7.1 Å reflection (Figure 5).

## DISCUSSION

*Nature of products*

X-ray diffraction patterns and infrared spectra indicate that the agglomerates formed by freezing are dehydrated colloidal halloysite or metahalloysite, but are in a form that has not been previously recognized. Standard references (Deer, Howie, and Zussman, 1962; Kerr, 1977; Phillips and Griffen, 1981) state that halloysite is too small to determine its complete optical properties. The properties listed describe the crystals as colorless (majority of our agglomerates were colored), the birefringence as very weak to almost isotropic (our agglomerates have higher birefringence), and the refractive index as 1.549–1.561 (refractive index of our agglomerates was 1.568–1.592). Fitzpatrick (1984) reported that halloysite is length-slow, similar to our lath-like forms. Analogous to our material, kaolinite is biaxial negative with a small 2V (Phillips and Griffen, 1981), and kaolinites can contain structural Fe and Fe-oxyhydroxide impurities (Jefferson *et al.*, 1975). Tazaki (1982) reported elevated levels of Fe in spherical halloysites. Kunze and Bradley (1964) reported 8.25% $Fe_2O_3$ in an air-dried sample of tabular halloysite from Texas. In addition, they concluded that much of the Fe was in the ferrous state. The ratio of Si/Al in our products is atypically high for halloysite (Jepson and Rowse, 1975). This excess silica may occur as opaline silica, which has been reported for some high-Si kaolinites (Langston and Pask, 1969).

It is generally stated that the optical properties of a mineral are a direct consequence of its crystallographic structure, and that uniform regions of optical activity imply a single crystal (Kerr, 1977). Our evidence indicates, however, that optically-uniform freeze-produced agglomerates are in fact polycrystalline. Apparently, colloidal halloysite crystals accrete together in a three-dimensional array that mimics a biaxial indicatrix. Yet they are oriented so as to produce ring-type

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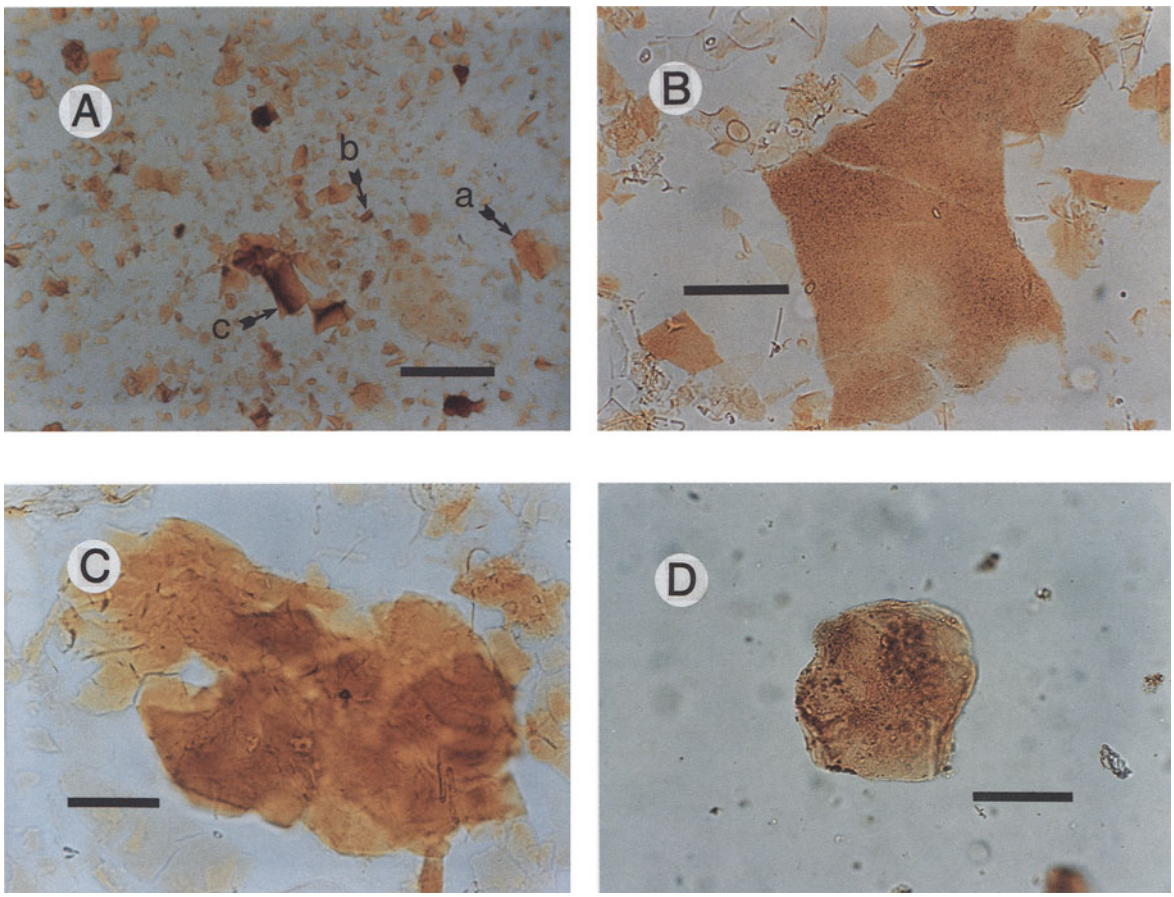



Figure 3. Photomicrographs (plane-polarized light) of freeze-produced agglomerates and suspected freeze-produced agglomerates from soil. (A) is a low magnification view showing several common forms including platy (a), lath-like (b), and cuspate (c). (B) is a magnified view of a large platy form showing the microgranular texture characteristic of the freeze-produced agglomerates. (C) shows agglomerate composed of several optically uniform domains, characteristic of many freeze-produced agglomerates. Optical domains are readily visible under cross-polarized conditions. (D) is a suspected freeze-produced agglomerate isolated from the very-fine sand fraction of a loess soil horizon by heavy liquid separation. These suspected halloysite agglomerates contain many dark inclusions not seen in laboratory-produced agglomerates. Line scale for A, D = 50 $\mu$m; for B, C = 10 $\mu$m.

electron diffraction patterns. We cannot, at present, offer a reasonable explanation for this incongruity, but speculate that Fe, either occupying a structural position in the halloysite, or as an Fe-oxyhydroxide compound between halloysite crystals, may be responsible.

*Mechanisms of formation*

We are unaware of any similar reported freezing phenomenon in which unit colloids weld or link together to produce larger, stable agglomerates. Experiments by Saunders *et al.* (1986) provide a potential explanation of this phenomenon. They concluded that slow freezing forces clay particles to "zone-refine" at the growth-interference faces of ice crystals. The surfaces are "ice-cleaned" or removed of surface contaminants that could inhibit particle bonding. Clay surfaces can then form bonds, or "cold-weld." Using Saunders *et al.* (1986) model, we hypothesize that, as a consequence of freezing aqueous suspension, colloidal halloysite is surface-cleansed of contaminants that could inhibit particle bonding. Once cleansed, the colloidal halloysite crystals are forced together by the growing ice in some mosaic. Although apparently polycrystalline by electron diffraction, the mosaic transmits light waves as if the entire grain was a biaxial indicatrix. Insight into the nature of the weld can be gleaned by the effect of citrate-dithionite on the agglomerates. That the crystals rapidly degraded and bleached in citrate-dithionite, suggests that an Fe-oxyhydroxide compound may be a welding agent. The fact that freeze-produced agglomerates have distinct habits suggests that the agglomeration process is not random. Random accretion would likely produce spherical agglomerates. It would seem unlikely that the growing ice "lattice" could mold ag-

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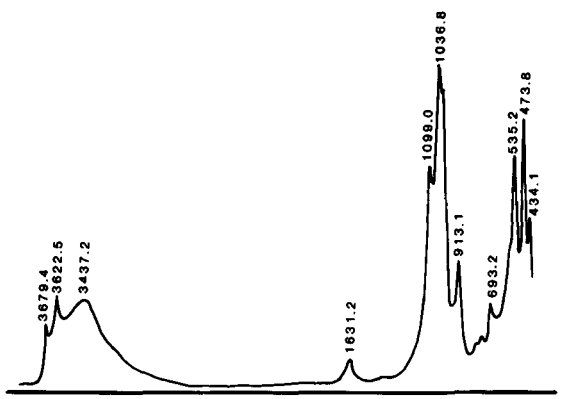



Figure 4. Infrared spectrum of bulk agglomerate products.

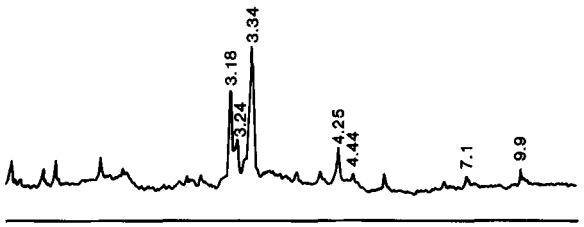



Figure 5. X-ray diffractograph of the very-fine sand fraction from loess soil horizons that were subjected to heavy liquid separation to concentrate suspected freeze-produced halloysite agglomerates.

glomerates into platy and lath-like habits. Clearly then, colloidal halloysite crystals accrete to thermodynamically-favored positions.

Only certain colloids are apparently capable of forming stable freeze-aided agglomerates. Weathered tephra-rich soil horizons containing short-range ordered minerals did not produce crystal aggregates upon freezing. Moreover, research has shown that freezing of aqueous suspensions of several types of smectite does not produce aggregates capable of remaining intact upon intense agitation (Lincoln and Tettenhorst, 1971; Rowell and Dillon, 1972; Saunders *et al.*, 1986). Given the similarity of metahalloysite to kaolinite, one might expect colloidal kaolinite to form freeze-produced agglomerates. However, unlike halloysites, kaolinites do not contain appreciable levels of Fe in the crystal structure that may aid in the agglomeration process.

### *Formation in soil*

When soil freezes in nature, particles migrate ahead of the freezing front (Corte, 1962). If the migrating particles include colloids conducive to agglomerate formation, extrapolation of our laboratory results would predict that capture and concentration of the colloid by the freezing front should lead to the formation of larger, stable agglomerates. The evidence for this process occurring in soils is only circumstantial at this point. We have isolated grains in the very-fine sand fraction of soil that are similar to laboratory freeze-produced halloysite agglomerates. Moreover, XRD data indicate the presence of halloysite in the very-fine sand fraction. Unfortunately, suspected freeze-produced halloysite agglomerates in soil are similar to some micaceous minerals. Biotite, or Fe-rich chlorites, can be excluded because they are strongly pleochroic and have greater refractive indices (Phillips and Griffen, 1981). Weathered biotites, particularly vermiculite, have optical properties very similar to the laboratory produced agglomerates. Vermiculite is biaxial negative with a 2V of 0–8°, is colorless, to pale yellow, to brown, is only weakly pleochroic, has a refractive index of 1.52–1.58, and occurs in plate-like forms (Phillips and Griffen, 1981). To determine the mineralogy of individual grains suspected to be freeze-produced halloysite unambiguously, may require better isolation techniques, or single-grain identification techniques such as the electron microprobe or use of the IR microscope. Given the high Si/Al ratios of laboratory-produced agglomerates, electron microprobe data could be misinterpreted.

## CONCLUSIONS AND IMPLICATIONS

The freezing of colloidal halloysite, extracted from north Idaho loess soils, results in the formation of silt- and sand-sized, stable, polycrystalline agglomerates. Although freezing of colloidal clays does alter the physiochemical properties of clays, we believe this is the first report to show that the freezing of colloids forces

Table 4. Elemental composition of agglomerates.[1]

| Sample | $Al_2O_3$ | $SiO_2$ | MgO | $K_2O$ | $Fe_2O_3$ | CaO | TiO | Mole ratio Si/Al | Mole ratio Si/Fe |
|---|---|---|---|---|---|---|---|---|---|
| | g $kg^{-1}$ | | | | | | | | |
| EDX1 | 258 | 423 | tr | 6 | 110 | 5 | 9 | 1.39 | 5.1 |
| EDX2 | 254 | 427 | tr | 7 | 106 | 6 | 10 | 1.42 | 5.3 |
| EDX3 | 234 | 458 | tr | 6 | 97 | 6 | 9 | 1.66 | 6.3 |
| HF | 195 | 502 | 16 | 3 | 95 | tr | nd | 2.18 | 7.0 |

[1] EDX values determined by energy-dispersive wavelength analysis of X-rays on three euhedral agglomerates selected by optical microscopy to have uniform optical properties. HF values determined by hydrofluoric acid digests of bulk sample of clay agglomerates.

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them to accrete together in the form of stable agglomerates. The formation of freeze-produced agglomerates could occur widely in temperate climates given the correct precursor colloidal mineralogy, which at this time appears to be halloysitic. Over time, the formation of such agglomerates could influence the physical and chemical properties of soils within the zone of freezing temperatures. This would certainly affect the particle-size distribution of the soil by changing clay to silt- and sand-sized material. Moreover, we cannot preclude the possibly that maturation of freeze-produced agglomerates may increase crystallinity. Trapping of the migrating colloids would likely occur at discontinuities in the soil where the freezing front would overtake these particles. We suspect this could occur in locations such as invertebrate burrows, unoccupied root channels, and soil structural voids. Under these conditions, freeze-produced agglomerates might resemble illuvial argillans.

The potential for observation of freeze-produced agglomerates in natural soil would preclude $H_2O_2$, citrate-dithionite, and possibly other mineralogical pretreatment agents that could destroy the agglomerates. Large halloysite agglomerates in soil may be overlooked because of optical similarities to some micaceous minerals.

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## REFERENCES

Ahlrichs, J. L. and White, J. L. (1962) Freezing and lyophilizing alters the structure of bentonite gels: *Science* **136,** 1116–1118.

Buckley, D. E. and Cranston, R. R. (1970) Atomic absorption analyses of 18 elements from a single decomposition of an aluminosilicate: *Chem. Geol.* **7,** 273–284.

Busacca, A. J. (1989) Long Quaternary record in eastern Washington, U.S.A., interpreted from multiple buried paleosols in loess: *Geoderma* **45,** 105–122.

Corte, A. E. (1962) Vertical migration of particles in front of a moving freezing plane: *J. Geophys. Res.* **67,** 1085–1090.

Deer, W. A., Howie, R. A., and Zussman, J. (1962) *Rock-forming Minerals. Vol. 3, Sheet Silicates:* Longmans, Green and Co. Ltd., London.

Dixon, J. B. (1989) Kaolin and serpentine group minerals: in *Minerals in Soil Environments,* 2nd ed., J. B. Dixon and S. B. Weed, eds., Soil Sci. Soc. Amer., Madison, Wisconsin, 467–526.

Farmer, V. C. (1974) The layer silicates: in *The Infrared Spectra of Minerals,* V. C. Farmer, ed., Mineralogical Society, London, 331–363.

Fitzpatrick, E. A. (1984) *Micromorphology of Soils:* Chapman and Hall, London.

Henmi, T. and Wada, K. (1976) Morphology and composition of allophane: *Am. Mineral.* **61,** 379–390.

Jackson, M. L. (1956) *Soil Chemical Analysis—Advanced Course:* published by the author, Dept. of Soils, Univ. of Wisconsin, Madison.

Jefferson, D. A., Tricker, M. J., and Winterbottom, A. P. (1975) Electron-microscopic and Mössbauer spectroscopic studies of iron-stained kaolinite minerals. *Clays & Clay Minerals* **23,** 355–360.

Jepson, W. B. and Rowse, J. B. (1975) The composition of kaolinite—An electron microscope microprobe study. *Clays & Clay Minerals* **23,** 310–317.

Kerr, P. F. (1977) *Optical Mineralogy:* McGraw-Hill, Inc., New York.

Kunze, G. W. and Bradley, W. F. (1964) Occurrence of a tabular halloysite in a Texas soil: *Clays & Clay Minerals* **12,** 523–527.

Langston, R. B. and Pask, J. A. (1969) The nature of anauxite: *Clays & Clay Minerals* **16,** 425–436.

Lincoln, J. and Tettenhorst, R. (1971) Freeze-dried and thawed clay: *Clays & Clay Minerals* **19,** 103–107.

Mubarek, A. and Olsen, R. A. (1976) An improved technique for measuring soil pH: *Soil Sci. Soc. Am. J.* **40,** 880–882.

Newman, A. C. D. and Brown, G. (1987) The chemical constitution of clays: in *Chemistry of Clays and Clay Minerals,* Mineralogical Society Monograph No. 6, A. C. D. Newman, ed., Longman Sci. & Technical, Essex, England, 1–128.

Phillips, W. R. and Griffen, D. T. (1981) *Optical Mineralogy—The Nonopaque Minerals:* W. H. Freeman, San Francisco.

Rowell, D. L. and Dillon, P. J. (1972) Migration and aggregation of Na and Ca clays by the freezing of dispersed and flocculated suspension: *J. Soil. Sci.* **23,** 442–447.

Saunders, R. S., Fanale, F. P., Parker, T. J., Stephens, J. B., and Sutton, S. (1986) Properties of filamentary sublimation residues from dispersions of clay in ice: *Icarus* **66,** 94–104.

Soil Survey Staff (1990) *Keys to Soil Taxonomy, 4th ed:* SMSS Technical Monograph **6,** Virginia Polytechnical Institute & State Univ., Blacksburg, Virginia.

Sudo, T. and Takahashi, H. (1956) Shapes of halloysite particles in Japanese clays: *Clays & Clay Minerals* **4,** 67–79.

Stoiber, R. E. and Morse, S. A. (1981) *Microscopic Identification of Crystals:* R. E. Krieger Publ. Co., Huntington, New York.

Taszaki, K. (1982) Analytical electron microscopic studies of halloysite formation processes—Morphology and composition of halloysite: in *Proc. Int. Clay Conf., Italy, 1981,* Elsevier, Amsterdam, 573–584.

van der Marel, H. W. and Krohmer, P. K. (1969) O-H stretching vibrations in kaolinite and related minerals: *Cont. Mineral. & Petrol.* **22,** 73–82.

Wada, K. and Yoshinaga, N. (1969) The structure of imogolite: *Am. Mineral.* **54,** 50–71.

Wada, S. I. and Mizota, C. (1982) Iron-rich halloysite (10 Å) with crumpled lamellar morphology from Hokkaido, Japan: *Clays & Clay Minerals* **30,** 315–317.

Whittig, L. D. and Allardice, W. R. (1986) X-ray diffraction techniques: in *Methods of Soil Analysis Part I—Physical and Mineralogical Methods.* No. 9, A. Klute, ed., Amer. Soc. Agron., Madison, Wisconsin, 331–362.

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