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LIM, HOWARD SOOKIL

EFFECTS OF DRYING METHODS, EXTENT, AND INORGANIC CEMENTING CONSTITUENTS ON THE STRUCTURAL PROPERTIES OF TYPIC HYDRANDEPTS OF HAWAII'S FORESTLAND

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EFFECTS OF DRYING METHODS, EXTENT, AND INORGANIC CEMENTING CONSTITUENTS ON THE STRUCTURAL PROPERTIES OF TYPIC HYDRANDEPTS OF HAWAII'S FORESTLAND

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN AGRONOMY AND SOIL SCIENCE DECEMBER 1979

by

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ABSTRACT

The effects of four well-defined drying treatments on the structural and physical characteristics of three Hawaii typic hydrandepts were investigated. The treatments were oven drying at 110°C, P₂O₅ drying at 25°C, freeze drying, and critical point drying. All three soils were developed from volcanic ash, but under different rainfall regimes. Effects of drying extent and roles of seven synthetic minerals (cementing agents) were also investigated. The properties investigated were particle size distribution, water stable aggregate, specific surface area, water retention characteristics, soil plasticity, shrinkage property, particle density, and soil viscosity.

Critical point drying was best for preserving the original structure and physical properties of both soils and synthetic minerals after dehydration. In terms of minimum changes in properties, the treatments ranked in the order of: critical point drying > freeze drying >
P₂O₅ drying > oven drying. However, none of the treatments fully investigated properties unchanged from original conditions. The alteration of physical properties of soils and synthetic minerals after critical point drying (producing minimum change in structural configuration) was blamed less on aggregation and more on the possible loss of original colloidal characteristics. Soil and mineral sensitivity to drying were well correlated with their original water retention characteristics, the higher the water retention, the severer were the changes that occurred upon drying. Thus the irreversible changes of soil physical properties of Typic Hydrandepts were in order of: Kaiwiki sub-surface > Puaulu sub-surface > Kaiwiki surface > Hilo sub- and surface > Puaulu surface. For synthetic minerals, they were in order of: aluminosilicates > iron hydrous oxide (A) > iron hydrous oxide (B) > aluminum hydroxide > iron oxide (hematite). However, the magnitude of change upon drying was calculated on the basis of unit surface areas. The minerals were ranked in order of: iron hydrous oxide monohydrated (B) (goethite) = aluminum hydroxide (gibbsite and bayerite mixture) > α-iron oxide (hematite) > iron hydrous oxide monohydrated (A) (akaganeite) > aluminosilicates. Severity of drying effects on aluminosilicates (SiO₂/Al₂O₃ = 0.5 to 2.0) was only slightly dependent on the silica/alumina ratio. The only unexpected
change upon drying was the definite reduction in particle
density for both soils and minerals.

The above results indicated that prediction of soil
sensitivity to drying would be possible by knowing the
type, form and content of prevailing mineralogical constitu­
ents. Then supplementary information such as texture,
dehydration history and content of organic constituents
would serve to improve such predictions.

Measurements of structural properties of the soils
subsequent to step-wise drying revealed that the region
between residual shrinkage and the shrinkage limit phases
represents the general water contents at which "irreversi­
bility" occurs. Residual shrinkage began at water poten­
tials of 0.1 to 1.0 bar and the shrinkage limit was reached
at potentials far beyond 15 bar (water contents of 41 to
65%).
TABLE OF CONTENTS

LIST OF TABLES ............... x

LIST OF ILLUSTRATIONS .......... xii

INTRODUCTION ................. 1

LITERATURE REVIEW ............. 5

A. Description of Hydrandepts .......... 5
   1. Definition and occurrence ........ 200
   2. Hawaii's Typic Hydrandepts ....... 203
   3. Characteristics of Hydrandepts ..... 207
      a. Thixotropy .................. 207
      b. Chemical properties .......... 211
      c. Physical properties .......... 214

B. Background on the contribution of drying to structural development and aggregate stability .......... 5

C. Effects of inorganic cementing agents on structural stability .......... 9

D. Effects of dehydration on physico-chemical properties .......... 14

E. Alternative dehydration techniques for study of soil structure .......... 18

MATERIALS AND METHODS .......... 25

A. Materials .......... 25
   1. Soils .......... 25
      a. Kaiwiki soil series .......... 25
      b. Hilo soil series .......... 25
      c. Puauulu soil series .......... 25

vi
2. Synthetic minerals

   a. Iron hydrous oxide monohydrated (A) 27
   b. Iron hydrous oxide monohydrated (B) 27
   c. α-iron oxide (hematite) 27
   d. Aluminum hydroxide 27
   e. Aluminosilicate (non-crystalline) (SiO₂/Al₂O₃=0.5) 27
   f. Aluminosilicate (non-crystalline) (SiO₂/Al₂O₃=1.0) 27
   g. Aluminosilicate (non-crystalline) (SiO₂/Al₂O₃=2.0) 27

B. Methods

1. Soil preparation 29
2. Synthesis of minerals 29
   a. Iron hydrous oxides 31
   b. Aluminum hydroxide 31
   c. Aluminosilicates (non-crystalline) 31
   d. α-iron oxide 32
3. Drying treatments 32
   a. Oven drying 32
   b. P₂O₅ drying 32
   c. Freeze drying 32
   d. Critical point drying 33
4. Chemical analysis 33
   a. pH measurement 33
   b. Organic matter determination 34
   c. Silica and aluminum determination 34
5. Physical Analysis 34
   a. Moisture content measurement 34
   b. Particle size distribution 34
   c. Water stable aggregate measurement 35
   d. Water retention measurement 35
   e. Control of sample moisture content 35
   f. Shrinkage measurement 35
   g. Plastic limit 36
   h. Liquid limit 37
i. Viscosity measurement ............ 37
j. Specific surface measurement by
   water vapor adsorption ........... 38
k. Specific surface measurement by
   N\textsubscript{2} gas adsorption ....... 40
l. Particle density measurement ....... 40
m. Scanning electron micrography (SEM) ... 41

6. Mineralogical analysis ............. 41
   a. X-ray diffraction analysis ....... 41

RESULTS AND DISCUSSION ............. 43

A. Effects of different dehydration methods
   on soil properties ................. 43

1. Characterization of soil samples .... 43
   a. Physico-chemical properties of
      original soil samples ............ 43
   b. Mineralogical properties of original
      soil samples ..................... 45

2. Effects of different dehydration
   techniques ........................ 56
   a. Particle size distribution ....... 56
   b. Water stable aggregate ........... 58
   c. Specific surface area measurements .. 61
   d. Water retention characteristics .... 62
   e. Soil plasticity ................... 71
   f. Soil viscosity ................... 76
   g. Shrinkage property ................ 81
   h. Particle density .................. 83
   i. Scanning electron micrography (SEM) ... 85

B. Contribution of cementing agents to changes of
   soil properties upon dehydration .... 93

1. Characterization of synthetic minerals .. 94
   a. Mineralogical identification ....... 94

2. Effects of different dehydration
   techniques ........................ 103
   a. Particle size distribution ....... 103
   b. Water stable aggregate .......... 106
c. Specific surface area .............. 107
d. Water retention characteristics .... 110
e. Shrinkage properties ............... 120
f. Particle density ............... 123
g. Scanning electron micrography (SEM) . 124

3. Analysis of responses of different soils in view of pure mineral data .......... 141

C. Assessment of the extent of irreversibility . . 143

1. Shrinkage property of the soils ....... 143

2. Determination of extent of drying on irreversible changes ................. 152
   a. Particle size distribution ....... 152
   b. Aggregate stability ........... 160
   c. Surface area by $H_2O$ vapor adsorption . 164
   d. Water retention characteristics ... 167
   e. Soil plasticity .............. 169
   f. Soil viscosity .............. 172

SUMMARY AND CONCLUSIONS ................. 179

LITERATURE CITED ................. 184

APPENDICES ................. 199
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sensitivity classifications</td>
</tr>
<tr>
<td>2</td>
<td>Some compounds and their critical temperature and critical pressure</td>
</tr>
<tr>
<td>3</td>
<td>Some information on selected soils</td>
</tr>
<tr>
<td>4</td>
<td>Sampling depths and codes for three soils</td>
</tr>
<tr>
<td>5</td>
<td>Some physico-chemical properties of original soil samples</td>
</tr>
<tr>
<td>6</td>
<td>Effect of drying treatments on water stable aggregate index (MWD) of undisturbed soils</td>
</tr>
<tr>
<td>7</td>
<td>Effect of drying treatments on water stable aggregate index (MWD) of disturbed soils</td>
</tr>
<tr>
<td>8</td>
<td>Specific surface area (m²/g) of soils by H₂O vapor adsorption</td>
</tr>
<tr>
<td>9</td>
<td>Specific surface area (m²/g) of soils by N₂ gas adsorption</td>
</tr>
<tr>
<td>10</td>
<td>Effect of drying treatments on Atterberg limits of soils</td>
</tr>
<tr>
<td>11</td>
<td>Effect of drying treatments on soil shrinkage (cm³/g) from saturation</td>
</tr>
<tr>
<td>12</td>
<td>Effect of drying treatments on soil particle density</td>
</tr>
<tr>
<td>13</td>
<td>Effect of drying treatments on water stable aggregate index (MWD)</td>
</tr>
<tr>
<td>14</td>
<td>Specific surface area (m²/g) by vapor adsorption technique for synthetic minerals</td>
</tr>
<tr>
<td>15</td>
<td>Specific surface area (m²/g) by N₂ gas adsorption technique for synthetic minerals</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>16</td>
<td>Effect of drying treatments on volume shrinkage (cm$^3$/g) of synthetic minerals</td>
</tr>
<tr>
<td>17</td>
<td>Water retention characteristics and volume shrinkage per unit surface area</td>
</tr>
<tr>
<td>18</td>
<td>Effect of drying treatments on particle density of synthetic minerals</td>
</tr>
<tr>
<td>19</td>
<td>Saturation water content, bulk density, and shrinkage limit of original (wet) soils</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Properties of thixotropic materials</td>
<td>209</td>
</tr>
<tr>
<td>2</td>
<td>Effect of pH on charge development of allophane (&lt;um)</td>
<td>212</td>
</tr>
<tr>
<td>3</td>
<td>Relation between interaction energy and particle separation when both short-range and long-range forces are significant</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Relation between interaction energy and particle separation when only long-range forces are significant</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>Proposed scheme of possible arrangements of quartz, clay domains, and organic matter in a soil aggregate</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>Phase diagram for CO₂, showing regions of existence of stages</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Soil sampling locations on the Island of Hawaii</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>Water retention characteristics of surface and sub-surface layers of three soils (gravimetric base)</td>
<td>46</td>
</tr>
<tr>
<td>9</td>
<td>Water retention characteristics of surface and sub-surface layers of three soils (volumetric base)</td>
<td>47</td>
</tr>
<tr>
<td>10</td>
<td>X-ray diffractogram for profile samples of Kaiwiki original soil</td>
<td>49</td>
</tr>
<tr>
<td>11</td>
<td>X-ray diffractogram for profile samples of Hilo original soil</td>
<td>51</td>
</tr>
<tr>
<td>12</td>
<td>X-ray diffractogram for profile samples of Puaulu original soil</td>
<td>53</td>
</tr>
<tr>
<td>13</td>
<td>Effect of drying treatments on particle size distribution of three soils</td>
<td>57</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>14</td>
<td>Effect of drying treatments on water retention characteristics of soil (Kaiwiki surface soil)</td>
<td>64</td>
</tr>
<tr>
<td>15</td>
<td>Effect of drying treatments on water retention characteristics of soil (Kaiwiki sub-surface soil)</td>
<td>65</td>
</tr>
<tr>
<td>16</td>
<td>Effect of drying treatments on water retention characteristics of soil (Hilo surface soil)</td>
<td>66</td>
</tr>
<tr>
<td>17</td>
<td>Effect of drying treatments on water retention characteristics of soil (Hilo sub-surface soil)</td>
<td>67</td>
</tr>
<tr>
<td>18</td>
<td>Effect of drying treatments on water retention characteristics of soil (Puaulu surface soil)</td>
<td>68</td>
</tr>
<tr>
<td>19</td>
<td>Effect of drying treatments on water retention characteristics of soil (Puaulu sub-surface soil)</td>
<td>69</td>
</tr>
<tr>
<td>20</td>
<td>Effect of drying treatments on Atterberg limits of soils</td>
<td>75</td>
</tr>
<tr>
<td>21</td>
<td>Viscosity of original (wet) soils</td>
<td>78</td>
</tr>
<tr>
<td>22</td>
<td>Effect of drying treatments on viscosity of soils</td>
<td>80</td>
</tr>
<tr>
<td>23</td>
<td>X-ray diffractogram for iron oxide and hydrous oxide</td>
<td>95</td>
</tr>
<tr>
<td>24</td>
<td>X-ray diffractogram for aluminum hydroxide</td>
<td>99</td>
</tr>
<tr>
<td>25</td>
<td>X-ray diffractogram for aluminosilicates and tetraethyl orthosilicate (Si source)</td>
<td>101</td>
</tr>
<tr>
<td>26</td>
<td>Effect of drying treatments on particle size distribution of synthetic minerals</td>
<td>105</td>
</tr>
<tr>
<td>27</td>
<td>Water retention characteristics of synthetic minerals</td>
<td>111</td>
</tr>
<tr>
<td>28</td>
<td>Effect of drying treatments on water retention characteristics of Fe-hydrous oxide (A)</td>
<td>112</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>29</td>
<td>Effect of drying treatments on water retention characteristics of Fe-hydrous oxide (B)</td>
<td>113</td>
</tr>
<tr>
<td>30</td>
<td>Effect of drying treatments on water retention characteristics of iron oxide (hematite)</td>
<td>114</td>
</tr>
<tr>
<td>31</td>
<td>Effect of drying treatments on water retention characteristics of aluminum hydroxide</td>
<td>115</td>
</tr>
<tr>
<td>32</td>
<td>Effect of drying treatments on water retention characteristics of aluminosilicate (0.5)</td>
<td>116</td>
</tr>
<tr>
<td>33</td>
<td>Effect of drying treatments on water retention characteristics of aluminosilicate (1.0)</td>
<td>117</td>
</tr>
<tr>
<td>34</td>
<td>Effect of drying treatments on water retention characteristics of aluminosilicate (2.0)</td>
<td>118</td>
</tr>
<tr>
<td>35</td>
<td>Volume shrinkage of fresh Kaiwiki surface soil upon drying</td>
<td>144</td>
</tr>
<tr>
<td>36</td>
<td>Volume shrinkage of fresh Kaiwiki sub-surface soil upon drying</td>
<td>145</td>
</tr>
<tr>
<td>37</td>
<td>Volume shrinkage of fresh Hilo surface soil upon drying</td>
<td>146</td>
</tr>
<tr>
<td>38</td>
<td>Volume shrinkage of fresh Hilo sub-surface soil upon drying</td>
<td>147</td>
</tr>
<tr>
<td>39</td>
<td>Volume shrinkage of fresh Puauulu surface soil upon drying</td>
<td>148</td>
</tr>
<tr>
<td>40</td>
<td>Volume shrinkage of fresh Puauulu sub-surface soil upon drying</td>
<td>149</td>
</tr>
<tr>
<td>41</td>
<td>Change of particle size distribution for fresh Kaiwiki surface soil upon drying</td>
<td>154</td>
</tr>
<tr>
<td>42</td>
<td>Change of particle size distribution for fresh Kaiwiki sub-surface soil upon drying</td>
<td>155</td>
</tr>
<tr>
<td>43</td>
<td>Change of particle size distribution for fresh Hilo surface soil upon drying</td>
<td>156</td>
</tr>
</tbody>
</table>

xiv
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>Change of particle size distribution for fresh Hilo sub-surface soil upon drying</td>
<td>157</td>
</tr>
<tr>
<td>45</td>
<td>Change of particle size distribution for fresh Puaulu surface soil upon drying</td>
<td>158</td>
</tr>
<tr>
<td>46</td>
<td>Change of particle size distribution for fresh Puaulu sub-surface soil upon drying</td>
<td>159</td>
</tr>
<tr>
<td>47</td>
<td>Change of aggregate stability index (MWD) of fresh soils upon drying</td>
<td>162</td>
</tr>
<tr>
<td>48</td>
<td>Change of specific surface area (m²/g) of fresh Kaiwiki soil upon drying</td>
<td>163</td>
</tr>
<tr>
<td>49</td>
<td>Change of specific surface area (m²/g) of fresh Hilo soil upon drying</td>
<td>164</td>
</tr>
<tr>
<td>50</td>
<td>Change of specific surface area (m²/g) of fresh Puaulu soil upon drying</td>
<td>165</td>
</tr>
<tr>
<td>51</td>
<td>Change of water retention characteristics of fresh soils upon drying</td>
<td>168</td>
</tr>
<tr>
<td>52</td>
<td>Change of liquid limit of fresh soils upon drying</td>
<td>171</td>
</tr>
<tr>
<td>53</td>
<td>Change of viscosity of fresh Kaiwiki soil upon drying</td>
<td>173</td>
</tr>
<tr>
<td>54</td>
<td>Change of viscosity of fresh Hilo soil upon drying</td>
<td>174</td>
</tr>
<tr>
<td>55</td>
<td>Change of viscosity of fresh Puaulu soil upon drying</td>
<td>175</td>
</tr>
<tr>
<td>Plate</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>Electron micrograph of Kaiwiki sub-surface soil</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>Electron micrograph of Hilo surface soil</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>Electron micrograph of Puaulu sub-surface soil</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>Electron micrograph of Fe-hydrous oxide (A)</td>
<td>125</td>
</tr>
<tr>
<td>5</td>
<td>Electron micrograph of Fe-hydrous oxide (B)</td>
<td>127</td>
</tr>
<tr>
<td>6</td>
<td>Electron micrograph of iron oxide (hematite)</td>
<td>129</td>
</tr>
<tr>
<td>7</td>
<td>Electron micrograph of aluminum hydroxide</td>
<td>131</td>
</tr>
<tr>
<td>8</td>
<td>Electron micrograph of aluminosilicate (0.5)</td>
<td>133</td>
</tr>
<tr>
<td>9</td>
<td>Electron micrograph of aluminosilicate (1.0)</td>
<td>135</td>
</tr>
<tr>
<td>10</td>
<td>Electron micrograph of aluminosilicate (2.0)</td>
<td>137</td>
</tr>
<tr>
<td>11</td>
<td>Electron micrograph of aluminosilicate (0.5) in high resolution</td>
<td>139</td>
</tr>
</tbody>
</table>
INTRODUCTION

Structural characteristics are highly correlated with other important soil physical properties and must be well understood for proper management of the soils. Characteristics of aggregates (shape, size, and stability) and mechanisms of their formation differ greatly from one soil to another. The important factors causing these differences are primarily differences in prevailing constituents and the history (e.g., exposure, dehydration cycles, or tillage) of the soil. All workers agree that dehydration is a necessary step for formation of stable aggregates. In the Hydrandepts of Hawaii, dehydration was shown to produce very significant, often called "irreversible," changes in some soil properties. However, not all the important changes in soil properties (particularly rheological properties) have been studied. Neither has the extent of dehydration needed to produce "irreversible" changes been determined. Missing yet is information on the roles played by different constituents, particularly the "cementing" fraction in the formation of ultimate structural units produced by drying. Establishing the nature of changes caused by drying and understanding the role of soil constituents are important if consequences of forest clearing are to be accurately predicted and if exposed soils are to be properly managed.

The occurrence of many Hydrandepts on the Island of
Hawaii provides an opportunity to study the effects of different constituents on changes in properties of soils upon dehydration. These soils are developed from basic volcanic ash which was deposited at different times in regions which are characterized by high rainfall throughout the year. Therefore, they seldom experience drying cycles in their natural setting. When dried in the laboratory or in the field after removal of natural vegetation they experience structural changes which should differ for soils of different ages as these undergo different degrees of Si removal or sesquioxide accumulation by chemical weathering. The roles of soil constituents in controlling structural changes can, therefore, be ideally investigated on soils selected from different weathering regimes.

Dehydration is prerequisite for the determination and study of many important soil properties such as specific surface area measurement by N₂ adsorption, organic matter content measurement, scanning electron microscopy, anion and cation adsorption capacity, and soil structure observation. Therefore, due to the significant changes of many properties of Typic Hydrandepts upon routine drying, it would be important to develop better drying techniques to preserve the natural soil properties and structure before such determinations. New techniques have been proposed for drying soils with little change in structural properties. However, these have not been examined on these soils.

The roles of soil constituents in effecting structural
changes due to drying may also be studied using a synthetic approach whereby defined constituents are added and their roles systematically determined. Although this approach has been used by various authors, there remains much need for information on the comparative contributions from cementing agents which are enriched in Fe, Al or Si. Recent information indicates that synthesis of such inorganic constituents can be performed simply and without too long an investment of time.

In examining the effect of drying on soil properties, one is required to define the exact extent of soil drying as well as the method. Because water is retained in soil by different mechanisms, not all water losses are expected to produce "irreversible" changes in soil properties. Indeed, it is expected that a critical water content exists, for a given soil, below which such irreversibility occurs. It may be suspected that, since the closest proximity between particles is needed to achieve maximum bonding, the critical water content is in the range of the shrinkage limit. However, no firm measurements have been made to establish this. New techniques have been proposed for drying soils with little change in structural properties. Such methods can be very useful for handling Hydrandepts but have not been examined on these soils.

This study was conducted on selected forest Typic Hydrandepts and synthetic systems with the following objectives:
1. To determine the effects of well-defined methods of drying on changes in structural and rheological properties of different Typic Hydrandepts.

2. To assess the roles played by and effectiveness of important inorganic constituents, particularly cementing ones, in stabilizing soil structure after drying.

3. To examine the effect of extent of drying on changes in structural and rheological properties of different Typic Hydrandepts.
LITERATURE REVIEW

A. Description of Hydrandepts

A detailed review of the properties of Hydrandepts is provided in Appendix I. Interested readers are referred to that section.

B. Background on the contribution of drying to structural development and aggregate stability

Baver, et al. (1972) defined the soil structure as the arrangement of primary and secondary particles into a certain structural pattern with consequential formation of pore spaces (intra- and inter-spaces) with various sizes. He described individual mechanical separates such as sand, silt and clay-sized fractions as primary particles and aggregates or structural elements which have been formed by aggregation of individual mechanical fractions as secondary particles. Because drying (and wetting) involves mostly changes in inter-particle separations, there are changes in interparticle energy forces associated with drying (or wetting) cycles. van Olphen (1963), following Verwey and Overbeek (1948), applied the diffuse double-layer theory to depict the mechanism of colloidal particle agglomeration in hydrophobic sols by various attractive and repulsive forces.
Low (1968) presented the following two diagrams (Fig. 3 and Fig. 4) obtained from algebraic summation of various repulsive (+) and attractive (−) energies between two soil particles. In brief, the long-range attraction is defined by all the attractive forces acting between two approaching particles in the presence of more than a single layer of intervening exchangeable cations. Other attractive forces arising from hydrogen bonding between oxygen atoms and hydroxyl groups in adjacent surfaces of particles were considered as short-range attractive forces. Relatively weak short-range attractive forces result in only one potential energy minimum as in Figure 4.

Fig. 3. Relation between interaction energy and particle separation when both short-range and long-range forces are significant.

Fig. 4. Relation between interaction energy and particle separation when only long-range forces are significant.
It must be realized that although flocculation is an important requisite to the formation of soil aggregates, it alone is insufficient for producing stable structural units.

Baver, et al. (1972) distinguished between the phenomena of aggregation and flocculation, quoting the statement of Bradfield (1936), "granulation is flocculation plus." From the point of view of soil structure, aggregation requires a cementation or binding together of soils resulting from shrinkage caused by tension formed by air-water interfaces at the surface of the soil-water systems in the process of drying.

Baver, et al. (1972) also emphasized that the dehydration is a basic requirement for the formation of secondary particles and electrostatic and van der Waal's forces are dominant and extremely important in aggregate formation.

Emerson (1959) proposed a scheme of possible arrangements and type of bonds among quartz, organic matter and domains, which he defined as a group of clay crystals that are oriented and sufficiently close together to behave in water as a single unit, as a possible mechanism of aggregate formation (Fig. 5). He also suggested that drying to the wilting point was apparently sufficient for transforming clay crystals in crumbs into aggregate domains in normal agricultural soils.
Fig. 5. Proposed scheme of possible arrangements of quartz, clay domains, and organic matter in a soil aggregate. (A) Quartz-organic colloid-quartz, (b) Quartz-organic colloid-clay domain, (C) Clay domain-organic colloid-clay domain, (C1) face-face, (C2) edge-face, (C3) edge-edge, (D) clay domain edge-clay domain face.

Emerson and Dettman (1960) found that the clay-clay attractive forces were greater in crumbs from acid soils than from soils containing free CaCO₃ because of two reasons: (1) positive charges on the edge faces of the clay crystals; (2) exchangeable trivalent cations on the clays.

Kingery and Francel (1954) believed that the major forces of attraction are due to capillary forces of the surface layer of water (and van der Waal's forces which are considerably smaller) which are expressed as:

$$ p = \frac{2\gamma}{r} $$

where the $\gamma$ is surface tension, $r$ is radius of capillary in the plastic range. They also found that the four common
major factors affecting drying behavior and plasticity are: (a) particle size, (b) surface tension, (c) adsorbed ions, and (d) water content.

On the other hand, El-Swaify and Emerson (1975) reported that the precipitation of Al- and Fe-hydroxides into dispersed clay suspensions followed by drying has been successful in increasing the net bonding between clay particles. They indicated that amorphous precipitated particles of both link the clay particles together by H bonding and/or van der Waal's attraction to the clay surface and to each other although Fe(OH)$_3$ was not as effective as Al(OH)$_3$.

El-Swaify (1976) indicated that drying cycles are essential for enhancing the roles played by both Fe- and Al-hydroxides by adding strong bonds which complement electrostatic interactions that are inherent to the colloidal constituents of soils.

C. Effects of inorganic cementing agents on structural stability

Kemper and Koch (1966) evaluated the correlation between aggregate stability and seven different soil constituents using over 500 samples from western United States and Canada. He reported that organic matter, clay, and free Fe$_2$O$_3$ and Al$_2$O$_3$ were important factors affecting aggregate stability. Baver, et al. (1972) also reiterated that the most common colloidal cementing agents are clay
particles, oxides and hydrous oxides of iron and aluminum, and organic matter. Greenland, et al. (1968) found on electron microscope examination of the clay fractions of some red soils, that "free" iron oxides were present as small (50-100Å in diameter) discrete particles frequently clustered to form large irregular aggregates. Based on these observations, they dismissed any large role for iron oxides in stabilizing soil structure. They also reported an association of some of the oxide particles with the edges, but not the faces of kaolinite plates. Later, Jones and Uehara (1973) also observed, using an electron microscope, that gel-like materials occurred as coatings on crystalline particles and not as discrete bodies. They speculated that these gel-like amorphous materials dried irreversibly in high oxide systems and reversibly in high silicon systems and that they played an important role in determining the stability of soil aggregates. El-Swaify (1969) found no changes in aggregate stability for two highly weathered oxidic soils from Hawaii after treatments with sea water, and sodium, calcium, and magnesium chlorides at different concentration levels. These results contrasted with earlier results on many temperate soils.

Briner and Jackson (1969) indicated that about 25% of allophane materials having high SiO₂/Al₂O₃ molar ratio (about 4.0) was present in some Australian soils. They postulated that occurrence of the amorphous phases both as
an external coating and discrete particles prevented not only parallel orientation of layered minerals, but also absorbed some of the diffraction from well-crystallized clay. The cation exchange and physical properties of the soils were affected as well, assessing phosphate fixation and fixing potassium as suggested by Sherman, et al. (1964) and Reeuwijk and de Villiers (1968), respectively.

In other cases, synthetic or extractive techniques have been adopted by many workers to discern the particular role of each of the organic cementing agents in stabilizing the structure of soils. Consequently, a large number of these synthetic and extractive techniques have been developed and applied (lutz, 1938; Greenland and Oades, 1968; El-Swaify and Emerson, 1975; Harder, 1978; Tamm, 1922; Deb, 1950; Mehra and Jackson, 1958; Schwertman, 1973; and others). Most of them concentrated on sesqui-oxides rather than aluminosilicate (allophanic) constituents. This is partially due to difficulties in selective extraction and synthesis of these compounds.

Deshpande, et al. (1968) examined the changes in soil properties associated with the removal of iron and aluminum oxides. They reported that Al oxides extraction from soils decreased the stability of aggregates, increased the proportion of recovered clay and silt but had little effect on the swelling. They suggested that the reduction of specific surface area due to the removal of iron oxides'
and the relatively slight changes in physical properties observed, indicated that iron oxides in the clay fractions were present primarily as small, discrete particles. Giovannini and Sequi (1976) observed changes in soil aggregate stability by introducing acetylacetone in benzene as a metal (iron and aluminum) extractant. They found, using soils containing total Fe:Al percent ratio were in between 7.8:8.6 and 4.3:10.1, that such extraction did not change particle size distribution but decreased the water stability of soil aggregates, and this decrease was closely related to the extent of the extraction of iron and aluminum. They postulated, through observation of the extraction of metals (essentially bound to organic matter) that the bonding, which exerts a protective action on soil aggregates, is weakened at the junctions of polymeric chains after the removal of metals so that the stability to the disrupting action of water is decreased. El-Swaify and Emerson (1975) criticized the destructive approach as a tool for investigating the role of cementing agents, advocating a synthetic approach instead. They illustrated that both Fe- and Al-hydroxides can be effective in reducing clay swelling and increasing aggregate stability. Later, El-Swaify (1976) showed that charge characteristics of the cementing agents and clay substrates are important parameters for deciding ultimate structural stability.
Wada and Kubo (1965) successfully synthesized and studied amorphous aluminosilicates as their analogues for better understanding of their natures. Aluminosilicates with SiO$_2$/Al$_2$O$_3$ molar ratios of 0 to about 4 were synthesized using SiO$_2$/Al$_2$O$_3$ molar ratios in parent solutions (tetraethyl orthosilicate and aluminum chloride) ranging from 0 to 8.5 by aging for periods from one day up to nearly one year.

Koizumi and Ueda (1976) also tried to synthesize aluminosilicates from aqueous solutions. They found that the solubility of solids gels depended upon the cementation of alumina. Consequently, increasing the initial alumina concentration resulted in decreasing the solubility of amorphous solids.

More recently, Perrot (1977a) also synthesized a range of amorphous aluminosilicates to study surface charge characteristics. He found that only negative charges could be detected in hydrous silica and the most siliceous aluminosilicate [(Al/Al+Si)=0.29], and only positive charges were detected in the more aluminous aluminosilicates and the soil allophenes. In all cases, the surface charges were pH dependent and in the aluminosilicate series, negative charge decreased and positive charge increased with increasing Al/Al+Si.

Fey and LeRoux (1977) tried to measure and quantify the properties of the poorly crystalline components in
sesquioxidic soil clays using synthetic aluminosilicates as well as sesquioxidic soil clays. They found that acid ammonium oxalate was superior to alkaline reagents for extracting amorphous aluminosilicates and alumina from these soils and from synthetic aluminosilicates \((\text{Si}_2\text{O}_5/\text{Al}_2\text{O}_3=0.91-2.25)\). It was also concluded that the role of amorphous (oxalate-soluble) alumina in governing physico-chemical properties is generally less than that of the poorly crystalline Al-substituted iron oxide component.

Cloos et al. (1969) reported, using synthetic amorphous silico-aluminates, that the Al:Al+Si ratio was the determining factor for phosphate adsorption and availability. Increasing aluminum content in the amorphous phase increased phosphate adsorption and decreased its availability, because of increasing complexity and hence a decreasing solubility of the hydroxyaluminum polymers in the amorphous phase.

**D. Effect of dehydration on Physico-Chemical properties**

Kanehiro and Sherman (1956) reported reduction in C.E.C. upon oven drying and sun drying for 100 days in glass house of 20-30% and 28-36% for Hilo soil, and 55-75% and 42-66% for Akaka soil, respectively. Sherman et al. (1964) showed that the drying of Typic Hydrandepts resulted in significant changes in many physico-chemical properties, and hydrated amorphous Al and Fe oxides rather than allophane were important in phenomena such as irreversible
shrinking and loss of C.E.C. occurring in the Akaka soil upon dehydration. Furthermore, when drying proceeded beyond a certain point, yet undefined, such changes were not reversible upon rewetting. They further presumed that the drying process, even at ordinary room temperature, enhanced transformation of X-ray amorphous colloidal constituents into crystalline minerals. Kubota (1972) investigated the approximate suction at which irreversible bonding of clay into sand-sized grains occurred upon drying. He revealed that (1) the clay and silt-sized fractions decreased by forming fine sand-sized grains when pF exceeded 3.5 (3.0 bar) and coarse sand-sized grains about pF 5.0 (100.0 bar), (2) no further change was observed in the distribution of particle sizes above pF 5.5 (316 bar). Following dehydration, Kavanagh, et al. (1976) examined the changes in surface reactivity for synthetic gibbsite, geothite, and naturally occurring clays. They observed a reduction in adsorption of a neutral polymer (polyvinyl alcohol) on synthetic minerals upon drying. This was attributed to a reduction in accessible surface area following aggregate formation rather than to a change in surface properties of the substrate. Electrophoretic data indicated that the thickness of the adsorbed layer on both clays and oxides is in excess of 10 nm at high concentrations of the polymer.
Similarly, Gallez, et al. (1976) found, in studies of surface and charge characteristics of tropical soils, that the surface area measured by Ethylene Glycol Monoethyl Ether (EGME) was higher (2-3 times) than by BET-N$_2$ gas adsorption. This was attributed to a loss of surface area by the drying of amorphous constituents in these soils and/or adsorption of a second layer of EGME on the surface following chemisorption of the first layer.

Warkentin and Maeda (1974) indicated that shrinkage and plasticity were the properties of allophane which changed most markedly upon drying. Both were altered in the following order of severity: oven drying > air drying > freeze drying. They also suggested that plasticity characteristics of allophane, namely a high liquid limit, high plastic limit, and a decreased plasticity index on drying could be a basis for rating the amount and nature of allophane in soils. Warkentin (1976) compared the changes in physical properties upon drying, among allophane, crystalline mineral soils and constant volume soils which do not exhibit much swelling. He found that the water retention for allophane soils followed a four parameter curve, i.e., it was determined by water potential, water content, bulk density or percent saturation, and the water content to which the sample was previously dried. The water retention curves for crystalline mineral soils, and for constant volume soils, however, were only determined
by the first three and the first two parameters, respectively. El-Swaify and Lim (1976) found, in their study of Hawaii's Typic Hydrandepts, that swelling was responsible for the majority of retained water in field moist soils, and that dehydration of these soils under defined low relative humidity resulted in significant reduction in water retention upon rewetting. They attributed observed changes to physical changes rather than mineralogical reasons. They also suggested that drying over $P_2O_5$ was favored over oven drying for more accurate assessment of water contents in such soils.

On the other hand, Yamamoto and Anderson (1967, 1973) revealed one of the practical implications of the dehydration of Hawaii's forest soils. They found that the erodibility indices were related to parent material, rainfall, and prevailing vegetative type. Parent material interaction with vegetative type was the most important factor affecting water stable aggregates. They consequently suggested a need for establishing extended ground covers to provide a satisfactory level of protection for different soils under prevailing rainfall conditions. El-Swaify and Dangler (1976) indicated that the erodibility of most of Hawaii's soils was well-related to aggregate stability, clay and sesquioxide contents, and soil acidity, all of which increased in magnitude with high intensity of weathering. Wood (1977) found, comparing hydrologic differences
between selected forested and agricultural soils in Hawaii, that the infiltration rates were higher for soils under forest than cultivated soils. The mean weight diameter (MWD) of soil aggregates were larger on most of his forested subsites than cultivated subsites. But the percent of aggregates less than 0.25mm in size was generally higher in the nonforest subsites. He concluded that the forested soils could be considered hydrologically superior in terms of water intake. They accept water faster and have greater porosities and larger, and probably less erodible aggregates than nonforest covered soils.

E. Alternative dehydration techniques for study of soil structure

Oven drying at 105°C has been a universally acceptable method of dehydration, assuming only adsorbed or hygroscopic water of substances are removed. However, Weiser and Milligan (1934), among many workers, elaborated on the dehydration process for synthetic gibbsite and presented an accurate dehydration isobar (curve), plotting $H_2O/Al_2O_3$ mole ratios against temperatures. This isobar showed a very steep decomposition of gibbsite in the range of 100-200°C. They showed that the $H_2O/Al_2O_3$ mole ratio changed from 3.0 to nearly 0.5 indicating a maximum possible water loss of 44.5% as a result of heating in this temperature range. Grim (1953) described the dehydration characteristics of various soil constituents against
temperature. He indicated that most soils, particularly allophane enriched, showed continuous loss of water from temperature range 0 to near 1000°C without any plateau. Jackson (1956) also indicated possible loss of structural water from gibbsite at around 100°C. These results created a necessity of conducting dehydration by means other than heat-drying, generally using certain substances as desiccants which provide a relative humidity of zero (O'Brien, 1948), with such drying by definition only "structural" water of soil mineral (Blackwood, et al., 1963). Lim (1976) reported that water content of selected volcanic ash soils dried equally under P$_2$O$_5$ drying and for freeze drying. Both were always higher than those for oven-dried samples. Most examined physico-chemical properties of these samples were drastically changed after oven and P$_2$O$_5$ drying. Brydon, et al. (1963) described the treatment of "lyophilization" or "freeze drying." A sample is quick-frozen to freeze the water in suspension in place without migration to prevent formation of ice-crystal. Secondly, the frozen water should be removed by sublimation without allowing liquid presence in the system so as to prevent capillary forces. They found, examining the samples dried by this technique, that Wyoming bentonite lost 3.0% H$_2$O when oven dried at 100°C. However, there was no mineralogical difference between original and oven dried samples. Due to the
importance of speed in freezing the samples, many workers tested freezing temperature against sample thickness. Pryde and Jones (1952), for example, found that the critical temperature at which migratory recrystallization stops was between \(-125^\circ C\) and \(-150^\circ C\), and this was confirmed by Meryman and Kafig (1955). Rosenquist (1959) suggested a lyophilized clay gel retained its original gel structure as essentially unaltered. However, Lopoz-Gonzalez and Vasquez (1959) suggested that the gel structure after lyophilization would be destroyed during the sublimation process but not the initial freezing stage. Ahlrichs and White (1962) showed that the basal spacing of freeze-dried Ca or Na bentonites was 12\(\AA\) and could be reduced to 10\(\AA\) on oven-drying. In addition, by microscopic observation of the lyophilized sample, they concluded that both the initial quick-freezing and the sublimation processes greatly altered the original gel structure. Rowell and Dillon (1972) reported that the ability of clay to move ahead of an ice-liquid interface was dependent upon the rate of freezing, the particle size, the release of dissolved air from the water through its probable effect on local freezing rates, and on the electrolyte concentration, all through their effects on interparticle forces and particle mobility. A freezing rate of less than 1 cm per hour still moved flocculated clay in most cases. Perrot (1977b) observed that the
crystallization of ice during the preparation of soil clays for freeze drying could cause aggregation. He suggested the addition of ethanol up to 4% into soil clay suspension to prevent undesirable aggregation during the freezing and to prevent the loss of fine clay particle through stream of vacuum during drying.

From the above, it is clear that capillary forces are principally responsible for formation of aggregates, upon shrinkage and drying of soil suspension. Therefore, reduction or elimination of liquid-vapor interfacial tension in drying process should result in a reduction of shrinkage. From this recognition has emerged a technique to eliminate capillary forces which is called critical point drying. Figure 6 illustrates the change of carbon dioxide from a gas to a liquid state as a function of temperature and pressure. It shows that at high temperature (48.1°C), CO₂ gas can never change to a liquid state regardless of the pressure applied. Increased pressure to 60 atm at 21.5°C can produce liquefied gas as indicated by the volume decrease at constant pressure between points D and B of the PV isotherm. At 31.3°C the portion BD (at 21°C) is reduced to a single point C, the critical point, at a pressure of 77 atm. The pressure, temperature, and volume associated with critical point are defined as critical point, critical pressure, temperature, and volume, respectively. Increases or decreases in pressure and
temperature from values of these critical points are required to change from the liquid to the gas state. At the critical point itself, however, the two phases coexist in a state of continuity with no meniscus or surface tension separations.

Fig. 6. Phase diagram for CO$_2$, showing regions of existence of states (Partington, 1949).

Diamond (1970) was the first to apply this technique for drying soil samples. By manipulating temperature and pressure, he brought the water in the sample slowly into the thermodynamic "critical region" without being expelled
from the clay. However, Greene-Kelly (1973) pointed out that the condition for critical point evaporation of water is precisely those hydrothermal conditions that favor rapid synthesis and alteration of clay minerals because of the high critical temperature of water (370°C). This fact prompted the substitution of water by other liquids in the soil pores prior to critical point drying. There are two major conditions (characteristics) required of a water substitute in this system: (1) it should be water miscible and (2) it should have a low critical temperature (at least below 100°C).

Table 2 summarizes the critical temperatures and pressures for a number of compounds.

Greene-Kelly (1973) found that the best method to minimize soil structural disturbance of soil water was by ethanol, then by liquid carbon dioxide which could then be removed at its low critical temperature. He reported that in this system, the soil shrinkage was minimal, no visible changes occurred, and no change on pore size distribution was observed by the mercury intrusion technique.
Table 2. Some compounds and their critical temperature and critical pressure

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>C.T. (°C)</th>
<th>C.P. (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>below -220°C</td>
<td>--</td>
</tr>
<tr>
<td>Fluorine</td>
<td>F₂</td>
<td>-155°</td>
<td>25</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>-146°</td>
<td>35</td>
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<td>Carbon Monoxide</td>
<td>CO</td>
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<tr>
<td>Argon</td>
<td>A</td>
<td>-121°</td>
<td>50.6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>-119°</td>
<td>50.8</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>NO</td>
<td>-93°</td>
<td>64</td>
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<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
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<td>73</td>
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<tr>
<td>Nitrous Oxide</td>
<td>N₂O</td>
<td>+35°</td>
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<td>HCl</td>
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<td>93</td>
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<td>Hydrogen Sulphide</td>
<td>H₂S</td>
<td>+100°</td>
<td>92</td>
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<td>Methane</td>
<td>CH₄</td>
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<td>57</td>
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<td>Ammonia</td>
<td>NH₃</td>
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<td>113</td>
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<td>Selenuretted Hydrogen</td>
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<td>Sulphur Dioxide</td>
<td>SO₂</td>
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<td>Ethane</td>
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<td>Ethanol</td>
<td>C₂H₅O</td>
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<tr>
<td>Acetylene</td>
<td>C₂H₂</td>
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<td>68</td>
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<td>Cyclopentane</td>
<td>C₅H₁₀</td>
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<td>Benzene</td>
<td>C₆H₆</td>
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<td>Chloroform</td>
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<td>Carbon Tetrachloride</td>
<td>CCl₄</td>
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<tr>
<td>Water</td>
<td>H₂O</td>
<td>+370°</td>
<td>196</td>
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</table>

MATERIALS AND METHODS

A. Materials

1. Soils

   The following three soil series were selected for this study: (a) Kaiwiki soil, (b) Hilo soil, and (c) Puaulu soil.

   The three soil sampling locations are shown on the Hawaii Island Map, Figure 7.

![Map of Hawaii Island showing soil sampling locations](image)

Fig. 7. Soil sampling locations on the Island of Hawaii (A Kaiwiki, B Hilo, C Puaulu)
As shown on the map (Fig. 7), sampling location A (Kaiwiki soil series) was at the end of Kaiwiki Road, near the top of the hill above Kaiwiki village and within the Kaiwiki forest. Location B for Hilo soil series was 5.0 miles north of Hilo and upper side of Highway 19 between Onamea and Hilo mills. Location C for Puaulu soil series was near the University of Hawaii's Volcano Experimental Station in an area of natural vegetation.

Some information on these three soil series is presented in Table 3. Selection of these soils was based on their varying stages and contents of amorphous materials. It is hypothesized that the "irreversible" behavior of Hydrandepts upon drying is strongly influenced by their contents of sesquioxidic constituents as well as the non-crystalline materials acting as "cementing" agents.

Volcanic ash soils, such as those selected for this study, were subjected to many previous investigations. Fieldes and Swindale (1954) stated that the weathering of volcanic glass produces allophane. Swindale and Sherman (1964) claimed that volcanic glass initially weathers to yellow, brown and orange colored amorphous aluminosilicates called paragonite and that more advanced stages of weathering produced allophane and then oxides. Loganathan (1967) observed that weathering was enhanced with increasing rainfall and temperature, and hence, the conversion of
allophane formed from the primary minerals to gibbsite or other minerals also increased.

The differences in profile characteristics, chemical and physical properties and mineralogy, including amorphous and organic matter contents of the three soils are presented in Table 5 and Figures 10 to 12. These have been discussed by Voss (1969), Chan (1972), Coswami (1972), Soil Conservation Service (1973), Keng (1974), and Balasubramanian and Kanehiro (1976). The Puaulu soil series, however, was not subjected to thorough investigation.

2. **Synthetic minerals**

The following seven minerals were synthesized for this study:

a. Iron hydrous oxide monohydrated (A) (akaganeite)
b. Iron hydrous oxide monohydrated (B) (goethite)
c. α-iron oxide (hematite)
d. Aluminum hydroxide (gibbsite and bayerite mixture)
e. Aluminosilicate (non-crystalline) (SiO₂/Al₂O₃=0.5)
f. Aluminosilicate (non-crystalline) (SiO₂/Al₂O₃=1.0)
g. Aluminosilicate (non-crystalline) (SiO₂/Al₂O₃=2.0)

These minerals are known as major constituents having their own characteristics in tropical soils which are developed through laterization. All or some of these minerals, except hematite, are known to exist in Hydran-depts, and may contribute to the irreversible behavior of
Table 3. Some information on selected soils

<table>
<thead>
<tr>
<th>Soils</th>
<th>Soil classification</th>
<th>Origin</th>
<th>Elevation of occurrence (m)</th>
<th>Rainfall (mm/year)</th>
<th>Total area on Island of Hawaii (ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiwiki</td>
<td>Thixotropic, isothermic, Typic Hydrandepts</td>
<td>Hydrol Humic Latosols</td>
<td>Volcanic ash</td>
<td>240-455</td>
<td>3,750-5,000</td>
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<tr>
<td>Hilo</td>
<td>Thixotropic, isohyperthermic, Typic hydrandepts</td>
<td>Hydrol Humic Latosols</td>
<td>Volcanic ash</td>
<td>near sea level to 240</td>
<td>3,050-4,600</td>
</tr>
<tr>
<td>Puaulu</td>
<td>Medial, over thixotropic, isomesic, Typic Hydrandepts</td>
<td>Regosols</td>
<td>Volcanic ash</td>
<td>1,150-1,370</td>
<td>2,280-3,050</td>
</tr>
</tbody>
</table>
these soils upon dehydration. Because of the importance of these minerals in Hydrandepts, studies on their inherent characteristics and roles have been performed individually.

B. Methods

1. Soil preparation

Each soil sample was collected at several different depths. These were selected visually in the field by variation in color and structure with the guidance of available profile descriptions (Soil Conservation Service, 1973). However, only two different depths for each soil series were intensively used throughout this particular experiment. The codes for all sampling locations and depths for the three soil series are shown in Table 4.

Upon collection, the individual soil samples were well-mixed and stored in triple vinyl bags at a low temperature (5°C) to preserve the original properties, especially moisture content, as well as possible.

2. Synthesis of minerals

The minerals used in this experiment were synthesized following the methods described by El-Swaify and Emerson (1975), for iron hydroxide monohydrated (A) and (B), by Gastuche (1964) and Lim (1976) for aluminum hydroxide, and by Siffert (1967) and Wada and Kubo (1975) for aluminosilicates (non-crystalline, SiO$_2$/Al$_2$O$_3$=0.5, 1.0, and 2.0), respectively.
<table>
<thead>
<tr>
<th>Code</th>
<th>Depth (cm)</th>
<th>Soil descriptions</th>
<th>Code</th>
<th>Depth (cm)</th>
<th>Soil descriptions</th>
<th>Code</th>
<th>Depth (cm)</th>
<th>Soil descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-6</td>
<td>5-30</td>
<td>Subangular blocky</td>
<td>H-3</td>
<td>15-20</td>
<td>Subangular blocky</td>
<td>P-13</td>
<td>10-30</td>
<td>Massive, sandy black soil layer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dark brown layer</td>
<td></td>
<td></td>
<td>Surface layer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-7</td>
<td>40-50</td>
<td>Massive structure</td>
<td>H-4</td>
<td>120-150</td>
<td>Subangular blocky</td>
<td>P-14</td>
<td>60-75</td>
<td>Subangular blocky</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reddish brown layer</td>
<td></td>
<td></td>
<td>Sub-surface layer</td>
<td></td>
<td></td>
<td>Dark reddish-brown layer</td>
</tr>
<tr>
<td>K-8</td>
<td>60-75</td>
<td>Subangular blocky</td>
<td>H-5</td>
<td>below 210</td>
<td>Subangular blocky</td>
<td>P-15</td>
<td>75-100</td>
<td>Subangular blocky</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blackish brown layer</td>
<td></td>
<td></td>
<td>Drown layer</td>
<td></td>
<td></td>
<td>Black resiliated layer</td>
</tr>
<tr>
<td>K-9</td>
<td>75-90</td>
<td>Subangular blocky</td>
<td>H-25</td>
<td>below 210</td>
<td>Hard clods of rotten rock within gray thin layer</td>
<td>P-16</td>
<td>100-120</td>
<td>Friable yellow accumulation within (P-17) layer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brown layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-10</td>
<td>90-100</td>
<td>Subangular blocky</td>
<td></td>
<td></td>
<td></td>
<td>P-17</td>
<td>100-120</td>
<td>Massive, friable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blackish brown layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dark reddish brown layer</td>
</tr>
<tr>
<td>K-11</td>
<td>105-120</td>
<td>Subangular blocky</td>
<td></td>
<td></td>
<td></td>
<td>P-18</td>
<td>120-125</td>
<td>Red consolidated layer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brown layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-12</td>
<td>below 120</td>
<td>Subangular blocky</td>
<td></td>
<td></td>
<td></td>
<td>P-19</td>
<td>below 125</td>
<td>Dark gray layer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dark reddish brown layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
a. **Iron hydrous oxides.**—Iron hydrous oxides were synthesized from $\text{N FeCl}_3$ solution by slow titration (more than 4 hours for 2 liters of $\text{FeCl}_3$ solution) with $\text{N NaOH}$ up to pH of 6.0 and 12.0 for the iron hydrous oxide monohydrated (A) and (B), respectively.

b. **Aluminum hydroxide.**—Aluminum hydroxide was synthesized from 0.1N-$\text{AlCl}_3$ solution by slow titration (more than 8 hours for 2 liters of $\text{AlCl}_3$ solution) with 0.1N-$\text{NaOH}$ to pH 4.5.

c. **Aluminosilicates (non-crystalline).**—Tetraethyl orthosilicate [$\text{Si(OCH}_2\text{CH}_3)_4]$ solution, 140 ppm, and three different concentrations of $\text{AlCl}_3\cdot6\text{H}_2\text{O}$ solutions, 390 ppm, 145 ppm, and 68 ppm (which produce $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 0.7, 1.5, and 4.0, in solution upon mixing, respectively) were prepared. The pH of these mixtures were adjusted to 7.0 by $\text{N NaOH}$ solution applied at a rate of 0.3-0.5 per minute. Siffert (1967) suggested use of tetraethyl orthosilicate as the Si source solution concentration maximum 140 ppm, because of silicon solubility.

Wada and Kubo (1975) reported that solutions with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 0.7, 1.5, and 4.0 produced precipitates with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 0.5, 1.0, and 2.0, respectively. The obtained precipitates were aged for 2 months. All above precipitates (synthesized minerals) were dialysed in deionized water within semi-permeable
visking cellulose bags until free of Cl\textsuperscript{−}. This was ascertained by AgNO\textsubscript{3} testing. They required 2-3 weeks for dialysis while changing the distilled water twice a day.

d. \textit{α-iron oxide}.--This mineral was obtained simply by the firing of either synthetic iron hydrous oxide (A) or (B) at 550°C for more than 4 hours. The resulting hematite was passed through a 140 mesh sieve (0.1mm opening), and then stored in a distilled water suspension.

3. Drying treatments

a. \textit{Oven drying}.--50g of soils and synthetic minerals were subjected to oven drying at 105°C for a period ranging from 24 to 48 hours until a constant weight was obtained.

b. \textit{P\textsubscript{2}O\textsubscript{5} drying}.--50g of soils and synthetic minerals were placed in a desiccator over P\textsubscript{2}O\textsubscript{5} (anhydrous phosphorus pentoxide) for three weeks or more until a constant weight was reached.

c. \textit{Freeze drying}.--Suspended soils and synthetic minerals were frozen quickly in liquid nitrogen in pyrex flasks. These frozen samples were then connected to a Virtis Freeze Dryer for a period of up to 5 days, the time required for complete drying being dependent on sample size.
d. Critical point drying.--The procedure described by Greene-Kelly (1973) was applied in this method. A certain quantity of each sample was immersed in successively higher concentrations of ethanol in water each for 24 hours to gradually replace water in samples by ethanol without structural damage. Ethanol concentrations of 25%, 50%, 75%, and absolute were employed. The remaining steps were conducted in a specially designed pressure bomb bearable to pressure up to 100 atm. The ethanol in samples was replaced with carbon dioxide by submerging the sample into liquid CO$_2$ for 30 minutes repeatedly about 3-5 times. The sample was dried out by evaporating the last batch of liquid carbon dioxide after warming the closed bomb to 35°C slowly and allowing the gas to escape slowly with venting speed at around 0.5 atmospheric-liter per minute.

4. Chemical analysis

   a. pH measurement.--The pH was measured for samples suspended in water at a ratio 1:5 for 30 minutes on an Orion Research Ionalyzer. For $\Delta$ pH measurement, the pH of each sample was measured following 24 hours equilibrating periods (stirring occasionally) both in water and in N KCl solution, at 1:1 sample to solution ratio. $\Delta$ pH was calculated as the difference between pH values in water and N KCl.
b. **Organic matter determination.**—Oxidizable organic matter was determined following the Walkley-Black method (Jackson, 1967).

c. **Silica and Aluminum determination.**—To determine SiO$_2$/Al$_2$O$_3$ ratio, precipitated aluminosilicate solids were digested using fluoric acid and hydrochloric acid in a specially designed bomb (Parr, 1976). Si and Al in this digested solution was determined with Perkin Elmer (Model 603) atomic absorption spectrometer.

5. **Physical analysis**

   a. **Moisture content measurement.**—To determine the moisture content of original soils and synthetic minerals, samples were placed in the oven at 105°C for 24 hours or until a constant weight was obtained.

   b. **Particle size distribution.**—10 to 20g samples were shaken for 20 minutes in a Spex Mixer Mill as mixtures containing a soil:water ratio of 1:5 and 1:3 for wet samples and dried samples, respectively. After shaking, samples were suspended in one liter cylinders using distilled water and <2um and <53um particles were measured at a depth of 20 cm using a plummet balance (modified from Marshall, 1956) after settling times of 16 hours and 80 seconds, respectively. The >53um particles were sieved directly through a 270 mesh sieve after silt and clay sizes were measured.
c. **Water stable aggregate measurement.**—10 to 20g samples were equilibrated at 28% relative humidity in a desiccator and then soaked in water at zero water suction for 30 minutes. They were subsequently subjected to a wet sieving operation as described by Kemper and Chepil (1965) for 30 minutes. The mean weight diameter (MWD) proposed by van Bavel (1950) was calculated as an index for changes in structural stability of samples from the data obtained by wet sieving operation.

d. **Water retention measurement.**—Water retention characteristics of samples were scanned following a drying cycle from saturation moisture content to oven drying range. The hanging water column technique was employed for water retention characteristics measurement from 0 to 150 cm suction, and the 15 bar ceramic extractor was used beyond this range and up to 15 bar pressure.

e. **Control of sample moisture content.**—In order to determine the extent of irreversibility, five to seven different moisture content levels, above, below, including the shrinkage limit were selected. Samples were allowed to attain selected moisture contents through drying from the original moisture content of the soils.

f. **Shrinkage measurement.**—Shrinkage was measured following ASTM procedure (Designation: D427-61) (ASTM, 1977). According to this method, an appropriate amount of
soil paste was made by mixing a soil sample with distilled water. A special shrinkage dish made of circular porcelain or monel metal (milk dish), having a flat bottom (with standard dimensions of 44.4 mm in diameter, and 12.7 mm in height), was completely filled with sample paste while excluding air bubbles and the excess paste was removed by straightedge. The weight of the wet sample and the shrinkage dish, the volume of the shrinkage dish, and the volume of dried sample were measured. The dish was placed on a bench until the sample reached desired moisture content. The dried sample volume was measured by immersing it in a known volume of mercury. The shrinkage limit (SL), was calculated as:

\[ SL = W \times \left( \frac{(V - V_o)}{W_o} \right) \times 100 \]  

where,

- \( W \) = moisture content of wet soil (weight basis),
- \( V \) = volume of wet soil pat,
- \( V_o \) = volume of dried soil pat, and
- \( W_o \) = mass of oven-dried soil pat, respectively.

g. **Plastic limit.**—Again the ASTM procedure (Designation: D424-59) (ASTM, 1977) was followed to measure plastic limit. A portion of the foregoing paste prepared for shrinkage limit was rolled in a glass plate by hand. This procedure was repeated at lower water contents so
that the moisture content at which the sample is shaped into a wire about 1/2 inch (12.7 mm) long and about 1/8 inch (3.2 mm) in diameter without crumbling (with rolling rate between 80 to 90 strokes per minute) could be determined.

h. **Liquid limit.**--The ASTM (ASTM, 1977) has recommended the procedure for liquid limit measurement (Designation: D423-66) as follows. An appropriate amount of sample was placed in a liquid limit apparatus and thoroughly mixed with water. The sample was levelled and trimmed to a depth of 1 cm at the point of maximum thickness. The sample was then divided into two parts by a firm stroke of the grooving tool through the center line. The number of crank blows necessary to bring the two paste halves into a contact of 1/2 inch long was determined. This procedure was repeated at different paste water contents so that the water content at which the two halves come into contact at 25 blows was graphically determined.

i. **Viscosity measurement.**--The viscosity measurement was conducted on a series of samples suspended within defined soil water ratios using a Fisher Improved MacMichael Viscometer (Cat. No. 15-346-500) (Dangler, 1973, and Fisher Scientific Instrument Manual for MacMichael Viscometer). The accuracy of this instrument and its operation was checked by measuring the viscosities of 20, 40, 60, and
70% of sucrose solutions at 22.5°C. The obtained viscosity values by this viscometer were converted to poise unit using the formula:

$$\mu = \frac{N \cdot A}{4 \pi h} \cdot \frac{1}{\omega}$$

(4)

where:

$\mu$ = viscosity in poises,

$N$ = the torsional moment of the wire in dyne-cm 
[981 x the g-cm/M° resistance of the wire (its certification constant) x the rotation of the wire in M° (dial deflection in degrees MacMichael)],

$A = \frac{1}{r_1} - \frac{1}{r_2}$, where $r_1$ = the outer radius of the plunger in cm and $r_2$ = the inner radius of the sample cup in cm,

$h$ = depth of immersion of the plunger in cm, and

$\omega$ = the speed of revolution of the cup in radians per second (1 revolution/sec. = $2\pi$ radians/sec.).

Necessary corrections for all measured sample viscosities were made by the equation that is obtained based on correlation between measured and tabulated sucrose viscosity values:

$$\log Y = 1.724 \log X + \log 0.04143$$

(5)

where:

$Y$ is corrected viscosity, and

$X$ is measured viscosity experimentally.

j. Specific surface measurement by water vapor adsorption.—A series of 5 sub-samples saturated with water
were placed in 5 different desiccators. The relative humidity of each desiccator was controlled by different chemicals. Saturated solutions of KNO₃, NaCl, Mg(NO₃)₂·6H₂O, MgCl₂·6H₂O, and LiCl·H₂O were used to control the relative humidities in these desiccators at 92.0, 76.0, 53.4, 33.2, and 12.0%, respectively. Water contents after 2-3 weeks of equilibrium were obtained by oven drying. Resulting sorption were analyzed for surface area calculations by the B.E.T. equation (Brunauer, et al., 1938) for multilayer adsorption:

\[
P/V(P_o-P) = 1/V_mC + (C-1)P/V_mC P_o
\]

where:

- \(P_o\) = saturation pressure of the adsorption vapor over the sample at the given temperature,
- \(P\) = partial pressure of the adsorption vapor,
- \(V\) = total volume (at STP) of adsorbed vapor on the surface of the sample,
- \(C\) = constant for the net adsorption energy, and
- \(V_mC\) = volume (at STP) of adsorbed vapor when whole sample surface is covered with a monomolecular layer.

In this equation, a plot of \(P/V(P_o-P)\) versus \(P/P_o\) is presumed to give a straight line whose slope and intercept are \((C-1)/V_mC\) and \(1/V_mC\), respectively. These values are used to solve for \(V_mC\) and \(C\). The following equation was then used to calculate sample surface area from \(V_mC\) with water vapor as an absorbate.
\[ S = (10.5 \times 10^{-20}) (V_m \cdot A/M) \]  

(7)

where:

- \( S \) = surface area in \( m^2 \),
- \( A \) = Avogadro number, and
- \( M \) = molecular weight of water, respectively.

k. Specific surface measurements by \( N_2 \) gas adsorption.--Surface area of all the samples subjected to drying were measured using a Perkin Elmer Shell Model 212D Sorptometer with the continuous He and \( N_2 \) gases flow method. Samples were first degassed overnight in a sand bath at a temperature of 110°C while a continuous stream of He gas was passed through them in order to drive off any interfering moisture or gases. The continuous flow method consists of \( N_2 \) gas as adsorbate and He gas as an inert gas carrier being passed over a sample which is in liquid nitrogen at -183°C. Measurement of the amount of adsorbed \( N_2 \) on the sample was then made following its displacement from the sample by a pure stream of He gas.

1. Particle density measurement.--10 to 20g of all the dried soil samples which passed through 140 mesh sieve as well as original (wet) soil samples were boiled in the presence of enough water (2/3 full of pycnometer) in pycnometer for 30 minutes and cooled overnight. The particle density was calculated on the oven-dry basis using the following formula (Blake, 1965):
\[
D_p = D_w (W_s - W_a) / (W_s - W_a) - (W_{sw} - W_w)
\]  
(8)

where,

- \(D_w\) = density of water in gram per cubic centimeter (g/cm\(^3\)) at temperature observed,
- \(W_s\) = weight of pycnometer plus soil corrected to oven-dry condition,
- \(W_a\) = weight of pycnometer filled with air,
- \(W_{sw}\) = weight of pycnometer filled with soil and water, and
- \(W_w\) = weight of pycnometer filled with water at temperature observed, respectively.

m. Scanning electron micrography.--Scanning electron micrographs of samples subjected to four different drying treatments were taken in an effort to observe differences in bonding association among constituents in samples subjected to different dehydration treatments. A Cambridge Stereoscan S-4-10 scanning electron microscope was used to examine samples subjected to four different drying treatments. Operating conditions included an applied voltage of 10 Kev, a working distance of 5-10 mm, and a take-off angle of 35°.

6. Mineralogical analysis

a. X-ray diffraction analysis.--Mineralogical identification of soils and synthetic minerals was carried out by a Philips Norelco X-ray Diffractometer using Cu ka radiation and a graphite monochrometer. For each soil, the diffraction analysis was conducted on two sub-samples
consisting of clay and silt sized particles following saturation with $\text{MgCl}_2$, and the other with $\text{KCl}$. Excess salts were washed out by repeated shaking with distilled water and centrifugation until a negative test was obtained for $\text{Cl}^-$ in the supernatant solution. The resulting wet pastes were subjected to analysis on glass slides. Synthetic minerals were directly subjected to X-ray analysis without any pretreatment.
RESULTS AND DISCUSSION

A. Effects of different dehydration methods on soil properties

1. Characteristics of soil samples

a. Physico-chemical properties of original soil samples.--The important physico-chemical properties of soil samples are given in Table 5. Kaiwiki series, which was covered with bush as heavily as Puaulu series had the highest water content at the time of sampling. Considering this fact along with annual rainfall amount on these three series (Table 3), it might be speculated that these initial moisture contents were affected at least partially by vegetative cover as well as annual rainfall distribution on them.

Puaulu series had the highest pH and the only positive ΔpH values. On the contrary, the Kaiwiki and Hilo series showed low pH and negative ΔpH values. This indicates that both Kaiwiki and Hilo series have been weathered more extensively, losing larger amounts of bases.

Organic matter distribution within the Kaiwiki and Puaulu series was irregular. This was not the case for the Hilo series. This irregularity is due either to organic matter leaching from the surface layer downward to a position where organic matter chelation occurs with metallic
### Table 5. Some physico-chemical properties of original soil samples

<table>
<thead>
<tr>
<th>Code</th>
<th>Moisture (%)</th>
<th>P tit. (H₂O)</th>
<th>P tit. (KCl)</th>
<th>ΔpH</th>
<th>O.N. (%)</th>
<th>Soil texture (%)</th>
<th>Water retention (%) by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>clay    silt    sand  total</td>
<td>0 cm</td>
</tr>
<tr>
<td>K-6</td>
<td>201.14</td>
<td>4.05</td>
<td>5.04</td>
<td>-0.19</td>
<td>16.45</td>
<td>62.0  20.0  9.3  99.3</td>
<td>296.9  234.9  210.1  192.0  156.1  144.0  123.0  105.7  104.0</td>
</tr>
<tr>
<td>K-7</td>
<td>271.61</td>
<td>5.00</td>
<td>5.56</td>
<td>-0.48</td>
<td>9.42</td>
<td>50.0  41.0  8.2  99.2</td>
<td>316.6  291.6  261.1  255.0  239.0  232.0  176.3  166.0  151.0</td>
</tr>
<tr>
<td>K-8</td>
<td>301.60</td>
<td>5.22</td>
<td>5.50</td>
<td>-0.36</td>
<td>26.13</td>
<td>51.0  43.0  5.7  99.7</td>
<td>503.3  443.9  393.2  389.2  357.7  325.7  244.6  242.4  224.0</td>
</tr>
<tr>
<td>K-9</td>
<td>413.67</td>
<td>5.08</td>
<td>5.73</td>
<td>-0.65</td>
<td>2.40</td>
<td>47.0  41.0  13.1  101.1</td>
<td>536.3  487.2  447.7  439.6  402.2  323.3  289.2  266.6  254.0</td>
</tr>
<tr>
<td>K-10</td>
<td>365.34</td>
<td>5.04</td>
<td>5.74</td>
<td>-0.70</td>
<td>7.91</td>
<td>51.0  35.0  13.2  99.2</td>
<td>409.6  420.3  415.0  316.1  354.6  316.3  255.0  226.1  225.4</td>
</tr>
<tr>
<td>K-11</td>
<td>462.20</td>
<td>4.90</td>
<td>5.80</td>
<td>-0.90</td>
<td>0.41</td>
<td>42.0  41.0  17.1  101.1</td>
<td>576.5  537.5  499.0  495.1  400.3  402.0  351.3  305.2  299.0</td>
</tr>
<tr>
<td>K-12</td>
<td>437.31</td>
<td>4.90</td>
<td>5.73</td>
<td>-0.83</td>
<td>9.42</td>
<td>56.0  32.0  13.0  101.0</td>
<td>553.8  508.7  464.7  444.3  405.7  355.6  325.1  280.2  202.0</td>
</tr>
<tr>
<td>H-3</td>
<td>129.00</td>
<td>4.65</td>
<td>5.42</td>
<td>-0.59</td>
<td>9.41</td>
<td>50.0  28.0  13.4  99.4</td>
<td>176.8  173.2  149.6  135.0  127.4  119.0  98.5  90.0  88.3</td>
</tr>
<tr>
<td>H-4</td>
<td>141.45</td>
<td>4.64</td>
<td>6.25</td>
<td>-1.61</td>
<td>2.50</td>
<td>62.0  24.0  14.2  101.2</td>
<td>165.5  150.9  147.4  145.3  132.0  126.7  107.2  97.7  96.2</td>
</tr>
<tr>
<td>H-5</td>
<td>91.66</td>
<td>4.94</td>
<td>5.30</td>
<td>-0.44</td>
<td>2.09</td>
<td>57.0  43.0  1.5  101.5</td>
<td>133.3  111.0  98.1  96.1  90.4  85.6  73.7  65.4  61.0</td>
</tr>
<tr>
<td>H-25</td>
<td>65.00</td>
<td>4.77</td>
<td>6.25</td>
<td>-1.74</td>
<td>0.55</td>
<td>34.0  74.0  2.3  100.3</td>
<td>174.5  102.3  82.7  76.5  74.0  72.6  62.3  59.9  57.0</td>
</tr>
<tr>
<td>P-11</td>
<td>100.61</td>
<td>6.72</td>
<td>6.27</td>
<td>0.45</td>
<td>5.74</td>
<td>18.0  26.0  55.6  99.3</td>
<td>146.5  132.0  113.9  97.9  87.3  75.1  56.7  43.7  35.4</td>
</tr>
<tr>
<td>P-14</td>
<td>152.17</td>
<td>6.66</td>
<td>5.90</td>
<td>0.68</td>
<td>0.07</td>
<td>29.0  45.0  25.3  99.3</td>
<td>198.2  170.6  161.2  160.2  131.6  117.6  68.8  63.1  60.3</td>
</tr>
<tr>
<td>P-15</td>
<td>263.33</td>
<td>6.49</td>
<td>5.91</td>
<td>0.66</td>
<td>11.75</td>
<td>44.0  30.0  17.0  99.9</td>
<td>321.2  263.3  259.6  252.1  236.0  213.7  181.0  161.6  153.6</td>
</tr>
<tr>
<td>P-16</td>
<td>342.31</td>
<td>6.44</td>
<td>5.94</td>
<td>0.50</td>
<td>14.28</td>
<td>43.5  37.0  19.2  99.7</td>
<td>412.8  396.7  359.1  331.1  298.2  261.6  194.2  170.5  161.0</td>
</tr>
<tr>
<td>P-17</td>
<td>119.53</td>
<td>6.49</td>
<td>5.95</td>
<td>0.54</td>
<td>5.74</td>
<td>38.0  33.0  28.0  99.0</td>
<td>146.3  132.4  121.5  110.5  105.4  94.9  77.1  75.4  70.0</td>
</tr>
<tr>
<td>P-18</td>
<td>68.83</td>
<td>6.52</td>
<td>6.09</td>
<td>0.43</td>
<td>3.77</td>
<td>10.2  65.0  25.6  100.8</td>
<td>97.4  81.3  74.2  64.5  62.9  60.9  55.4  50.1  45.0</td>
</tr>
<tr>
<td>P-19</td>
<td>37.11</td>
<td>6.58</td>
<td>6.25</td>
<td>0.33</td>
<td>1.29</td>
<td>4.0  74.7  21.1  99.8</td>
<td>52.7  43.1  36.7  33.1  25.6  22.0  21.2  20.9  19.0</td>
</tr>
</tbody>
</table>
ions, or to burial of an organic surface horizon by subsequent volcanic ash deposits.

Particle size distribution analysis showed the Puaulu series to have the coarsest texture among the three series, thus emphasizing that it has been subjected to the least intensive weathering among the three soils. However, this soil also displays enrichment of clay sized particles in the 75-120 cm depth. Kaiwiki series shows irregular but relatively uniform contents of clay-sized particles throughout the profile.

Water retention data showed that Kaiwiki series is characterized by higher water retention throughout all layers than the other two soil series. It is apparent from the data that water retention is directly related to clay and/or organic matter contents, in these soils. Typical water retention characteristics of two profiles (surface and one sub-surface at depths of about 5-30 cm and 75-120 cm) from each soil series are compared in Figures 8 and 9. It is noted that water retention increased in the order of: Puaulu surface<Hilo surface and sub-surface<Kaiwiki surface<Puaulu sub-surface<Kaiwiki sub-surface.

b. Mineralogical properties of original soil samples. --Mineralogical constituents in all samples were identified by X-ray diffraction analysis. Figures 10-12
Figure 8. Water retention characteristics of surface and sub-surface layers of three soils (gravimetric base). (K-6), (K-12), (H-3), (H-4), (P-13), and (P-15) refer to Kaiwiki surface and sub-surface, Hilo surface and sub-surface, and Puaulu surface and subsurface, respectively.
Figure 9. Water retention characteristics of surface and sub-surface layers of three soils (volumetric base). (K-6), (K-12), (H-3), (H-4), (P-13), and (P-15) refer to Kaiwiki surface and subsurface, Hilo surface and sub-surface, and Puaulu surface and sub-surface, respectively.
show X-ray diffractogram patterns for the Kaiwiki, Hilo and Puaulu series, respectively.

The Kaiwiki series consists mainly of amorphous materials with some goethite and other iron oxides, and small amount of aluminum oxides. Non-crystallinity was gradually increased from profile top to bottom as reflected by virtually a single broad amorphous band encompassing the whole X-ray diffractogram. The enrichment of amorphous constituents throughout whole profiles is a result of the volcanic ash origin and the intensive weathering regime to which the soil is subjected. As shown from X-ray diffraction analysis for mostly clay fraction of the Hilo series, the three upper horizons contain a predominance of X-ray amorphous materials. However, the horizon H-25 (about 5 cm thick) which was a distinctive gray layer underlain below 200 cm, consisted of crystalline minerals. Diffraction peaks occurred at 4.82Å, 4.13Å, 3.33Å, and 2.52Å in all four horizons indicate the presence of gibbsite, goethite, quartz, and maghemite, respectively. In this soil, the X-ray amorphous band was gradually lowered and crystalline mineral portions were increased going down to lower horizons. The lowest gray horizon sampled contained a large proportion of hydrated iron and aluminum oxide minerals.

It should be mentioned also that there was difficulty in identifying minerals in the diffraction range of 2θ<10. Chan (1972) analyzed the mineralogy of selected
Figure 10. X-ray diffractogram for profile samples of Kaiwiki original soil.
Figure 11. X-ray diffractogram for profile samples of Hilo original soil.
Figure 12. X-ray diffractogram for profile samples of Puaulu original soil.
profile samples from the Hilo series to a depth of 124+ cm. He obtained exactly the same X-ray diffractograms as shown here for untreated (mostly clay) fractions. However, he obtained 14Å, 10Å, and 7Å peaks clearly after treatments with hydrogen peroxide and "Tweneboah solution." The 10Å and 7Å were previously detected by Voss (1969). Earlier, Kawasaki and Aomine (1965) have reported that vermiculite-chlorite intergades and imogolite possessed similar peaks. Consequently, Chan (1972) supplemented his work by electron micrographs and concluded that the 14Å, 10Å, and 7Å peaks were likely for chloritic minerals and also indicated the possible presence of imogolite.

Wada and Wada (1976) have reported, investigating clay mineralogy of B horizons of two Hydrandepts (Akaka, and Hilo series), that the B horizons of Hydrandepts were characterized by predominance of hydrous non-crystalline alumina and iron oxides associated with considerable amounts of humus and with very small amounts of silica. Allophane, allophane-like constituents and imogolite were present but in minor amounts. Gibbsite, geothite, chlorite and illite were also detected. Lim (1976) estimated the contents of major minerals in Hilo surface soil (5-20 cm) of 60-65% amorphous minerals, 20-25% gibbsite, and around 10% of quartz.

The X-ray diffractogram of Puaulu series profile samples (Fig. 12) revealed that this soil also consisted
of mainly amorphous materials except for the lowest horizon. The broad amorphous diffraction bands became gradually less prominent with increasing soil depth, showing the highest amount of crystalline minerals in the lowest horizon. These were feldspar, olivine, quartz with small amounts of goethite, maghemite and TiO$_2$ minerals. The predominance in this horizon of primary minerals (such as feldspar, olivine, and quartz) indicated that profile development in this young soil is still occurring from top to bottom by weathering fresh original volcanic ash deposit.

2. Effects of different dehydration techniques

   a. Particle size distribution.--Figure 13 shows the changes in particle size distribution of three soils due to various dehydration treatments. The content of less than 2um-sized particles in the young Puaulu series, developed under low rainfall, was the least among the three soil series. A decrease in the amount of less than 2um-sized particles and an increase in the amount of larger than 2um-sized particles in soils was observed upon drying, indicating that some of the fine particles were aggregated into larger size upon drying. As expected, the effects of drying treatments were in the following order: oven drying > $P_2O_5$ drying > freeze drying > critical point drying,
Figure 13. Effect of drying treatments on particle size distribution of three soils. (K-6), (K-12), (H-3), (H-4), (P-13), and (P-15) refer to Kaiwiki surface and sub-surface, Hilo surface and sub-surface, and Puaulu surface and sub-surface, respectively.
for all the soils. In addition, the effect was more pronounced in sub-soils of all three soil series, probably because the surface soils have already been partially subjected to some natural drying as compared to sub-soils.

The results of the present study are in agreement with an earlier study (Lim, 1976) with exception of the critical point drying treatment which had not been studied by that author.

b. Water stable aggregate.---Water stable aggregates of soils were used to evaluate the strength of secondary particles formed during the dehydration process. Among the various ways of expressing aggregation characteristics of soils, the mean weight diameter (MWD) of soil aggregates introduced by van Bavel (1949) was used in this investigation as an index of aggregation. The MWD is expressed mathematically as follows:

\[
NWD = \sum_{i=1}^{n} x_i \cdot w_i
\] (9)

where \(x_i\) and \(w_i\) are the weight of a given size fraction of aggregates and the mean (average) diameter of that fraction, respectively.

Schaller and Stockinger (1953) have reported correlation coefficient of 0.958 and 0.913 between the MWD and the percentage of aggregates >2 mm and >1 mm, respectively, while comparing five different methods for expressing aggregation data.
The water stable aggregate index (MWD) (Table 6) indicates that the size of aggregate formed and its stability in wet and oven- and P$_2$O$_5$-dried conditions were quite similar. Wood (1977) has reported almost similar results but he found a higher MWD for five Inceptisols than reported in this study. However, soils subjected to freeze- and critical point-drying treatments have formed very small size and unstable aggregates. Critical point drying in particular produced the smallest size of aggregates.

Table 6. Effect of drying treatments on water stable aggregate index (MWD) of undisturbed soils

<table>
<thead>
<tr>
<th>soils</th>
<th>wet</th>
<th>oven</th>
<th>P$_2$O$_5$</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiwiki surface</td>
<td>2.288</td>
<td>2.451</td>
<td>2.531</td>
<td>1.076</td>
<td>0.412</td>
</tr>
<tr>
<td>Kaiwiki sub-surface</td>
<td>2.238</td>
<td>2.719</td>
<td>2.584</td>
<td>0.687</td>
<td>0.540</td>
</tr>
<tr>
<td>Hilo surface</td>
<td>1.595</td>
<td>1.593</td>
<td>1.423</td>
<td>0.945</td>
<td>0.813</td>
</tr>
<tr>
<td>Hilo sub-surface</td>
<td>2.259</td>
<td>1.959</td>
<td>1.481</td>
<td>0.681</td>
<td>0.541</td>
</tr>
<tr>
<td>Puauulu surface</td>
<td>1.548</td>
<td>1.592</td>
<td>1.216</td>
<td>0.867</td>
<td>0.714</td>
</tr>
<tr>
<td>Puauulu sub-surface</td>
<td>1.455</td>
<td>1.665</td>
<td>1.602</td>
<td>0.669</td>
<td>0.612</td>
</tr>
<tr>
<td>Average</td>
<td>1.897</td>
<td>1.997</td>
<td>1.806</td>
<td>0.821</td>
<td>0.605</td>
</tr>
</tbody>
</table>

LSD (0.05) = 0.21

The effect of drying treatments of disturbed (puddled) soils on water stable aggregation is shown in Table 7. In contrast to the undisturbed wet soils, aggregate size of all wet (puddled) samples at saturation moisture condition has been reduced drastically as compared
to undisturbed wet samples. Oven- and P₂O₅-drying treatments of puddled soils, however, produced larger aggregates than aggregates formed in undisturbed soils.

Table 7. Effect of drying treatments on water stable aggregate index (MWD) of disturbed soils

<table>
<thead>
<tr>
<th>soils</th>
<th>moisture (%)</th>
<th>wet</th>
<th>oven</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiwiki surface</td>
<td>298.3</td>
<td>1.371</td>
<td>2.796</td>
<td>2.689</td>
</tr>
<tr>
<td>Kaiwiki sub-surface</td>
<td>587.2</td>
<td>0.549</td>
<td>2.844</td>
<td>2.892</td>
</tr>
<tr>
<td>Hilo surface</td>
<td>190.6</td>
<td>0.894</td>
<td>2.635</td>
<td>2.584</td>
</tr>
<tr>
<td>Hilo sub-surface</td>
<td>175.8</td>
<td>0.821</td>
<td>3.010</td>
<td>3.145</td>
</tr>
<tr>
<td>Puaulu surface</td>
<td>148.3</td>
<td>0.677</td>
<td>2.285</td>
<td>2.271</td>
</tr>
<tr>
<td>Puaulu sub-surface</td>
<td>332.4</td>
<td>0.586</td>
<td>2.768</td>
<td>2.862</td>
</tr>
<tr>
<td>Average</td>
<td>--</td>
<td>0.817</td>
<td>2.725</td>
<td>2.740</td>
</tr>
</tbody>
</table>

LSD (0.05) = 0.290

It is postulated that the physical agitation with water addition made all wet soil samples impossible to sustain original aggregates against slow vertical oscillation (30 cycles per minute) in the Yoder apparatus (1936). On the contrary, physical agitation distributed inter-particle attraction forces uniformly throughout the whole soil mass. Consequently, oven- and P₂O₅-drying treatments enabled formation of larger aggregates due to gradual increase of capillary forces upon soil water evaporation.
c. **Specific surface area measurements.**--In this particular experiment, two different techniques, i.e., water vapor adsorption and $N_2$ gas adsorption techniques were used to determine surface areas. From adsorption isotherms, surface areas (tables 8 and 9) were calculated by the B.E.T. equation (Brunauer, et al., 1939). It was not possible to measure the surface area of wet soils by $N_2$ gas adsorption technique because the degassing procedure (on a hot sand bath at 100-110° C for more than 4 hours) would have resulted in undefined drying anyway. Data showed that the three Typic Hydrandepts have undergone remarkable decrease of surface area in order of: wet > critical point drying > freeze drying > $P_2O_5$ drying > oven drying. Overall, surface areas obtained in this experiment were slightly larger than previous results (Wadsworth, 1944; Quirk, 1955; Lim, 1976; and El-Swaify and Lim, 1976). Also the surface area measured by $H_2O$ vapor adsorption (Table 8) were larger than by $N_2$ gas adsorption (Table 9). It is believed that the polar character of $H_2O$ molecules enables them to better penetrate into interlayer spaces and attach themselves to surface ions ($H_2O$ dipole moment = 1.84 debye) than the non-polar molecules $N_2$ (dipole moment = none). The magnitude of specific surface areas was in order of: Kaiwiki sub-surface > Puaulu sub-surface > Kaiwiki surface > Hilo sub-surface > Hilo surface > Puaulu surface.
Table 8. Specific surface areas ($m^2/g$) of soils by $H_2O$ vapor adsorption

<table>
<thead>
<tr>
<th>soils</th>
<th>wet</th>
<th>oven</th>
<th>$P_{2O5}$</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiwiki surface</td>
<td>325</td>
<td>191</td>
<td>203</td>
<td>249</td>
<td>298</td>
</tr>
<tr>
<td>Kaiwiki sub-surface</td>
<td>439</td>
<td>280</td>
<td>313</td>
<td>349</td>
<td>383</td>
</tr>
<tr>
<td>Hilo surface</td>
<td>239</td>
<td>189</td>
<td>194</td>
<td>212</td>
<td>231</td>
</tr>
<tr>
<td>Hilo sub-surface</td>
<td>287</td>
<td>153</td>
<td>172</td>
<td>191</td>
<td>243</td>
</tr>
<tr>
<td>Puauulu surface</td>
<td>200</td>
<td>123</td>
<td>153</td>
<td>173</td>
<td>182</td>
</tr>
<tr>
<td>Puauulu sub-surface</td>
<td>380</td>
<td>116</td>
<td>182</td>
<td>303</td>
<td>332</td>
</tr>
<tr>
<td>Average</td>
<td>312</td>
<td>175</td>
<td>203</td>
<td>246</td>
<td>278</td>
</tr>
</tbody>
</table>

LSD (0.05) = 25

Table 9. Specific surface areas ($m^2/g$) of soils by $N_2$ gas adsorption

<table>
<thead>
<tr>
<th>soils</th>
<th>oven</th>
<th>$P_{2O5}$</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiwiki surface</td>
<td>140</td>
<td>139</td>
<td>189</td>
<td>236</td>
</tr>
<tr>
<td>Kaiwiki sub-surface</td>
<td>193</td>
<td>188</td>
<td>205</td>
<td>314</td>
</tr>
<tr>
<td>Hilo surface</td>
<td>172</td>
<td>158</td>
<td>180</td>
<td>223</td>
</tr>
<tr>
<td>Hilo sub-surface</td>
<td>174</td>
<td>166</td>
<td>186</td>
<td>208</td>
</tr>
<tr>
<td>Puauulu surface</td>
<td>4</td>
<td>6</td>
<td>14</td>
<td>24</td>
</tr>
<tr>
<td>Puauulu sub-surface</td>
<td>41</td>
<td>46</td>
<td>56</td>
<td>93</td>
</tr>
<tr>
<td>Average</td>
<td>121</td>
<td>117</td>
<td>138</td>
<td>183</td>
</tr>
</tbody>
</table>

LSD (0.05) 24

d. Water retention characteristics.—Since previous experimental results on particle size distribution, water stable aggregates, and specific surface areas have shown considerable changes due to different drying treatments,
changes in water retention characteristics of wet soils were also examined (Figs. 14-19). The oven- and P₂O₅-drying treatments reduced water retention capacity of soils most drastically. As shown in Figure 13, both treatments reduced recoverable clay-sized particles as a result of their agglomeration into silt and sand-sized particles. Consequently, exposed surface area of soils subjected to these treatments was reduced significantly (Tables 8 and 9). Furthermore, a large number of fine intra-aggregate pores probably coalesced and became unavailable for water retention. Manifestation of cementing effects by drying (El-Swaify and Emerson, 1975) also eliminates swelling forces which account for much of the water retention in natural soils.

Tsuji, et al. (1975), indicated that the rapid release of water at low suctions and the high water content at high suctions were attributed to the presence of microstructure or intra-aggregate and macro-structure or inter-aggregate voids in Oxisols and Ultisols but not in Vertisols and Inceptisols. However, the smooth water release curves of wet soil samples throughout the entire range probably indicate presence of intra-aggregate voids in these Typic Hydrandepts as well.

It is noted that water retention at any given suction of freeze- and critical point-dried samples were markedly higher than oven- and P₂O₅-dried samples even
Figure 14. Effect of drying treatments on water retention characteristics of soil (Kaiwiki surface soil).
Figure 15. Effect of drying treatments on water retention characteristics of soil (Kaiwiki sub-surface soil).
Figure 16. Effect of drying treatments on water retention characteristics of soil (Hilo surface soil).
Figure 17. Effect of drying treatments on water retention characteristics of soil (Hilo sub-surface soil).
Figure 18. Effect of drying treatments on water retention characteristics of soil (Puaulu surface soil).
Figure 19. Effect of drying treatments on water retention characteristics of soil (Puaulu sub-surface soil).
though they were always lower than water retention of wet samples. This points out that there is substantial difference between oven- and P₂O₅-drying treatments and freeze and critical point-drying treatments; the former drying treatments induced a larger soil structural alteration than the latter two dehydration treatments. The critical point-drying treatment is considered to be the best among all the drying treatments to preserve water retention closest to original soil characteristics after dehydration. However, it should not be overlooked that the loss of water retention characteristics of soils rich in amorphous constituents upon dehydration is due to dual effects. First is the effect of structural alteration upon changes in recoverable particles followed by drying as shown in Figure 13. The other is the loss of colloidal properties of amorphous materials upon drying.

Wells and Furkert (1972) investigated the bonding of water to New Zealand allophane, using differential thermal analysis (DTA) and infrared absorption analysis (IR). They reported that the main portion of water in natural allophane was held in hydrogen bonded clusters of water molecules in micropores in addition to single water molecules hydrogen bonded to common clay surfaces. They also found that air-drying or mechanical working (rubbing with fingers for a few seconds) to produce a slurry of allophane breaks the clusters to distribute the water as
single linked molecules on the clay surface only, and hydrogen bonded clusters of water molecules cannot be recovered by rewetting. Warkentin (1976) observed a change in shrinkage property of allophane upon drying as Lim (1976) and El-Swaify and Lim (1976) did who suggested that the swelling mechanism was responsible for the majority of high water retention capacity of Hawaii's Typic Hydrandepts.

e. Soil plasticity.—In order to investigate the effects of dehydration on the dynamic properties of soils, plasticity was selected as an index and its measurement procedure is described in the preceding section. Mellor (1922) defined plasticity as "the property which enables a clay to change its shape without cracking when it is subjected to a deforming stress." Plastic flow is mathematically expressed with the Bingham formula (Baver, et al., 1972):

$$ V = k \mu (F-f) $$

where $V$ is the volume of plastic flow, $\mu$ is the coefficient of mobility, $F$ is the external force applied, $f$ (called "yield value") is the internal force necessary to overcome the cohesive forces within the system to begin the flow, and $k$ is a constant. The essential difference between viscous and plastic flow is $f$ (yield value) in the formula. Therefore, this equation may be used to express viscous flow also if $f = 0$ for certain substances.
Baver, et al. (1972) stated that "plasticity is a function of the number and thickness of the water film in a given system. The number of films depends upon the size of particles and their specific surfaces. The thickness of the film is a function of the nature of the clay minerals, which determines the quantity of water that is adsorbed before a distinct film around each point of contact is formed, and the amount of water added to the system." Early in 1931, Nichols described the cohesive force of a water film (F) between two plate-shaped particles by the following equation:

\[ F = \frac{k4\pi rT \cos \alpha}{d} \]  

(11)

where \( T \) is the surface tension, \( \alpha \) the angle of contact between the liquid and the particle (generally assumed to be zero), \( d \) the distance between particles, \( r \) the radius of the particles, and \( k \) is a constant. He has also mentioned that not only do cohesive forces vary inversely with the moisture content for a given size and number of particles, but also that the product of the cohesive force and moisture content is constant as long as no excess water is present.

Table 10 shows the Atterberg limits (collective term for liquid limit, plastic limit, and plastic index) of the soils in this experiment. Here again, all original wet soils exhibited the highest Atterburg limits and the
Table 10. Effect of drying treatments on Atterberg limits of soils

<table>
<thead>
<tr>
<th></th>
<th>wet</th>
<th>oven</th>
<th>P_2O_5</th>
<th>freeze</th>
<th>critical point</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kaiwiki surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid limit</td>
<td>194.2</td>
<td>49.6</td>
<td>61.6</td>
<td>105.0</td>
<td>165.9</td>
</tr>
<tr>
<td>plastic limit</td>
<td>138.0</td>
<td></td>
<td>no cohesion</td>
<td>84.4</td>
<td>129.4</td>
</tr>
<tr>
<td>plastic index</td>
<td>56.2</td>
<td></td>
<td>no cohesion</td>
<td>20.6</td>
<td>36.5</td>
</tr>
<tr>
<td><strong>Kaiwiki sub-surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid limit</td>
<td>418.7</td>
<td>46.5</td>
<td>51.9</td>
<td>96.0</td>
<td>244.4</td>
</tr>
<tr>
<td>plastic limit</td>
<td>320.3</td>
<td></td>
<td>no cohesion</td>
<td>78.9</td>
<td>180.0</td>
</tr>
<tr>
<td>plastic index</td>
<td>98.4</td>
<td></td>
<td>no cohesion</td>
<td>17.1</td>
<td>64.4</td>
</tr>
<tr>
<td><strong>Hilo surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid limit</td>
<td>141.3</td>
<td>54.0</td>
<td>57.0</td>
<td>90.5</td>
<td>103.4</td>
</tr>
<tr>
<td>plastic limit</td>
<td>121.8</td>
<td>50.0</td>
<td>53.0</td>
<td>75.9</td>
<td>106.5</td>
</tr>
<tr>
<td>plastic index</td>
<td>19.5</td>
<td>4.0</td>
<td>4.0</td>
<td>14.6</td>
<td>16.9</td>
</tr>
<tr>
<td><strong>Hilo sub-surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid limit</td>
<td>145.1</td>
<td></td>
<td>no cohesion</td>
<td>60.3</td>
<td>105.2</td>
</tr>
<tr>
<td>plastic limit</td>
<td>90.7</td>
<td></td>
<td>no cohesion</td>
<td>57.7</td>
<td>85.3</td>
</tr>
<tr>
<td>plastic index</td>
<td>54.4</td>
<td></td>
<td>no cohesion</td>
<td>2.6</td>
<td>19.9</td>
</tr>
<tr>
<td><strong>Puaulu surface</strong></td>
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<td></td>
<td></td>
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<tr>
<td>liquid limit</td>
<td>137.7</td>
<td>33.4</td>
<td>45.0</td>
<td>45.4</td>
<td>58.6</td>
</tr>
<tr>
<td>plastic limit</td>
<td>85.6</td>
<td></td>
<td>no cohesion</td>
<td>47.6</td>
<td></td>
</tr>
<tr>
<td>plastic index</td>
<td>52.1</td>
<td></td>
<td>no cohesion</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td><strong>Puaulu sub-surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid limit</td>
<td>277.8</td>
<td>47.3</td>
<td>49.1</td>
<td>61.8</td>
<td>74.6</td>
</tr>
<tr>
<td>plastic limit</td>
<td>184.5</td>
<td></td>
<td>no cohesion</td>
<td>no cohesion</td>
<td></td>
</tr>
<tr>
<td>plastic index</td>
<td>93.3</td>
<td></td>
<td>no cohesion</td>
<td>no cohesion</td>
<td></td>
</tr>
</tbody>
</table>
closest values to original wet soils were obtained on critical point-dried soils. Lowest values (or even entirely no cohesion) were observed with oven- and P₂O₅-drying, reflecting changes of particle size distribution and surface area values measured previously. As in sands, the dehydration products lacked sufficient contact points and subsequently lacked rigidity caused by surface tension forces resulted from water films in the system. These changes in Atterberg limits were least pronounced in critical point drying-treatments. Atterberg values were in order of: wet>critical point drying>freeze drying>P₂O₅>oven drying. The Unified Soil Classification System Chart which is being intensively used to predict the engineering properties of soils demonstrates all these soils falling below "A" line which separates inorganic clay (above), and inorganic silt and organic soils (below), and slide down stepwise upon dehydration treatment in order of: wet+critical point drying+freeze drying+P₂O₅ drying=oven drying due to lowering liquid limit gradually (Fig. 20). Depending upon this classification system, soils belonging to either above or below "A" line and to higher than liquid limit 50% are not suitable for foundation. On the contrary, soils which belong to below "A" line and liquid limit lower than 50% are known to be the most desirable for foundation.

Yamazaki and Takenaka (1965) presented results similar to these of the present experiment, showing the
Figure 20. Effect of drying treatments on Atterberg limits of soils. (K-6), (K-12), (H-3), (H-4), (P-13), and (P-15) refer to Kaiwiki surface and sub-surface, Hilo surface and sub-surface, and Puaulu surface and sub-surface, respectively.
Atterberg limits obtained from (original) wet and air-dried of Japanese allophane on Cassagrande plastic chart. Many workers (van Schuylenborgh, 1953; Warkentin, 1972; Warkentin and Maeda, 1974; and Maeda, et al., 1977) suggested the use of the typical plasticity values to classify allophane soils from others. The allophane soils, unlike others, fall far from the "A" line on Cassagrande plasticity chart. This is because allophane soils have a high liquid limit and the low plastic index.

f. Soil viscosity.—In order to understand the changes in rheological properties (deformation and flow behavior) of Hawaiian Typic Hydrandepts, original soil viscosities and their changes due to different dehydration treatments were measured by using the Fisher Improved MacMichael Viscometer (Fisher instruction manual). All the viscosity values (poise) presented here are revised by equation (5) derived by relating sucrose viscosity values presented in "The Fisher Improved MacMichael Viscometer Instruction Manual" and actual sucrose viscosity values obtained in this laboratory.

According to the van Wazer, et al. (1963): "Ideal viscous bodies exhibit two types of flow, that is, viscosity in shear which is commonly known, and the little known bulk viscosity which must occur when the volume changes upon applying or relieving compression. The best-known ideal viscous body is the Newtonian fluid for which the
coefficient of viscosity (called simply viscosity) is a constant and is measured in terms of poise (dyne·sec./cm²).

It is known that generally the dispersed systems exhibit non-Newtonian behavior (van Olphen, 1963).

For a given soil:water ratio, viscosities of the original soils (Fig. 21) were in order of: Kaiwiki sub-surface soil > Puaulu sub-surface soil > Kaiwiki surface soil > Hilo surface soil > Hilo sub-surface soil > Puaulu surface soil. Careful study of these results indicated that the trends for these viscosity values correspond closely with moisture contents and water retention characteristics (Table 5), degree of non-crystallinity, i.e., amount of X-ray amorphous materials (Figs. 10-12), and the surface area by water vapor adsorption techniques (Table 8). As was pointed out by van Olphen (1963), the rheological properties of dispersion systems were influenced by four factors, namely the concentration of suspended matter, the size and shape of the suspended particles, interparticle forces, and viscosity of the dispersion medium. In contrast, Baver, et al. (1972) stated that the increase in viscosity of a colloidal system depended on the total volume of suspended particles and was independent of the degree of dispersion (interparticle forces). The volume implies the total volume associated with the particles, i.e., any water hull around individual particles or water enmeshed within aggregates. Consequently, an increase in viscosity was
Figure 21. Viscosity of original (wet) soils. (K-6), (K-12), (H-3), (H-4), (P-13) and (P-15) refer to Kaiwiki surface and sub-surface, Hilo surface and sub-surface, and Puaulu surface and sub-surface soil, respectively.
also caused by adsorption of highly hydrated ions on the soil particles. The above views helped to explain why the Kaiwiki sub-soil which had the largest water holding capacity exhibited the highest viscosity due to the larger total volume of the particles in the system. In addition, various dehydration treatments reducing viscosities upon reduction of the water holding capacity of soils, caused by the loss of non-crystallinity in the mechanism reported by Wells and Furkert (1972), the reduction of surface area, and decrease of particle attraction by increasing particle size.

Viscosity of a soil suspension has significant implications with respect to soil erodibility. Water erosion is due to two distinctive actions, detaching and transporting action of water, and these are determined by the detachable effects of falling raindrops and the amount and velocity of runoff. Therefore, the resistivity of the soil to detachment and movement is the internal factor determining soil erodibility. Examining soil aggregate stability (Tables 6-7) only, it would be mistakenly concluded that oven and P₂O₅-drying treatments which produce larger and more stable aggregates than untreated (wet) soils are to be beneficial in terms of soil erodibility. However, that is not true, closely examining the changes of Atterberg limits (Table 10) and viscosity (Fig. 22) upon dehydration treatments (especially oven- and P₂O₅-drying). Although aggregate sizes and stability of soils
Figure 22. Effect of drying treatments on viscosity of soils. (K-6), (K-12), (H-3), (H-4), (P-13), and (P-15) refer to Kaiwiki surface and sub-surface, Hilo surface and sub-surface, and Puaulu surface and sub-surface, respectively.
were increased upon drying, instead, viscosities were tremendously decreased due to drastic reduction of cohesion of soil particles. In addition, actual field observation revealed that only a thin surface layer (approximately 2-5 cm) was subjected to dehydration, and loosely-bounded from very cohesive layer. Consequently, this loosely-bounded, non-resistant to shear and soil surface layer is rather easily stripped off upon rainfall.

g. Shrinkage.—Subsamples subjected to each drying treatment were saturated with water, and volume reduction was measured after oven drying at 105°C for 24 hours. Among the six wet samples, Kaiwiki sub-surface soil showed the largest volume reduction (Table 11). The following sequence was found for different soil series: Kaiwiki sub-surface soil>Kaiwiki surface soil>Puaulu sub-surface soil>Hilo sub-surface soil>Hilo surface soil>Puaulu surface soil. As for previous results, the shrinkage was also influenced by soil mineralogy (Figs. 10-12) and texture (Table 5), especially mineralogy. The results may be explained satisfactorily as follows (Wells and Furkert, 1972). The large quantity of water originally present in natural amorphous materials (e.g., allophane) is held in hydrogen-bonded clusters of water molecules which extend beyond single water molecules ordinarily bonded to the clay surfaces. These clusters of water molecules cannot be recovered upon rewetting once broken
by mechanical work (rubbing) or dehydration. This reduces the swelling property of all soils subjected to dehydration.

Table 11. Effect of drying treatments on soil shrinkage (cm$^3$/g) from saturation

<table>
<thead>
<tr>
<th>soils</th>
<th>wet</th>
<th>oven</th>
<th>$P_2O_5$</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiwiki surface</td>
<td>3.195</td>
<td>0.114</td>
<td>0.124</td>
<td>0.641</td>
<td>0.936</td>
</tr>
<tr>
<td>Kaiwiki sub-surface</td>
<td>8.775</td>
<td>0.083</td>
<td>0.086</td>
<td>3.018</td>
<td>4.368</td>
</tr>
<tr>
<td>Hilo surface</td>
<td>0.885</td>
<td>0.000</td>
<td>0.060</td>
<td>0.417</td>
<td>0.604</td>
</tr>
<tr>
<td>Hilo sub-surface</td>
<td>1.194</td>
<td>0.000</td>
<td>0.000</td>
<td>0.442</td>
<td>0.465</td>
</tr>
<tr>
<td>Puauulu surface</td>
<td>0.617</td>
<td>0.287</td>
<td>0.303</td>
<td>0.226</td>
<td>0.337</td>
</tr>
<tr>
<td>Puauulu sub-surface</td>
<td>2.450</td>
<td>0.000</td>
<td>0.075</td>
<td>0.234</td>
<td>0.307</td>
</tr>
<tr>
<td>Average</td>
<td>2.86</td>
<td>0.085</td>
<td>0.110</td>
<td>0.829</td>
<td>1.172</td>
</tr>
<tr>
<td>LSD (0.05)</td>
<td></td>
<td></td>
<td></td>
<td>0.989</td>
<td></td>
</tr>
</tbody>
</table>

Observed magnitudes of shrinkage due to various dehydration treatments followed the order: critical point drying<freeze drying<$P_2O_5$ drying<oven drying. This order followed the closely-observed changes in particle size distribution, surface area, and water retention characteristics upon these four dehydration treatments. Ross (1978) also reported that the surface area was highly correlated (linearly) with free swelling index (F.S.I.) ($r^2 = 0.96$) and clay content. The clay content and surface area were in turn closely related to the coefficient of linear extensibility (COLE) ($r^2 = 0.81$ and $r^2 = 0.91$), respectively. Consequently, it is evident that there is
noticeable difference among the four drying treatments on soil structure changes. Reduction of soil clay content (Fig. 13) caused by aggregation, reduction of surface area accordingly, and possibly loss of colloidal property of amorphous materials as well upon drying (Wells and Furkert, 1972) resulted reduction of shrinkage property of dried soils in this experiment.

h. Particle density.--The particle densities of six soils with and without various dehydrations are presented in Table 12. It was found that the particle densities of soils subjected to drying were constantly lower than those of wet soils. In the literature, reported data on the "allophane" soils gave values ranging from 1.8 g cm\(^{-3}\) to 2.9 g cm\(^{-3}\) (Gradwell, 1955; Forsythe, et al., 1964; Bonfils and Moinereau, 1971; Wada and Wada, 1975, Fieldes and Claridge, 1975; Wada, 1976a; and others). Gradwell (1955) stated that the difference between the particle densities of clay soils measured by water displacement and by non-polar liquids displacement are characteristic of soils. He also reported that not only were the particle densities measured by water displacement higher than those by toluene displacement, but also the original wet samples showed higher values than the oven-dried samples of allophanic soils. In addition, this trend was prominent with increasing the content of allophane in soils. Subsequently, he speculated that the lower particle
density values by toluene displacement were probably caused by poor penetration into the fine pores of the soil amorphous. Wada (1976b) proposed the hollow, spherule structure of allophane minerals. The void space inside of the hollow spherule wall was filled with water molecule and the wall was probably constructed from defective layer structures consisting of Al-O, OH octahedral sheet and a Si, Al-O, OH tetrahedral sheet. This defect in structure could provide openings (approximately 3Å) in the wall which would permit water molecule transmission. This proposed hollow, spherule structure unit might explain the low particle density of allophane soils upon dehydration treatments and results in this experiment as well. Evacuation of water from the void space inside the wall without complete collapse would cause difficulty of refilling water through small openings within the wall unit because of entrapped air. Thus, the particle density decrease with drying may be only apparent.

Table 12. Effect of drying treatments on soil particle density

<table>
<thead>
<tr>
<th>soils</th>
<th>wet</th>
<th>oven</th>
<th>P₂O₅</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiwiki surface</td>
<td>3.03</td>
<td>2.50</td>
<td>2.49</td>
<td>2.61</td>
<td>2.36</td>
</tr>
<tr>
<td>Kaiwiki sub-surface</td>
<td>2.93</td>
<td>2.33</td>
<td>2.41</td>
<td>2.25</td>
<td>2.43</td>
</tr>
<tr>
<td>Hilo surface</td>
<td>2.81</td>
<td>2.43</td>
<td>2.37</td>
<td>2.33</td>
<td>2.21</td>
</tr>
<tr>
<td>Hilo sub-surface</td>
<td>3.00</td>
<td>2.58</td>
<td>2.42</td>
<td>2.43</td>
<td>2.62</td>
</tr>
<tr>
<td>Puaulu surface</td>
<td>2.94</td>
<td>2.66</td>
<td>2.47</td>
<td>2.58</td>
<td>2.51</td>
</tr>
<tr>
<td>Puaulu sub-surface</td>
<td>2.98</td>
<td>2.82</td>
<td>2.86</td>
<td>2.83</td>
<td>2.74</td>
</tr>
<tr>
<td>Average</td>
<td>2.95</td>
<td>2.55</td>
<td>2.50</td>
<td>2.51</td>
<td>2.48</td>
</tr>
</tbody>
</table>

LSD (0.05) = 0.12
i. **Scanning Electron Microscopy (SEM)**

The importance of soil structure that influences the soil physico-chemical characteristics has recently accelerated intensive study on soil structure. SEM is one of the useful techniques to study structure of soils among many sophisticated methods such as vapod adsorption, transmission and reflection electron microscopy, mercury intrusion, quantimet, light microscopy, and so forth.

Results reported so far show that dehydration techniques used in this study had quite different effects on soil characteristics with close similarity between the effects of oven-drying and $\text{P}_2\text{O}_5$-drying treatments. Therefore, in order to inspect visually the effects of dehydration techniques on resulting soil structure, a few selected samples that had been subjected to drying were examined by a Scanning Electron Microscope (Model: Cambridge Stereoscan S-4-10). The unit was operated at 10 Kev at a working distance of 5-10 mm with a take of angle of 35°.

It was difficult to find visual structural differences among soil samples subjected to different dehydration techniques (as compared with the synthetic minerals discussed in a later section). The difficulty was because of
sample heterogeneity problems, such as presence of many different kinds and sizes of constituents in soils. The following are some of the readily observable differences as noted from plates 1, 2, and 3.

All soil samples subjected to oven and $P_2O_5$ drying have similarly formed into large masses of sub-angular blocky, dense, and closed crumbs with large pore spaces separating individual units. These are aggregates formed by both electrostatic and van der Waal's attraction forces between primary and/or secondary constituents in soils. This is a manifestation of large cohesive forces (surface tension) acting among the constituents under natural conditions. On the contrary, the freeze and critical point-drying techniques which were devised to reduce or eliminate such cohesive forces among particles resulted in small, fluffy, and open spongy structure. Furthermore, there were some differences between formations resulting from freeze drying and critical point drying. Generally, freeze drying produced plate or sheet-like structure while critical point drying produced bulkier and more open structure. The latter appeared closer to original soil aggregate configuration indicating that freeze drying also did disturb original interparticle associations as alluded to by Greene-Kelly (1973). Notwithstanding this fact, many investigators still consider the freeze drying technique to be the best for soil structure determination.
Plate 1. Electron micrograph of Kaiwiki sub-surface soil. 
(A) oven-dried, (B) $P_2O_5$ dried, (C) freeze-dried, 
(D) critical point-dried.
Plate 2. Electron micrograph of Hilo surface soil.
(A) oven-dried, (B) P_{2}O_{5} dried, (C) freeze-dried,
(D) critical point-dried.
HILO_SURFACE_SOIL

A

B

100u

100u

C

D

100u

100u
Plate 3. Electron micrograph of Puaulu sub-surface soil.  
(A) oven-dried, (B) $P_2O_5$ dried, (C) freeze-dried,  
(D) critical point-dried.
PUAULU_SUB-SURFACE_SOIL

A

50u

B

50u

C

25u

D

10u
Greene-Kelly (1973) criticized this trend and encouraged using the critical point drying for study of soil structure. These above results confirmed his intuitive conclusions.

**B. Contribution of cementing agents to changes of soil properties upon dehydration**

The irreversibility of Hydrandepts upon dehydration has been blamed primarily on presence of large amounts of organic and highly hydrated inorganic X-ray amorphous constituents (Fieldes, *et al.*, 1952; Sherman, *et al.*, 1953; Kanehiro and Sherman, 1956; and Lim, 1976). The roles of some such constituents in stabilizing soil structure upon drying were analyzed by El-Swaify and Emerson (1975) and El-Swaify (1976). It was suggested that size, shape, and charge characteristics of constituents all affected their effectiveness as cementing agents.

The foregoing X-ray diffraction analysis (Figs. 10-12) and others (Dias, 1965; Lai and Swindale, 1967; Voss, 1969; Chan, 1972; and Lim, 1976) have shown that the predominant mineralogical constituents of Typic Hydrandepts in Hawaii are X-ray amorphous or poorly-crystallized silicates, and sesquioxides. Other studies (Wada and Wada, 1976; Sherman, *et al.*, 1964; Chan, 1972; and Wada, *et al.*, 1972) have revealed that the X-ray amorphous fraction consists of hydrous non-crystalline alumina, iron, and silica oxides, allophane, allophane-like, imogolite and humus. Lim (1976) studied the contribution of organic
matter to irreversible behavior. Here, it was decided to study the inorganic substances themselves to understand the mechanism of irreversibility in soils. The two distinctive approaches, i.e., synthetic and selective extraction techniques, have long been employed to study the precise effects of individual soil constituents. Yet, neither technique is entirely satisfactory (El-Swaify and Emerson, 1975; and Lim, 1976). The latter technique in particular, raises considerable question of validity because the extraction process is never absolutely selective for a specific soil constituent.

In this particular experiment, the responses of two synthetic iron hydrous oxides, one iron oxide, one aluminum hydroxide, and three aluminosilicate minerals to drying have been investigated.

1. Characterization of synthetic minerals

   a. Mineralogical identification. --X-ray diffraction analysis of synthetic iron oxide and hydrous oxides of iron are shown in Figure 23. Fe-hydrous oxide (A) which was precipitated at pH 6.0 and aged for two weeks during dialysis exhibited the β-FeOOH (akaganeite) peaks. Fe-Hydrous oxide (B) which was precipitated at pH 12.0 and aged for two weeks during the dialysis showed α-FeOOH (goethite) peaks. On the other hand, Fe-hydrous oxide (A) and/or (B) fired at 550°C for 4 hours, showed α-Fe₂O₃
Figure 23. X-ray diffractogram for iron oxide and hydrous oxides.
(hematite) peaks. However, many investigators have observed the delicacy of mineral synthesis in laboratory such as influence of pH, anions, cations, and other impurities, temperature, aging conditions, and so forth.

For instance, Mackenzie (1957) and Mackenzie and Meldau (1959) reported that a ferric hydroxide precipitated with ammonium hydroxide at pH 10.0 was crystallizing to goethite. But the one precipitated at pH 5.0 retained its amorphous status even after 155 days. It was reported by Schellman (1959) that the ionic impurities in the crystallization of hydrous iron oxides was important. The goethite was found at high pH of 11 to 12, hematite favored at a low pH, and both minerals appeared in neutral solutions. However, cation impurities such as Mg$^{++}$, or Ca$^{++}$ favored the formation of hematite while anions such as SO$_4$$^{--}$, or CO$_3$$^{--}$ induced the formation of goethite in neutral solutions. El-Swaify and Emerson (1975), and El-Swaify (1976) reported that the forms of Al or Fe precipitated in the presence of clay systems were generally amorphous. But the precipitated Al or Fe in pure system (absence of clay) were always either gibbsite or bayerite and goethite. Gastuche, et al. (1964) found that in a dialysis medium, hematite was rapidly formed from precipitated ferric gel at low pH (4.5). Under the same condition except high pH (above pH 8.0), however, goethite appeared together with hematite. Landa and Gast (1973) investigated
the nature of freshly-precipitated and aged hydrated ferric oxides by the use of scanning electron microscopy, transmission electron microscopy, X-ray diffraction, I.R. adsorption, and pH 3.0 ammonium oxalate extraction technique. The results revealed that the fresh material was essentially non-crystalline hydrated ferric oxide, which rapidly crystallized as geothite, without any indication of coexisting hematite when aged at 60°C and high pH. However, for the one prepared at lower pH (less than pH 8.0), only partial crystallization was evidenced after four weeks of aging. That also reported that I.R. analysis could be used to distinguish clearly between α-FeOOH (goethite) and its polymorphs, β-FeOOH (akaganeite) and γ-FeOOH (lepidocrocite) because of differences in the O-H bending vibration frequencies.

The prepared and aged Al-hydroxide was identified as a mixture of gibbsite (γ-Al₂O₃·3H₂O) and bayerite (α-Al₂O₃·3H₂O) of around 50:50 ratio similar to the results reported by Lim (1976). However, possibly due to insufficient dialysis, there was some X-ray amorphous aluminum chloride compound showing a hump maximum at 6.51Å (Figure 24). In addition, Figure 25 shows X-ray diffractogram of synthetic aluminosilicate minerals in three different SiO₂/Al₂O₃ molar ratios and powder of dried mother solution (tetraethyl orthosilicate: Si(OCH₂CH₃)₄). The three different SiO₂/Al₂O₃ molar ratios (0.5, 1.0, and
Figure 24. X-ray diffractogram for aluminum hydroxide.
Figure 25. X-ray diffractogram for aluminosilicates and tetraethyl orthosilicate (Si source).
2.0) were chosen according to various SiO$_2$/Al$_2$O$_3$ molar ratios reported for allophane or allophane-like amorphous such as 0.81-1.93 by Henmi and Wada (1974), 0.8-1.4 and 1.5-2.3 for sesquioxidic and halloysitic allophanes by Jackson (1965), and 2.4-4.0 for siliceous allophane by Rirner and Jackson (1969). As shown in Figure 25, these three synthetic minerals and mother solution all showed X-ray amorphous humps in between 20-30 of 2θ range. Judging from whole X-ray diffractogram, however, the powder of dried mother solution was identified as cristobolite from three synthetic aluminosilicate amorphous substances. Wada and Kubo (1975) precipitated amorphous aluminosilicates from varying amounts of solutions containing monomeric silica (tetraethyl orthosilicate) and aluminum ions (AlCl$_3$ or Al(OH)$_{2.55}$Cl$_{0.45}$) molar ratio ranged from 0.0 to 8.0) which allow the SiO$_2$/Al$_2$O$_3$ molar ratio of the precipitates from 0.5-3.0 for investigating effects of environmental factors on precipitation of aluminosilicates genesis, structure, and properties of their natural counterparts. The three aluminosilicates synthesized in this experiment agreed with the results of Wada and Kubo (1957).

2. Effects of different dehydration techniques

a. Particle size distribution.—Clay-sized particle content in the synthetic minerals subjected to drying
treatments were in the order of (Fig. 26): oven drying \( \text{P}_2\text{O}_5 \) drying \( \text{freeze drying} \) critical point drying. It was shown that among iron oxide minerals, the iron hydrous oxide (A) was by far the closer to soil pattern (particularly for soils which consisted of a large amount of amorphous materials) than the well-crystallized iron hydrous oxide (B). Furthermore, hematite mineral was almost completely inert to drying treatments, probably due to its synthetic history by firing at 550°C for more than 4 hours. These results suggest that "irreversible" drying in Typic Hydrandepts must be more due to Fe-hydrous oxide type (A) than type (B) and hematite. \( \text{Al(OH)}_3 \) did not exhibit severe changes upon different dehydration treatments, possibly due to its well-crystallized nature. It was interesting to note that the effect of dehydration treatments on the synthetic aluminosilicates in three different \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) molar ratios were in order of: \( \text{SiO}_2/\text{Al}_2\text{O}_3=0.5 \rangle \text{SiO}_2/\text{Al}_2\text{O}_3=1.0 \rangle \text{SiO}_2/\text{Al}_2\text{O}_3=2.0 \). This indicates that the high Si content within the structure produces more reversibility in behavior, a case which is represented by (silicate) clay minerals in the extreme. Jones and Uehara (1973) had speculated that some amorphous minerals which are the high oxide systems lose their viscous property upon drying and that high silicon systems appear to be able to alter reversibly between the viscous and elastic states upon wetting and drying. Consequently, they stated that these features might have strong
Figure 26. Effect of drying treatments on particle size distribution of synthetic minerals. Fe(A), Fe(B), Al-hydroxide, Si(0.5), Si(1.0), and Si(2.0) refer to synthetic akaganeite, goethite, mixture of gibbsite and bayerite, and aluminosilicate SiO$_2$/Al$_2$O$_3$=0.5, 1.0 and 2.0, respectively.
implications in irreversible crusting of laterites, reversible crusting in irrigated soils of arid regions and soil aggregation in general. It is clear from these results, however, that all amorphous silicates display changes upon drying but that their changes differ in magnitude depending on the Si content. The formation of water stable aggregates confirmed this conclusion. In addition, the synthetic aluminum hydroxide mineral in the present study was the least affected one by drying treatment among the three different kinds of synthetic minerals (iron hydrous oxides, aluminum oxide, and aluminosilicate minerals).

b. Water stable aggregate.—The water stability of secondary particles formed upon drying treatments including fresh minerals was compared by means of mean weight diameter (MWD). The magnitude of mean weight diameter (MWD) was in order of: oven drying > P₂O₅ drying > freeze drying > critical point drying > fresh, indicating that the oven drying treatment was the most inducive to forming large and water stable secondary particles (Table 13). It ought to be pointed out that all fresh (wet) samples used here for MWD measurement were over-saturated in water. Unlisted data showed that by simply decreasing water content of these synthetic minerals unlike common reversible soils (or minerals) up to even saturation point (zero suction), the undried (fresh) minerals' MWDs
increased nearly to oven or \( P_2O_5 \)-dried samples' MWDs. Consequently, it indicates that aggregates in the abundance of water at zero suction (saturation point) were not bound just by hydrogen bond of ordinary free water, but evidently some other additive attraction forces were involved. In other words, the particle distance even at zero suction was short enough to affect each other by electrostatic, van der Waal's forces or both. This fact was explained by El-Swaify and Emerson (1975) and/or Well and Furkert (1972) phenomenologically, as mentioned earlier.

Table 13. Effect of drying treatments on water stable aggregate index (MWD)

<table>
<thead>
<tr>
<th>minerals</th>
<th>wet</th>
<th>oven</th>
<th>( P_2O_5 )</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-hydrous oxide (A)</td>
<td>0.012</td>
<td>2.851</td>
<td>2.328</td>
<td>0.412</td>
<td>0.254</td>
</tr>
<tr>
<td>Fe-hydrous oxide (B)</td>
<td>0.021</td>
<td>2.467</td>
<td>2.018</td>
<td>0.418</td>
<td>0.189</td>
</tr>
<tr>
<td>Fe-oxide (hematite)</td>
<td>0.014</td>
<td>1.132</td>
<td>1.132</td>
<td>0.050</td>
<td>0.028</td>
</tr>
<tr>
<td>Al-hydroxide</td>
<td>0.027</td>
<td>1.912</td>
<td>1.323</td>
<td>0.031</td>
<td>0.030</td>
</tr>
<tr>
<td>Aluminosilicate (0.5)</td>
<td>0.030</td>
<td>1.516</td>
<td>1.377</td>
<td>0.040</td>
<td>0.034</td>
</tr>
<tr>
<td>Aluminosilicate (1.0)</td>
<td>0.025</td>
<td>1.956</td>
<td>2.079</td>
<td>0.028</td>
<td>0.026</td>
</tr>
<tr>
<td>Aluminosilicate (2.0)</td>
<td>0.018</td>
<td>2.182</td>
<td>2.028</td>
<td>0.214</td>
<td>0.190</td>
</tr>
<tr>
<td>Average</td>
<td>0.021</td>
<td>2.003</td>
<td>1.756</td>
<td>0.170</td>
<td>0.107</td>
</tr>
</tbody>
</table>

LSD (0.05) = 0.05

c. **Specific surface area.** As soil samples, the two different techniques, i.e., water vapor adsorption technique and \( N_2 \) gas adsorption technique were applied to synthetic minerals to determine surface areas.
The surface areas obtained by both techniques applying B.E.T. equation are integrated in Tables 14 and 15. The magnitude of surface area of the freshly-synthesized minerals was as follows: aluminosilicates > Fe-hydrous oxides > aluminum hydroxide > iron oxide. It should be mentioned that among three iron minerals, Fe hydrous oxide (A) has the largest surface area and Fe oxide (hematite) has the least.

As described in the methods and materials, FeCl₃ was titrated with NaOH up to pH 6.0 for Fe-hydrous oxide (A) and up to pH 12.0 for Fe-hydrous oxide (B). El-Swaify and Emerson (1975) mentioned that pH 6.5 and 4.6 were equivalent points (inflection points in the titration curves) on the titration of FeCl₃ and AlCl₃ with NaOH to synthesize Fe-hydrous oxide and aluminum hydroxide, respectively. In other words, these two pH's are the points at which exact amount of both solutions are needed to begin forming iron hydrous oxide and aluminum hydroxide compounds of amorphous or the smallest possible crystalline sizes. Proper aging methods can induce the formation of either poor or well-crystallized (large) minerals. For Fe, this proved to be correct and successful for yielding smaller-sized mineral particles by controlling the aging pH at 6.0 than at 12.0. It was Fe-hydrous oxide (A) which underwent the most drastic decrease in surface area upon dehydration due to the large number of contact points.
among particles thus leading to strong aggregation. Lim (1976) calculated the surface area of synthetic iron hydrous oxide (A) as ranging from 238.3 to 350.5 m²/g using El-Swaify and Emerson's results (1975) (particle diameter of 40 Å, particle density of 4.28 g/cm³) for cylindrical shape or spherical shape, respectively. El-Swaify and Emerson (1975) had calculated the surface area of precipitated goethite and bayerite as 259 and 57 m²/g respectively, based on the B.E.T. N₂ gas adsorption.

As for other characteristics, the effect of drying methods on surface areas was also in the order of: oven drying>P₂O₅ drying>freeze drying>critical point drying.

Table 14. Specific surface area (m²/g) by H₂O vapor adsorption technique for synthetic minerals

<table>
<thead>
<tr>
<th>minerals</th>
<th>wet</th>
<th>oven</th>
<th>P₂O₅</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-hydrous oxide (A)</td>
<td>385</td>
<td>280</td>
<td>269</td>
<td>292</td>
<td>321</td>
</tr>
<tr>
<td>Fe-hydrous oxide (B)</td>
<td>178</td>
<td>156</td>
<td>157</td>
<td>160</td>
<td>167</td>
</tr>
<tr>
<td>Fe-oxide (hematite)</td>
<td>20</td>
<td>18</td>
<td>17</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Al-hydroxide</td>
<td>69</td>
<td>46</td>
<td>57</td>
<td>59</td>
<td>64</td>
</tr>
<tr>
<td>Aluminosilicate (0.5)</td>
<td>814</td>
<td>532</td>
<td>603</td>
<td>643</td>
<td>738</td>
</tr>
<tr>
<td>Aluminosilicate (1.0)</td>
<td>836</td>
<td>658</td>
<td>640</td>
<td>706</td>
<td>804</td>
</tr>
<tr>
<td>Aluminosilicate (2.0)</td>
<td>868</td>
<td>737</td>
<td>731</td>
<td>749</td>
<td>836</td>
</tr>
<tr>
<td>Average</td>
<td>452</td>
<td>347</td>
<td>353</td>
<td>375</td>
<td>421</td>
</tr>
<tr>
<td>LSD (0.05) = 49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 15. Specific surface area (m$^2$/g) by N$_2$ adsorption technique for synthetic minerals

<table>
<thead>
<tr>
<th>minerals</th>
<th>oven</th>
<th>P$_2$O$_5$</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-hydrous oxide (A)</td>
<td>235</td>
<td>225</td>
<td>256</td>
<td>262</td>
</tr>
<tr>
<td>Fe-hydrous oxide (B)</td>
<td>144</td>
<td>148</td>
<td>152</td>
<td>160</td>
</tr>
<tr>
<td>Fe-oxide (hematite)</td>
<td>15</td>
<td>15</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td>Al-hydroxide</td>
<td>37</td>
<td>37</td>
<td>49</td>
<td>58</td>
</tr>
<tr>
<td>Aluminosilicate (0.5)</td>
<td>408</td>
<td>420</td>
<td>436</td>
<td>620</td>
</tr>
<tr>
<td>Aluminosilicate (1.0)</td>
<td>422</td>
<td>417</td>
<td>436</td>
<td>617</td>
</tr>
<tr>
<td>Aluminosilicate (2.0)</td>
<td>548</td>
<td>531</td>
<td>606</td>
<td>628</td>
</tr>
<tr>
<td>Average</td>
<td>258</td>
<td>256</td>
<td>279</td>
<td>338</td>
</tr>
</tbody>
</table>

LSD (0.05) = 49

It was also noticed that among three aluminosilicate minerals, surface area tends to increase with increasing SiO$_2$/Al$_2$O$_3$ ratio and a larger reduction of surface area upon oven- and P$_2$O$_5$-drying resulted with decreasing SiO$_2$/Al$_2$O$_3$ molar ratio.

d. Water retention characteristics.—The magnitude of water retention characteristics of seven fresh (wet) synthetic minerals were in order of: aluminosilicate (2.0) > aluminosilicate (1.0) > aluminosilicate (0.5) > iron hydrous oxide (A) > iron hydrous oxide (B) > aluminum hydroxide > iron oxide. The iron oxide (hematite) retained remarkably less water than other synthetic minerals (Fig. 27). The data reflect surface areas rather closely.
Figure 27. Water retention characteristics of synthetic minerals.
Figure 28. Effect of drying treatments on water retention characteristics of Fe-hydrous oxide (A).
Figure 29. Effect of drying treatments on water retention characteristics of Fe-hydrous oxide (B).
Figure 30. Effect of drying treatments on water retention characteristics of iron oxide (hematite).
Figure 31. Effect of drying treatments on water retention characteristics of aluminum hydroxide.
Figure 32. Effect of drying treatments on water retention characteristics of aluminosilicate (0.5).
Figure 33. Effect of drying treatments on water retention characteristics of aluminosilicate (1.0).
Figure 34. Effect of drying treatments on water retention characteristics of aluminosilicate (2.0).
As in previous results, effects of drying treatments on water retention characteristics by the synthetic minerals (Figs. 28-34) was in order of: oven drying > P₂O₅ drying > freeze drying > critical point drying. That is, critical point drying technique was always the best to sustain the structural condition of original (fresh) minerals even though the magnitude was still lower than the original minerals. However, it should be pointed out here that the difference between critical point drying and original samples was not simply because of defects of the dehydration technique itself, but because of some other reasons. Evidence from surface area (Table 14) shows that surface areas after critical point drying were as much as 85.9-98.2% of those of original (wet) synthetic minerals. The water retention characteristics of critical point dried minerals, however, were only maximum of 52.2% (17.5-52.2%) of original (wet) synthetic minerals except for the hematite (75.3%). The discrepancy may be explained in view of the findings of Wells and Furkert (1972) who found that the larger quantity of water present in natural allophane was held in hydrogen-bonded clusters of water molecules. Subjecting the allophanes to drying or mechanical work to produce a slurry broke the clusters and distributed the water as single-linked molecules on the clay surface. El-Swaify and Lim (1975), through extensive study on the mechanisms of water retention by Hawaii's Typic Hydrandepts,
attributed the majority of excessive amount of water held by wet Typic Hydrandepts to the swelling mechanism. This mechanism is sensitive to drying in that large interparticle forces manifested upon drying (close proximity) must be overcome (energy barrier) to gain reversibility.

El-Swaify and Emerson (1975) showed that precipitation of iron and aluminum hydrous oxides directly into the soil clays (illite, kaolinite and kaolinite-illite mixture) and subjected to freeze drying reduced water retention drastically as compared to natural soil clays. This was due to triple effects of drying. Firstly, dehydration of iron or aluminum hydrous oxides reduced their own surface areas upon drying. Secondly, dehydration of these minerals also deprived their own water-holding power associated with other than surface areas as depicted by Wells and Furkert (1972). Lastly, soil clays coated by these iron and aluminum hydrous oxides were inhibited from free water retention by restriction of clay swelling.

e. Shrinkage properties.—As shown in Table 16, the severity of volume shrinkage of original (fresh) synthetic materials upon oven drying was in the order of: aluminosilicates>iron hydrous oxides>aluminum hydroxide> iron oxide. As in the previous results, oven drying was the most and critical point drying was the least severely effective method on the change of shrinkage property of synthetic minerals. However, even critical point drying
technique which was the best among four drying methods to sustain original shrinkage was far from reaching the swelling property of original fresh minerals. The best possible explanation for this fact was given by Wells and Furkert (1972) described previously.

Table 16. Effect of drying treatments on volume shrinkage (cm$^3$/g) of synthetic minerals

<table>
<thead>
<tr>
<th>minerals</th>
<th>wet</th>
<th>oven</th>
<th>P$_2$O$_5$</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-hydrous oxide (A)</td>
<td>17.54</td>
<td>0.05</td>
<td>0.07</td>
<td>1.54</td>
<td>4.20</td>
</tr>
<tr>
<td>Fe-hydrous oxide (B)</td>
<td>13.07</td>
<td>0.78</td>
<td>0.84</td>
<td>1.90</td>
<td>4.14</td>
</tr>
<tr>
<td>Fe-oxide (hematite)</td>
<td>0.87</td>
<td>0.45</td>
<td>0.48</td>
<td>0.63</td>
<td>0.75</td>
</tr>
<tr>
<td>Al-hydroxide</td>
<td>10.43</td>
<td>0.70</td>
<td>0.74</td>
<td>1.48</td>
<td>2.74</td>
</tr>
<tr>
<td>Aluminosilicate (0.5)</td>
<td>18.96</td>
<td>0.30</td>
<td>0.32</td>
<td>1.84</td>
<td>3.37</td>
</tr>
<tr>
<td>Aluminosilicate (1.0)</td>
<td>19.43</td>
<td>0.32</td>
<td>0.35</td>
<td>2.01</td>
<td>4.85</td>
</tr>
<tr>
<td>Aluminosilicate (2.0)</td>
<td>20.14</td>
<td>0.34</td>
<td>0.41</td>
<td>3.65</td>
<td>7.89</td>
</tr>
<tr>
<td>Average</td>
<td>14.34</td>
<td>0.43</td>
<td>0.46</td>
<td>1.86</td>
<td>4.00</td>
</tr>
<tr>
<td>LSD (0.05) = 4.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is evident that shrinkage was closely related (positive correlation) to water retention characteristics rather than to surface area of minerals. This is in contrast to the report by Ross (1977) who found that the free swelling index (FSI) and coefficient of linear extensibility (COLE) were highly correlated (positively) with specific surface area of soils. It was shown previously that these original (wet) minerals lost both their shrinkage and water
retention properties upon drying, but in two quite different ways. The shrinkage property was reduced drastically upon drying regardless of drying methods. However, the surface areas were reduced not only less drastically compared with shrinkage property, but also differently upon drying methods applied. This result induced deviation from possible positive correlation between shrinkage property and specific surface areas.

Table 17. Water retention characteristics and volume shrinkage per unit surface area

<table>
<thead>
<tr>
<th>minerals</th>
<th>water retention (g/m²)</th>
<th>water shrinkage (m²/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iron hydrous oxide monohydrated (A)</td>
<td>0.044</td>
<td>0.045</td>
</tr>
<tr>
<td>iron hydrous oxide monohydrated (B)</td>
<td>0.173</td>
<td>0.168</td>
</tr>
<tr>
<td>α-iron oxide (hematite)</td>
<td>0.065</td>
<td>0.045</td>
</tr>
<tr>
<td>aluminum hydroxide</td>
<td>0.272</td>
<td>0.151</td>
</tr>
<tr>
<td>aluminosilicate (SiO₂/Al₂O₃ = 0.5)</td>
<td>0.025</td>
<td>0.023</td>
</tr>
<tr>
<td>aluminosilicate (SiO₂/Al₂O₃ = 1.0)</td>
<td>0.026</td>
<td>0.023</td>
</tr>
<tr>
<td>aluminosilicate (SiO₂/Al₂O₃ = 2.0)</td>
<td>0.026</td>
<td>0.023</td>
</tr>
</tbody>
</table>

However, it should be pointed out that the high reactive properties of fresh aluminosilicates among synthetic minerals (reflected in highest irreversibility) was primarily due to large specific surface areas rather than effectiveness of surface molecular groups. (See Tables 14 and 15). Thus, water retention and shrinkage volume were recalculated for different minerals per unit surface area
(by H₂O) as shown in Table 17. Based on these recalculations, the magnitude of these characteristics per unit surface area was ranked differently from per gram basis as: iron hydrous oxide monohydrated (B)=aluminum hydroxide>a-iron oxide (hematite)>iron hydrous oxide monohydrated (A)>aluminosilicates.

f. **Particle density.**—Particle densities of seven original (wet) synthetic minerals and pre-dried synthetic minerals using four different drying techniques were measured following the same procedure as soil samples (Table 18). Particle densities of these synthetic minerals are shown in Table 18.

<table>
<thead>
<tr>
<th>minerals</th>
<th>wet</th>
<th>oven</th>
<th>P₂O₅</th>
<th>freeze</th>
<th>critical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-hydrous oxide (A)</td>
<td>3.83</td>
<td>3.33</td>
<td>3.46</td>
<td>3.67</td>
<td>3.45</td>
</tr>
<tr>
<td>Fe-hydrous oxide (B)</td>
<td>4.00</td>
<td>3.95</td>
<td>3.79</td>
<td>3.85</td>
<td>3.69</td>
</tr>
<tr>
<td>Fe-oxide (hematite)</td>
<td>4.25</td>
<td>4.35</td>
<td>4.43</td>
<td>4.19</td>
<td>4.29</td>
</tr>
<tr>
<td>Al-hydroxide</td>
<td>2.53</td>
<td>2.37</td>
<td>2.31</td>
<td>2.28</td>
<td>2.32</td>
</tr>
<tr>
<td>Aluminosilicate (0.5)</td>
<td>2.51</td>
<td>1.95</td>
<td>1.90</td>
<td>1.88</td>
<td>1.71</td>
</tr>
<tr>
<td>Aluminosilicate (1.0)</td>
<td>2.17</td>
<td>1.91</td>
<td>1.85</td>
<td>1.82</td>
<td>1.78</td>
</tr>
<tr>
<td>Aluminosilicate (2.0)</td>
<td>2.46</td>
<td>1.96</td>
<td>1.98</td>
<td>1.91</td>
<td>1.94</td>
</tr>
<tr>
<td>Average</td>
<td>3.11</td>
<td>2.86</td>
<td>2.83</td>
<td>2.81</td>
<td>2.74</td>
</tr>
</tbody>
</table>

LSD (0.07) = 0.12
minerals followed the same trends as in soils, i.e., the particle densities of synthetic minerals subjected to drying were constantly lower than the original samples except for the iron oxide (hematite). This is probably due to the history of this synthetic minerals, which involved high temperature drying and redispersion. The particle density values presented here are within the ranges tabulated by Jackson (1956). For instance, values of 4.9-5.3, 4.28, 2.3, and 2.65 were given for hematite, goethite, gibbsite, and quartz, respectively. The observed reduction of mineral particle density upon drying was similar to observed reductions in soils and may be explained as done earlier in view of the reasons discussed by Gradwell (1955), Wada (1976), Wada and Wada (1975) and many other workers on the particle density of soil sample section.

g. Scanning Electron Micrography (SEM).—The scanning electron micrographs of seven different minerals are shown on Plates 4 to 11. These pictures were taken under the same working conditions as for the soil samples (section i in A). It was much easier to observe the structural differences here than it was for soil samples because of homogeneity of synthetic minerals. Examination of the micrographs indicated that oven and $P_2O_5$ drying have similarly resulted in the formation of large masses of sub-angular blocky, hard, closed crumbs. On the other hand, freeze drying and critical point drying resulted in rather
(A) oven-dried, (B) P$_2$O$_5$-dried, (C) freeze-dried,
(D) critical point-dried.
Fe-HYDROUS OXIDE (A)
Plate 5. Electron micrograph of Fe-hydrous oxide (B). (A) oven-dried, (B) $\text{P}_2\text{O}_5$-dried, (C) freeze-dried, (D) critical point-dried.
Fe-HYDROXIDE(B)
(A) oven-dried, (B) $\text{P}_2\text{O}_5$-dried, (C) freeze-dried,
(D) critical point-dried.
Plate 7. Electron micrograph of aluminum hydroxide. 
(A) oven-dried, (B) $P_2O_5$-dried, (C) freeze-dried, 
(D) critical point-dried.
AL-HYDROXIDE

A

B

100 u

50 u

C

D

100u

100u
Plate 8. Electron micrograph of aluminosilicate (0.5).
(A) oven-dried, (B) $P_2O_5$-dried, (C) freeze-dried,
(D) critical point-dried.
ALUMINOSILICATE
(SiO$_2$/Al$_2$O$_3$ = 0.5)
Plate 9. Electron micrograph of aluminosilicate (1.0).  
(A) oven-dried, (B) \( \text{P}_2\text{O}_5 \)-dried, (C) freeze-dried, 
(D) critical point-dried.
ALUMINOSILICATE
\((\text{SiO}_2/\text{Al}_2\text{O}_3=1.0)\)
Plate 10. Electron micrograph of aluminosilicate (2.0).
(A) oven-dried, (B) $\text{P}_2\text{O}_5$-dried, (C) freeze-dried,
(D) critical point-dried.
ALUMINOSILICATE
\((\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.0)\)
Plate 11. Electron micrograph of aluminosilicate (0.5) in high resolution. (A) oven-dried, (B) $P_2O_5$-dried, (C) freeze-dried, (D) critical point-dried.
ALUMINOSILICATE
\((\text{SiO}_2/\text{Al}_2\text{O}_3=0.5)\)
fluffy and open structure as compared to oven and P\textsubscript{2}O\textsubscript{5} drying. However, there were considerable differences between freeze and critical point drying as expected. In general, freeze dried samples always displayed plate sheet-like structure while critical point dried samples were characterized by more soft, fluffy, and open structure. Plate 11 is of the same synthetic aluminosilicate (0.5) mineral as Plate 8, but under higher resolution for closer observation of structural differences among different drying treatments.

3. Analysis of responses of different soils in view of pure mineral data

It can be observed by examining all the experimental results obtained with synthetic minerals, that the magnitude of surface reactivity and sensitivity to dehydration were in order of: aluminosilicates>iron hydrous oxide (A)>iron hydrous oxide (B)>aluminum hydroxide>α-iron oxide.

On the other hand, it was shown for the soils that the magnitude of surface reactivity and their sensitivity to dehydration were in the order of: Kaiwiki sub-surface>Puaulu sub-surface>Kaiwiki surface>Hilo sub-surface>Hilo surface>Puaulu surface. Analysis of both these results reveals that the surface reactivity and their sensitivity to dehydration were most closely related (positively correlated) with water retention characteristics (Table 5 and Figure 27). As shown on X-ray diffractograms (Figs. 10-12), amorphous materials were predominant in these three
soils displaying non-crystallinity in order of: Kaiwiki soils > Puaulu soils > Hilo soils. Careful study of X-ray diffractograms revealed that X-ray diffractograms of Kaiwiki and Puaulu soils were quite similar to X-ray diffractograms of aluminosilicates which are the highest in water retention characteristics and the highest in surface reactivity and their sensitivity thereupon. As described previously, however, it was noted that these soil characteristics deviated from precise order of non-crystallinity. Large differences in reactivity and sensitivity were noted between surface and sub-surface soils in both Kaiwiki and Puaulu soil series, notwithstanding the similarity of non-crystallinity. For the Kaiwiki soil, the X-ray diffractogram showed mineralogical differences between surface and sub-surface soils. On the contrary, a difference in non-crystallinity between surface and sub-surface Puaulu soil can hardly be seen. Instead, it was noted that clay content of Puaulu surface soil was remarkably low. Therefore, soil surface reactivity sensitivity upon drying may be readily predicted from the type, form, and content of different mineralogical constituents prevailing in the soils. Supplementary information on texture, previous dehydration history, and content of organic constituents may also be necessary.
C. Assessment of the extent of irreversibility

The observed irreversibility in the properties of Typic Hydrandepts upon drying has been examined in section (A). Furthermore, it was evident that even routine air drying induced irreversible cation exchange capacity reduction (Kanehiro and Sherman, 1956). Lim (1976) reported, in the study of dehydration on physico-chemical properties of selected volcanic ash soils from Hawaii, that air drying of Typic Hydrandepts (Akaka and Hilo soils) resulted in water content of 26.3% and 21.1%, respectively. It was of interest, therefore, to identify whether specific water contents were associated with such irreversibility. This was investigated using several indices, namely, particle size distribution, aggregate stability, surface area, water retention characteristics, soil consistency, and soil viscosity.

1. Shrinkage property of the soils

Dehydration has been known to be the necessary step for the formation of stable aggregates in soils. Consequently, the understanding of shrinkage behavior of soils is an important cornerstone for the study of the extent of irreversibility.

Figures 35 to 40 show overall shrinkage behavior of soils in relation to moisture content of soils. The volume reduction was expressed as a percentage of that at saturation and moisture content as a percentage of oven-dry
Figure 35. Volume shrinkage of fresh Kaiwiki surface soil upon drying.
Figure 36. Volume shrinkage of fresh Kaiwiki sub-surface soil upon drying.
Figure 37. Volume shrinkage of fresh Hilo surface soil upon drying.
Figure 38. Volume shrinkage of fresh Hilo sub-surface soil upon drying.
Figure 39. Volume shrinkage of fresh Puaulu surface soil upon drying.
Figure 40. Volume shrinkage of fresh Puaulu sub-surface soil upon drying.

Volume reductions (%) vs. Water content (%) after drying.
weight. The dotted lines indicate normal shrinkage of soils. The results revealed that the total soil volume reduction (shrinkage) of wet original soil was in the order of: Kaiwiki sub-surface > Puaulu sub-surface > Kaiwiki surface > Hilo sub-surface > Hilo surface > Puaulu surface. In each case, total volume reduction was positively related with the saturation moisture content (%) of these soils. Reeve and Hall (1978) reported that structural shrinkage occurred at the beginning of the soil-drying cycle from saturation moisture content, while normal shrinkage was in the middle portion of the curve, and residual shrinkage took place in between end of normal shrinkage and shrinkage limit.

These distinctions were based on the definitions of the three phases given by Stirk (1954). He defined these three shrinkage phases as: normal shrinkage (when the ratio of volume change to water loss was greater than 0.9), residual and structural shrinkage (when the volume change ratio was 0.05 to 0.9), and no shrinkage if the ratio was less than 0.05, respectively. In view of these definitions, results of this particular study showed no structural shrinkage at the beginning of the volume reduction. Slight normal shrinkage was noticed before residual shrinkage began. It should be mentioned that a clear distinction was not noted for the transition from normal shrinkage to residual shrinkage. Nor was an abrupt point noted at the "shrinkage limit." As can be seen in all the curves,
normal shrinkage generally ceased in the range between 0.1 and 1.0 bar suction. This was quite different from Reeve and Hall's observation (1978) on two clayey alluvial and two boulder clay soils in West Northamptonshire that the normal shrinkage phase continued far beyond 15 bar suction moisture content. Because of the ambiguity of the "shrinkage limit," a mathematical calculation for the shrinkage limit was paralleled (Table 19) together with visual estimation, applying equation (3) given in A.S.T.M. (Designation: D427-61)(1977). It is quite interesting to note that the two values for shrinkage limit of each soil in this experiment were close. The range of values shown in Table 19 indicates that the water content at which particles come in "closest" contact is not widely different for all soils under study, with subsequent implications to attractive forces and the water content for irreversibility. However, it must be stated that two distinguishable steps are involved in dehydration and subsequent interparticle cementation. In the range from saturation to shrinkage limit, particle interaction based on the DLVO theory may prevail without effective action by cementing agents. Initially at saturation, the particles are at maximum distance; the distance gets closer as drying proceeds down to the end of the normal shrinkage phase. Upon further dehydration to shrinkage limit, the soil particles achieve maximum contact. This suggests that the second dehydration
step, i.e., residual shrinkage phase, is more effective for enhancing interparticle attractions than the first one, i.e., the normal shrinkage phase. It may be possible, however, even at the shrinkage limit, that water films surrounding soil particles are sufficiently large as to keep cementing agents of very fine size from manifesting effective interparticle bonding. The following discussion will be revealing in this regard.

Table 19. Saturation water content, bulk density, and shrinkage limits for original (wet) soils.

<table>
<thead>
<tr>
<th>soils</th>
<th>saturated moisture (%)</th>
<th>bulk density calculated</th>
<th>shrinkage limit (%)</th>
<th>graphic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiwiki surface</td>
<td>296.89</td>
<td>0.303</td>
<td>43.56</td>
<td>43.00</td>
</tr>
<tr>
<td>Kaiwiki sub-surface</td>
<td>576.49</td>
<td>0.170</td>
<td>46.68</td>
<td>41.00</td>
</tr>
<tr>
<td>Hilo surface</td>
<td>176.89</td>
<td>0.471</td>
<td>65.12</td>
<td>59.00</td>
</tr>
<tr>
<td>Hilo sub-surface</td>
<td>165.47</td>
<td>0.503</td>
<td>60.09</td>
<td>55.00</td>
</tr>
<tr>
<td>Puaulu surface</td>
<td>146.48</td>
<td>0.554</td>
<td>67.29</td>
<td>65.00</td>
</tr>
<tr>
<td>Puaulu sub-surface</td>
<td>321.23</td>
<td>0.282</td>
<td>49.23</td>
<td>48.01</td>
</tr>
</tbody>
</table>

2. Determination of extent of drying on irreversible changes

a. Particle size distribution.—The particle size distribution was measured as one of the several indices for irreversible changes of the Typic Hydrandept soils upon drying. The particle size distributions of six samples of Typic Hydrandept soils, each subjected to various moisture
levels stepwise from saturation to oven dry were analyzed. The results are given in Figures 41 to 46, showing the changes of clay-, silt- and sand-sized particle contents upon gradual dehydration. It was observed that when these results were compared with the shrinkage curves of each soil (Figs. 35-40), the clay content began to decrease slowly at around 0.1-1.0 bar suction which was the end of normal shrinkage or the beginning of the residual shrinkage phase. The changes persisted slightly beyond the shrinkage limits of soils.

On the other hand, the changes of sand sized content upon dehydration were not so prominent compared with the changes of clay content. In other words, the increase of sand sized content was observed after the clay content was considerably decreased. This indicated that the change of particle sizes upon dehydration involved mostly the association of the more reactive clay-sized particles into silt-sized particles firstly. It is also speculated that any sand sized aggregates formed upon dehydration probably were less coherent and experienced higher impacts upon collision than silt sized aggregates, while samples were being shaken for particle size distribution analysis. Hence, sand sized particles were broken down into silt-sized prior to silt-sized particles into clay.

As expected, the most significant changes in clay and sand sized particle contents occurred near the shrinkage limit of each soil.
Figure 41. Change of particle size distribution for fresh Kaiwiki surface soil upon drying.
Figure 42. Change of particle size distribution for fresh Kaiwiki sub-surface soil upon drying.
Hilo surface soil

Suction (bars)

Recoverd particle content (%)

Water content (%) after drying

Figure 43. Change of particle size distribution for fresh Hilo surface soil upon drying.
Figure 44. Change of particle size distribution for fresh Hilo sub-surface soil upon drying.
Figure 45. Change of particle size distribution for fresh Puaulu surface soil upon drying.
Figure 46. Change of particle size distribution for fresh Puauulu sub-surface soil upon drying.
Kubota (1972), on the basis of measurements of approximate soil suction at which irreversible bonding of clay into sand sized particles occurred on drying, reported that the clay and silt contents started to decrease when suction exceeded pF 3.5 (i.e., 3.1 bars) forming fine sand sized particles. Increase in coarse sand sized particles was not observed until suction was increased to about pF 5.0 (i.e., 100 bars) at which the clay and silt sized particles were at a minimum. He also observed that no further changes in particle size distribution occurred at suction above pF 5.5 (i.e., 315 bars).

b. Aggregate stability.--In addition to the extent of soil aggregates, the stability of the aggregates is very important in the evaluation of soil structure, particularly in relation to soil susceptibility to water or wind erosion. The mean weight diameter (MWD) was adopted as the aggregate stability parameter to evaluate the extent of irreversibility of soils in drying. This parameter of soil aggregates was introduced by van Bavel (1949). Maximum aggregate stabilities (plateaus) (Fig. 47) were reached in the early stage of dehydration. In terms of soil shrinkage, these plateaus were already reached at the end of the normal shrinkage phase or even before the end of that phase. In contrast, it may be recalled from section (a), that no changes occurred in particle size distribution upon gradual dehydration (Figs. 41-46), until the soils reached the
Figure 47. Change of aggregate stability index (MWD) of fresh soils upon drying. (K-6), (K-12), (H-3), (H-4), (P-13), and (P-15) refer to Kaiwiki surface and sub-surface, Hilo surface and sub-surface, and Puaulu surface and sub-surface soils, respectively.
residual shrinkage phases. This discrepancy between changes in particle size distribution and aggregate stability could be explained by the differences of physical forces associated with the analysis of these two properties. For aggregates of given strength, the 20-minute vigorous shaking for particle size analysis was much more destructive than the 30-minute simple up and down movement in the water for water stable aggregate analysis. Thus, the abrupt rather than gradual changes in the content of sand sized particles were observed at the last extent of drying.

c. Surface area by H₂O vapor adsorption.--The changes of surface area of soils upon drying to different moisture levels (between saturation and oven dry) were measured by water vapor adsorption technique. The amount of water adsorbed by soils at water vapor P/P₀=0.2 (Quirk, 1955) was considered to provide monolayer coverage and was attained by using a saturated solution of CH₃COOK in water. The surface areas at different drying stages are given in Figures 48-50. The changes in surface areas were hardly recognizable until the soils were dried quite extensively. Abrupt reductions of surface area were observed after the moisture content was at least less than 20-25% in all soil cases. The extent of change was more prominent in subsurface soils than in surface soils probably because of partial experience in dehydration of the surface soils. The maximum reductions of surface area were 49%, 36%, 45%,
Figure 48. Change of specific surface area (m²/g) of fresh Kaiwiki soil upon drying.
Figure 49. Change of specific surface area (m²/g) of fresh Hilo soil upon drying.
Figure 50. Change of specific surface area (m$^2$/g) of fresh Puaulu soil upon drying.
21%, 61%, and 42% in Kaiwiki sub-surface, Kaiwiki surface, Hilo sub-surface, Hilo surface, Puaulu sub-surface, and Puaulu surface soil, respectively.

On the other hand, the relative humidity can be related in terms of water suction units (bars or pF) citing following formulas. From the Kelvin equation (Marshall, 1959), the vapor pressure $P/P_0 = 0.2$ can be converted into suction by the expression:

$$h = \frac{RT}{g} \ln \left(\frac{P}{P_0}\right)$$

(12)

where $R$ is the gas constant per gram, $T$ is the absolute temperature, $g$ is the acceleration due to gravity, $P$ is the vapor pressure of the water in chemical saturated water, and $P_0$ is the vapor pressure of the water in bulk. The conversion may also be made by the relationship:

$$\log_{10} h = 6.5 + \log(2 - \log \text{R.H.})$$

(13)

where $\log_{10} h = \text{pF}$, and R. H. (Relative Humidity) is $P/P_0 \times 100$, respectively. The calculated suction equivalent to $P/P_0 = 0.2$ through both equations was 2210340 cm (2210 bars). All dried samples within each soil series, yet, above vapor pressure of $P/P_0 = 0.2$ (not above suction of 2210 bars) sustain higher amounts of water than the water amount which could be adsorbed by these soils at relative humidity of 20%. Consequently, it can be readily understandable that there should not be any difference in
adsorbed water amount among soil samples drying further to measure surface area at relative humidity of 20%.

On the contrary, the soils which were dried to lower than vapor pressure of $P/P_0 = 0.2$ or above the water suction of 2210 bars (oven dried soils in this particular experiment) were not able to adsorb water as much as other moist soils which had been dried less extensively, demonstrating an irreversibility of soils because of structural alteration.

d. Water retention characteristics.--Since the reduction of water retention by Typic Hydrandepts on complete drying by oven, $P_2O_5$, freeze, and critical point drying was evident, effort was made to find the extent of such reduction. Consequently, the changes of water retention at 50 cm water suction (Fig. 51) by a series of soils dehydrated stepwise from saturation to oven dry were traced.

It was found that all sub-surface soils always showed higher water retention characteristics than surface soils in the same soil series until soils were extensively dried. This may be due to pre-experienced drying of surface soils to some extent, by one reason or another, in the natural environment, prior to soil sampling. It can also be noted that at the beginning of drying, the water retention properties were not changed in any soil, up to a certain level.
Figure 51. Change of water retention characteristics of fresh soils upon drying. (K-6), (K-12), (H-3), (H-4), (P-13), and (P-15) refer to Kaiwiki surface and sub-surface, Hilo surface and sub-surface, and Puaulu surface and sub-surface soils, respectively.
However, further pre-dehydration beyond this level induced the reduction of water retention gradually until complete drying cycle. Comparing water retention characteristics to the shrinkage curve of each soil, it was found that the critical water content occurs beyond the end of the normal shrinkage phase (or beyond the beginning of residual shrinkage phase). However, it was evident, comparing the water stable aggregate curve (Fig. 47) to this water retention characteristic (51), that the attraction forces (electrostatic or hydrogen bonds) acting between particles continued to increase upon progressive dehydration even within the normal shrinkage region. The estimated inter-particle distances based on moisture contents and surface areas of each soil near the end of normal shrinkage ranged approximately from 115 to 140Å. Therefore, it can be concluded that the irreversibility in terms of water retention characteristics occurred when the particle distance became closer than this distance, or when soils were dehydrated beyond the end of normal shrinkage phase (beginning of residual shrinkage phase).

e. Soil plasticity (liquid limit, plastic limit, and plastic index).—As for the other soil properties, soil consistency is one of the physical properties which distinguishes non-crystalline soils from other materials. Wet non-crystalline soils normally have a high liquid limit and plastic limit which result in a low plastic index.
Other than this property, these soils are plastic when wet, and non-plastic when dry. Accordingly, the change of consistency on gradual drying was measured in order to investigate the extent of drying at which the irreversibility occurred in terms of soil consistency. Data for changes of the liquid limit are presented in Figure 52. Because the plastic limit and plastic index were well positively correlated with liquid limit values, their data are shown in Appendix III. Figure 52 showed that the overall pattern of liquid limit changes was quite similar to the water retention characteristics curve. The liquid limit remained high until the end of normal shrinkage phase was approached. Then the liquid limit was reduced upon further dehydration beyond the normal shrinkage phase indicating that the change of liquid limit was induced irreversibly from within the residual shrinkage phase. Soma and Maeda (1974) have reported similar results by measuring liquid limits on allophane soils. Their results indicated that allophanic soils which were gradually dried showed a sharp break at a specific water content where liquid limit decreased linearly indicating that the irreversible changes began at that dehydration level. They also reported that the liquid limit was constant while the soil was still in the normal shrinkage phase. The liquid limit then began to decrease continuously after the normal shrinkage phase had passed. Therefore, it was evident that the reduction
Figure 52. Change of liquid limit of fresh soils upon drying. (K-6), (K-12), (H-3), (H-4), (P-13), and (P-15) refer to Kaiwiki surface and sub-surface, Hilo surface and sub-surface, and Puaulu surface and sub-surface soils, respectively.
of moisture content beyond the normal shrinkage caused a gradual reduction of soil plasticity (soils becoming non-plastic) due to irreversible loss of soil cohesion. It may also be observed here, comparing the liquid limit curves (Fig. 52) and/or soil shrinkage curves (Figs. 35-40) to plastic limit (Appendix III), that the soil moisture content at the end of normal shrinkage was below the plastic limit of each soil, hence causing soils to be non-cohesive, "friable." The soil friability is defined as the moisture range where the moisture is sufficient to minimize the cementation effects between the individual particles but not enough to cause the formation of distinct films around particle contacts that produce the cohesion. Consequently, cohesion of individual granules is at a minimum. Such structural formation restricts regaining the original plasticity.

f. Soil viscosity.--Figures 53-55 illustrate the changes of viscosity upon gradual dehydration of soils from saturation to oven drying. These changes of viscosity were compared at a specific soil suspension concentration for each soil. This concentration was 26% and 14% for Kaiwiki surface and sub-surface soils, 36% and 35% for Hilo surface and sub-surface soils, and 40% and 25% for Puaulu surface and sub-surface soils, respectively. It is interesting to note that the changes of viscosity in every soil occurred in two phases with transition zone in between. This
Figure 53. Change of viscosity of fresh Kaiwiki soil upon drying.
Figure 54. Change of viscosity of fresh Hilo soil upon drying.
Figure 55. Change of viscosity of fresh Puaulu soil upon drying.
transition zone reflected a rather slow reduction (changes) of viscosity upon dehydration. In addition, the wider transition zone (wide range of moisture percentage) was observed in soils with higher saturation moisture content. It is also pointed out that the transition zones (slow viscosity change range) overlapped with their residual shrinkage phases of each soil. These results suggest that drastic viscosity changes of soil suspension occurred at two different stages, i.e., at the beginning of the dehydration (from beginning to end of normal shrinkage phase) and at the end of complete dehydration (from shrinkage limit to oven dry). This behavior is completely different from that observed for all other changes of soil characteristics upon dehydration.

The viscosity of a liquid expresses the internal friction between the molecules of liquid. Hence, viscosity is a structural and temperature sensitive property of liquid. However, the viscosity of the soil suspension expresses the integrated effects of the molecules of the water, the influence of the particles on the structure of the associated water, and the impact of particle interaction as it acts upon status of the soil particles (size, shape, and dispersability) and their degree of hydration. Earlier, it had been shown that the viscosity of soil suspensions decreased not only with the concentration of soil suspension but also with dehydration of soils (Fig. 22).
The effects of both factors (concentration of soil suspension, and dehydration of soils) are obvious when examining the mathematical relationship proposed by Einstein (1905) (Reiner, 1969):

\[ \eta_s = \eta_m (1 + 2.5\phi) \]  

(14)

where \( \eta_s \) is the viscosity of the colloidal system, \( \eta_m \) the viscosity of the dispersion medium, and \( \phi \) the volume of the dispersed phase per unit volume of sol. The volume \( \phi \) includes the total volume associated with the particles such as any water hull around individual particles or water enmeshed within aggregates.

van Olphen and Waxman (1958) tested the relationships between specific viscosity \( (\eta_{sp} = \eta_{rel} - 1) \) and clay concentration and particle size in soil suspension, and found that the change of specific viscosity was sigmoid shaped as Figures 53-55 show, upon change of clay concentration, and the sigmoid shape was more enhanced as the size of particle increased. They also pointed out that the higher initial clay concentration to increase the specific viscosity hereupon was required as increasing particle size in soil suspension, because of the higher clay concentration required for the initiation of particle interactions in larger clay particle suspension.

Therefore, an explanation of the sigmoid type of viscosity change upon gradual dehydration in this experiment
could be speculated as follows:

The change of water structure associated with non-crystalline materials from that of bulk water as described by Wells and Furkert (1972) or Boutron and Alben (1975) was responsible for the drastic change of viscosity at the beginning stage of dehydration (normal shrinkage phase). At the same time, the granulation initiated in this dehydration stage was great enough to accelerate decreasing viscosity (by reducing internal friction). On the other hand, at the end of dehydration stage, again the rate of viscosity change was sharp because of the shifting sigmoid curves from left to right upon increasing soil particle size as the reason explained by van Olphen and Waxman (1958) previously.
SUMMARY AND CONCLUSIONS

Three Hawaii Typic Hydrandepts and seven synthetic minerals, known for cementing effects, were subjected to four different drying techniques and subsequent changes in physical and rheological properties were investigated. The extent of drying necessary to cause "irreversible" changes of soil physical and rheological properties was also investigated.

A. Effects of alternative drying techniques on soil characteristics

Three Hawaii Typic Hydrandepts developed from the same volcanic ash under three different climatic regimes were subjected to drying at zero relative humidity at "room temperature," in a 105°C oven, by freeze drying and by a new method, i.e., critical point drying. It was concluded that:

1. Critical point drying was the best technique to preserve original soil structure as visually confirmed by scanning electron microscope inspection, and quantitatively assessed by measuring soil physical properties after dehydration. Drying treatments ranked with respect to preservation of original soil properties in the order of: critical point drying > freeze drying > P₂O₅ drying >
oven drying. However, none of the methods was fully successful in preserving original properties.

2. The severity of changes in soil properties upon dehydration was positively related to the moisture content of the original (natural wet) soils, thus in the order: Kaiwiki sub-surface soil > Puaulu sub-surface soil > Kaiwiki surface soil > Hilo sub-surface soil > Hilo surface soil > Puaulu surface soil.

3. Comparison between reductions of surface area and water retention characteristics upon dehydration indicated that the loss of water retention capacity was not simply due to structural alteration (and subsequent reduction of surface area) but more so because of the loss of original (colloidal) water order at the soil surface upon drying.

4. All drying treatments produced apparent reductions of particle density in all soils. This was explained by the difficulty in refilling small openings (intra-voids) within dehydrated aggregates by water.

B. Roles of individual cementing agents

Using individual synthetic minerals, it was concluded that:

1. The effect of four drying techniques on changes of synthetic mineral properties were exactly in the same order and magnitude as on soils.
2. The severity of changes of synthetic mineral properties observed upon dehydration were in order of:
Aluminosilicates > iron hydrous oxides > aluminum hydroxide > iron oxide (hematite). This indicated that fine graded "sesquioxide poor" constituents are almost as likely to cause irreversible dehydration as pure sesquioxides. However, the effectiveness of the synthesized soil constituents based on their unit surface areas were in the order of: iron hydrous oxide monohydrated (B) (goethite) = aluminum hydroxide (gibbsite and bayerite mixture) > α-iron oxide (hematite) > iron hydrous oxide monohydrated (A) (akaganeite) > aluminosilicates. This indicated that particle size or the extent of crystallinity are also decisive factors in causing irreversibility.

3. Particle densities of all synthetic minerals were also reduced after being subjected to any dehydration technique.

4. The magnitudes of surface area and also of water retention characteristics of original (wet) minerals and their changes upon dehydration were in the order of: aluminosilicates > iron hydrous oxides > aluminum hydroxide > iron oxide (hematite).
C. Effects of drying stage on change of soil physical characteristics of Typic Hydrandepts

1. Shrinkage measurements revealed that the greater the soils' original moisture content (saturation), the longer the normal shrinkage phase. However, normal shrinkage was always ended between 0.1-1.0 bar suction. The shrinkage limits of these soils ranged from 41% to 65%, far beyond 15 bar suction.

2. The severity of irreversible change of soil physical properties of these three Typic Hydrandepts were in the order of: Kaiwiki sub-surface soil>Puaulu sub-surface soil>Kaiwiki surface soil>Hilo sub-surface soil>Hilo surface soil>Puaulu surface soil, indicating that the irreversibility is positively related to original moisture content and to the content of non-crystalline material, which, in turn, is positively correlated with rainfall regime associated with soil formation.

3. In general, the threshold point for irreversible change was the soil's residual shrinkage phase. However, the observed changes were different for different soil properties, as follows:

(a) Soil viscosity was the most sensitive characteristic on soil dehydration. The viscosity started to decrease from the beginning of dehydration continuously to the end (oven drying).
(b) Water stable aggregate content also began to increase from the beginning of dehydration but ended approximately at the end of the residual shrinkage phase.

(c) No changes were observed in either water retention or soil consistency (liquid limit, plastic limit, and plastic index) until the end of the normal shrinkage phase and gradual decreases were observed from the beginning of the residual shrinkage phase to oven drying.

(d) Reduction in clay-sized particle content first occurred at the end of the normal shrinkage phase while increases in the content of sand-sized particle appeared after near the end of the residual shrinkage phase. Both changes were nearly completed at a point somewhere between the shrinkage limit and complete (oven) drying.

(e) A considerable reduction of surface area (measured by water vapor adsorption at $P/P_0=0.2$) was observed only after intensive dehydration, i.e., within the range of shrinkage limits (41% to 65%) far beyond 15 bar suction and after oven (complete) drying.
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APPENDIX I

A. Description of Hydrandepts

1. Definition and occurrence

Hydrandepts, in the strict sense, is a term in Soil Taxonomy which represents one of the seven great soil groups within the order Inceptisols. In the U. S. Taxonomy (Soil Survey Staff, 1975), Hydrandepts are generally described as having the following characteristics: (1) deep profiles, usually with distinct depositional stratification, (2) mostly dark, reddish color in regions with very high, well-distributed rainfall and perudic moisture regime, (3) water above "field capacity" during most of each year, (4) almost continuous leaching with weathering products that consist of a gelatinous mixture of "allophane," organic matter, free sesquioxides, and usually gibbsite, (5) low bulk density because of open-structure and high content of water and organic matter, (6) high water holding capacity, and (7) formation of large segregated aggregates or crumbs as a result of "irreversible" dehydration.

These soils were called Hydrol Humic Latosols in the 1938 USDA Great Soil Group Classification System (Baldwin et al., 1938).

It would be meaningful to clarify a term "allophane" which is being widely misconstrued relative to Hydrandepts,
prior to further literature review in this section. In view of the recent specific definition, allophane minerals are stated as being "member of a series of naturally occurring minerals which are hydrous aluminosilicates of widely varying chemical composition, characterized by short range order, by the presence of Si-O-Al bonds, and by a differential thermal analysis (DTA) curve displaying a low temperature endotherm and a high temperature exotherm with no intermediate endotherms" (van Olphen, 1971; and Wada, 1977).

Maeda, et al. (1977) and Wada (1977) distinguished between allophane, imogolite, and amorphous materials. Allophane gives an X-ray diffraction characteristic of non-crystalline materials because of only short-range crystalline order, but does have an identifiable spherule form in electron micrographs. "Imogolite" was first described by Yoshinaga and Aomine (1962) in a soil derived from a glassy volcanic ash known as "imogo." This has a defined X-ray diffractogram with a number of broad reflections. Those with maxima at 12-20, 7.8-8.0, and 5.5-5.6Å are enhanced by "parallel" orientation of specimen during X-ray exposure. It also has a characteristic morphological form (smooth and curved threads varying in diameter from 100-300Å and extending several um in length) in electron micrographs. On the other hand, amorphous materials in soils do have X-ray diffraction
characteristics of non-crystalline materials also but no
definite and structural arrangement in electron micrographs.
Accordingly, non-allophanic Hydrandepts such as Hawaii
Typic Hydrandepts can be readily distinguishable from most
allophanic Typic Hydrandepts (Typic Hydrandepts consisting
of large portion of allophane minerals).

In a less specific sense, however, "allophane" can
be used to describe soils having observed properties common
to soil materials which arise from weathering of pyroclastics as "volcanic ash soils" or "Andepts" or "Andosols."
The distribution of these Hydrandepts is known to be in
intertropical regions, more frequently in the Caribbean and
Andean lands, as well as in the Pacific areas of Indonesia,
Japan, New Zealand, and parts of the United States (Allen,
1977). The occurrence of these soils is recognized from
weathering volcanic ash and other saprolitic volcanic rocks
(pyroclastic materials) (Maeda, et al., 1977; and Allen,
1977). It should be noted, however, that the reverse is
not necessarily true. Tokashiki and Wada (1972) and Shoji
and Masui (1972) reported that montmorillonite, humus,
hydrous aluminum and iron oxides, opaline, and silica were
present but no imogolite and allophane, during the early
stage of volcanic ash weathering. Tokashiki and Wada
(1972) noted that there seemed to be an inverse relation­
ship between the abundance of opaline silica and allophane
in volcanic ash soils. They also noted that allophane was
absent in the presence of opaline silica and humus containing more than 15% organic carbons. Fieldes (1955) and others pointed out the importance of sequential relationships such as allophane B - allophane AB - allophane A - metahalloysite - kaolinite in the formation and transformation of non-crystalline clay materials. Swindale (1975) presented the development of mineralogical sequences from volcanic glass as follows, showing that allophane is an intermediate product for amorphous materials:

\[
\begin{align*}
\text{volcanic glass} \quad \text{(obsidian, etc.)} & \quad \text{montmorillonite} \\
\text{palagonite} & \quad \text{halloysite} \quad \text{gibbsite}
\end{align*}
\]

\[
\begin{align*}
\text{allophane} & \quad \text{amorphous oxides}
\end{align*}
\]

Wada and Harward (1974) noted, reviewing the literature, that nearly all varieties of volcanic ash (rhyolitic, dacitic, andesitic, and basaltic) produced allophane, although different in chemical composition, stability and amount. Henmi and Wada (1974) observed, by high resolution electron microscopy, that imogolite was always associated with allophane in different amounts. However, the inverse of this observation did not seem to be necessarily true.

2. **Hawaii's Typic Hydrandepts**

The Hamakua Coast area of the Island of Hawaii was recognized as being the site of extensively weathered
volcanic ash soils by Maxwell (1898). Extraordinary characteristics of these soils such as relatively high organic matter content, high water holding capacity, and irreversible drying were noticed by Richter (1931), Dean (1947) and others. Sherman (1949) suggested that weathering occurred rapidly in the high rainfall, or perhumid climate area and caused development of distinctive stratification of the parent ash and the formation of the Hydrol Humic Latosols. The occurrence of these soils on the Island of Hawaii was surveyed by Cline (1955). Bates (1960) believed allophane and imogolite to be major products of relatively early weathering of basalt in a perhumid climate of Maui. However, products of weathering depend primarily upon the rainfall, slope, and texture of rocks. He also postulated that desilication appeared to be the rule in the Hawaiian weathering picture, even though resilication may be locally important. Volcanic glass was the apparent source of most Al, Fe, Si gel materials which became allophane, cliachite, or gibbsite, depending on the kind and relative proportion of the cations present. Tamura, et al. (1953) reported that allophane was identified in substantial amounts (approximately 30%) in the 0.2um fractions of two Hydrol Humic Latosols (Akaka, and Hilo soils). Other minerals present included gibbsite (25-35%), goethite (10-35%), magnetite (5-20%), mica (1-10%), and quartz (0-3%). Sherman (1957) observed that
the sheet-like gibbsite formed when Hydrol Humic Latesols in Hamakua Coast were dried, but little evidence usually existed for gibbsite when soils were in field moisture condition. Variable amounts of chemical constituents and minerals were reported in Typic Hydrandepts by many others (Sherman, 1958; Irving, 1961; Calhoun and Hill, 1962; Tenma, 1965; Lai and Swindale, 1967; and Lim, 1976). Voss (1969) reported that the Hilo and Akaka soils were situated on a weathering sequence in between common allophane-containing volcanic ash soils and bauxite deposits, but in reality were neither. He had negative views on the presence of allophane in these soils, though positive on the presence of non-crystalline allophane-like materials of amorphous hydrated aluminum and iron oxides. These materials, however, appeared to have similar characteristics as allophane. Patterson (1963) found white, soft, and open-structured allophane as well as aluminosilicate gels on Maui, Hawaii. Both the allophane and air-dried gel were similar in composition containing approximately 50% of Al₂O₃ and 22-26% of SiO₂. He postulated that the weathering of volcanic rock to form saprolite began soon after lavas cooled, and the formation of clays by weathering volcanic rock proceeded in places for more than half a million years. He also suggested the mineralogical sequence of:

\[ \text{SiO}_2 - \text{Al}_2\text{O}_3 \text{ gels} \rightarrow \text{allophane} \rightarrow \text{gibbsite and halloysite} \]
Wada, et al. (1972) examined the inorganic gel and allophane from basaltic saprolite on Maui, Hawaii studied by Patterson (1963) previously. They found that the main constituents of the gel were imogolite and gibbsite, with allophane being the minor constituent. They suggested the crystallization of imogolite from allophane and revealed differences in structural organization between imogolite and allophane through high resolution electron micrographs. Jones and Uehara (1973) observed non-crystalline material in the Akaka soil which appeared to be "amorphous" even in high resolution electron micrographs but not allophane. Chan (1972) revealed the morphology of Hilo soil by electron micrographs and X-ray diffraction analysis. He thought that imogolite was dominant as variable amounts of short fibrous materials were present together with translucent gels, minor amounts of gibbsite, quartz, feldspar, micas, goethite, magnetite, and kaolinite.

Most recently, Wada and Wada (1976) reported that B horizons of two Hydrandepts (Hilo and Akaka) were characterized by predominance of hydrous non-crystalline alumina and iron oxides associated with considerable amounts of humus and with very small amounts of silica because of strong desilication in the weathering of volcanic ash. Allophane, allophane-like constituents and imogolite were present but in minor amounts. Gibbsite, goethite, chlorite and illite were also present as accessory minerals.
3. Characteristics of Hydrandepts

It is known that the two most distinctive characteristics of Hydrandepts are "thixotropy" and "irreversible dehydration," although they also possess other unusual properties. "Thixotropy" and other properties have been reviewed in this section, providing another section for review of "irreversible dehydration."

a. Thixotropy.---The term "thixotropy," a rheological term the definition of which is reported to have been introduced in 1927 by A. F. Peterfi, appears in the taxonomic family unit of many Hydrandepts in association with mineralogical class. It was originally defined by H. Freundlich as the phenomenon of isothermal, reversible gel-sol transformation in colloidal suspensions (Seed and Chan, 1957). Another definition provided by van Wazer, et al. (1963) refers to the case whereby a mineral reversibly exhibits more fluidity with increasing time of flow under steady-state conditions. If, on the contrary, the mineral exhibits more resistance to flow with increasing time while being subjected to steady-state shear, it is said to display "rheopesy." On a phenomenological basis, pseudoplastic flow occurs at the immediate conclusion of thixotropic behavior and dilatant flow occurs at the immediate conclusion of rheopectic behavior.
Rahman (1974) categorized thixotropic materials into thixotropic and partially thixotropic categories, using the thixotropic strength ratio which is defined as follows:

\[
T.S.R. = \frac{\text{Strength of specimen tested after time } "t"}{\text{Strength of identical specimen tested immediately after disturbance}}
\]

Figure 1 shows the cyclic curves which characterize both types. Many workers, however, criticize the use of the term "thixotropy" in soil genesis and classification, because of the subjective interpretations of thixotropic characteristics of soils in the field, even though the term is correctly understood. It is partly for this reason that Smith (1978) proposed the reclassification of Andepts.

Terzaghi (1944), as reported by Penner (1965), used the term clay sensitivity synonymously with thixotropy, defining both in terms of the unconfined compressive strength, as the ratio of the natural (undisturbed) strength of a soil to its remoulded strength. Later, Smalley (1972) reported that sensitivity values varied from 1 for a London clay to 1,500 for a Canadian Leda clay. There have been many proposed classifications of soils with respect to sensitivity. The comparison of four such classifications by Mitchell, et al. (1972) is presented in Table 1. Pusch (1966) defined another term, "quick clay," as a clay whose sensitivity exceeds a certain value, usually 30-50. Mitchell, et al. (1972) also gave a descriptive definition
A. PURELY THIXOTROPIC MATERIAL

B. PARTIALLY THIXOTROPIC MATERIAL

Thixotropic Strength Ratio = \( \frac{S_A}{S_R} \)

Acquired Sensitivity After Time \( t = \frac{S_T}{S_R} \)

Thixotropic Regain After \( t = S_T - S_R \)

Percent Thixotropic Regain After \( t = \left( \frac{S_T - S_R}{S_R} \right) \times 100 \)

Figure 1. Properties of thixotropic materials
(A after Mitchell, 1960)
(B after Skemoton and Northey, 1953)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S=1: insensitive clays</td>
<td>S=1-2: clays of low sensitivity</td>
<td>S=3-5: low sensitivity</td>
<td>S&lt;20: normal clays</td>
</tr>
<tr>
<td>S=1-2: clays of low sensitivity</td>
<td>S=1-2: slightly sensitive clays</td>
<td>S=5-7: medium sensitivity</td>
<td>S=20-50: semi-quick clays</td>
</tr>
<tr>
<td>S=2-4: clays of medium sensitivity</td>
<td>S=2-4: medium sensitive clays</td>
<td>S=7-11: medium to high sensitivity</td>
<td>S&gt;50: quick clays</td>
</tr>
<tr>
<td>S=4-8: sensitive clays</td>
<td>S=4-8: very sensitive clays</td>
<td>S=11-14: high sensitivity</td>
<td></td>
</tr>
<tr>
<td>S&gt;8: extra-sensitive clays</td>
<td>S=8-16: slightly quick clays</td>
<td>S=14-20: high to very high sensitivity</td>
<td></td>
</tr>
<tr>
<td>S&gt;16: quick clays</td>
<td>S=16-32: medium quick clays</td>
<td>S=20-40: very high sensitivity</td>
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<td></td>
<td>S=32-64: very quick clays</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>S&gt;64: extra-quick clays</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*As reported by Mitchell, et al. (1972)
of quick clay as a clay of such high sensitivity that it behaves as a viscous fluid in the remoulded state.

Rahman (1974) studied the interrelationships involving sensitivity, thixotropy, and electrokinetic phenomena in some Hawaiian soils. He found for the Hilo soil (Typic Hydrandept) that bulk density, shear strength, hydraulic conductivity, electrokinetic coefficient, and soil-water tension were changed upon remoulding. Electrical conductivity was one exception. As expected, changes of these properties were also discovered upon aging of the remoulded samples.

b. **Chemical properties.**—Chemical properties of Typic Hydrandepts (particularly soils containing imogolite and allophane) are summarized as follows: cation exchange capacity values of 20-50 meq./100g and anion exchange capacity values of 5-30 meq./100g were obtained by equilibrating allophane soil clay (<2μm) with 0.2N-NH₄Cl solution at pH 7.0 (Wada and Ataka, 1958; Fieldes and Schofield, 1960). The cation exchange capacity values of 135 meq./100g for allophane (SiO₂/Al₂O₃ ratio=2.0 and <2μm) and 30 meq./100g for imogolite were obtained by equilibrating with 0.05 N-NaCH₃OO at pH 7.0 (Henmi and Wada, 1974). Iimura (1966) measured the apparent negative and positive charges with an allophane having SiO₂/Al₂O₃ ratio of 1.43, and Wada (1977) reproduced the data and calculated net charges in between pH 4.0-8.0 as shown in
Figure 2. It is believed that the development of apparent negative and positive charges in response to pH is due to the sorption of H\(^+\) or OH\(^-\) ions on surfaces, and that allophane having other SiO\(_2\)/Al\(_2\)O\(_3\) ratios might exhibit somewhat different cation exchange capacity and anion exchange capacity versus pH curves.

![Figure 2: Effect of pH on charge development of allophane (<2\(\mu\)m) (Wada, 1977)](image)

The effects of salt concentration on cation exchange capacity of soils containing imogolite and allophane were summarized to be positive, cation exchange capacity increased with increasing salt concentration. The effects of ion species on cation exchange capacity and anion exchange capacity of soils containing imogolite and allophane were in increasing order of:

\[ K > Ca = NH_4 = Na > Mg \] on cation exchange capacity and
S_4O_4^2->CH_3COO^->Cl^->NO_3 on anion exchange capacity (Wada and Tsuji, 1973).

The effects of temperature, drying, and cation selectivity were also reported by many workers (Wada and Harada, 1969 and 1971; Egashira and Aomine, 1974; Yoshida, 1961; and Wiklander, 1964). It was reported that the electrodialized suspensions of allophane clays showed pH range of 4.0-6.5 (Iimura, 1966) and that all exchange sites were occupied by H^+, whereas 60% of sites on layer silicates were occupied by Al. This high affinity of allophane and imogolite for H^+ indicates weak acid properties. It was also reported that allophane and imogolite showed weak acidity in most environments, and that the strength of their acidity was enhanced upon decreasing water content of soils (Mortland, 1970).

It is known that interactions between anions and non-crystalline aluminosilicates occur in three different ways: specific adsorption, non-specific adsorption, and decomposition of these aluminosilicates induced specifically by adsorbed anions. These reactions have been intensively studied specifically for hydrous Fe-oxides (Hingston, et al., 1967; Greenland, 1971).

The high accumulation of humus constitutes one important feature of Andepts. Recently, linear correlation between humus and 0.1M-Na_4P_2O_7 extractable Al for a number of Andepts was shown by Wada and Higashi (1976). It has been
reported that allophane and imogolite are effective in non-specific and specific adsorption of organic anions but adsorb little or no organic cations (Greenland and Quirk, 1962; Kinter and Diamond, 1960). It has also been found that allophane clays adsorb considerable amounts of enzymes (Kobayashi and Aomine, 1967) and that allophane exhibits catalytic effects on oxidative changes of polyphenols (Kyuma and Kawaguchi, 1964; Kumada and Kato, 1970).

c. Physical properties.--The physical properties of allophane soils, in summary, are low bulk density, high water holding capacity, high liquid and plastic limit, difficulty to disperse, slippery but non-sticky consistency, anomalous compaction behavior, and irreversible changes in all these properties on drying.

The 15 bar retention, plasticity, and surface area were used for index properties of allophane (Packard, 1957; Flach, 1964; Birrell, 1966; Colmet-Daage, et al., 1967; and Warkentin, 1972) instead of particle size distribution for most soils. The difficulty of inducing dispersion is one of the limitations of using particle size in predicting physical properties of allophane soils.

There is a bulk of papers on the dispersion of allophane soils (Gautheyrou, et al., 1976). Optimum pH for good dispersion of Kanto loam was reported to be pH range 2.5-3.5 (Tada and Yamazaki, 1963). However, it was reported that surface soil generally dispersed better at high pH of 10-11
with NaOH, while sub-soils at pH 3.0 with HCl (Colmet-Daaget, et al., 1972). It was found that usual dispersing agents could not be used for allophane soils (Sherman, et al., 1964). Ultrasonic dispersion is known to release clay size particles from aggregates (Oba and Kobo, 1965) but still much lower values for clay content than values estimated from the 15 bar water content (Espinoza, et al., 1975).

The complete description of the water retention curve of swelling crystalline clay soils depends on water content, suction, and sample volume. However, the complete description of the water retention curve for allophane soils depends on one more variable, i.e., initial degree of sample drying in addition to above three variables (Warkentin, 1976). Water retention by allophane, unlike the swelling clay minerals, was determined by the size distribution of voids, not by the magnitude of surface area (Fujwara and Baba, 1973). Maeda and Warkentin (1975) found that soils with a high content of allophane have an S-shaped water retention curve, similar to the shape for coarse grained soils. The approximately linear portion on the water content:log suction plot was between 0.01 and 0.1 bar suction in contrast to between 0.01 bar to around 100 bar for swelling crystalline clays. Forsythe (1972) mentioned that the loss of water retention in allophane soils upon drying was greater at low suctions than at high
suctions. Maeda and Warkentin (1975) found that allophane soil had a higher saturated hydraulic conductivity than soils with montmorillonite at same void ratio, and that drying increased the saturated hydraulic conductivity at constant bulk density.

Some measured mineral densities of wet allophanes were the range of 1.80 to 2.78 (Fieldes and Claridge, 1975; Forsythe, et al., 1964; Bonfils and Moinereau, 1971; and Wada and Wada, 1975). Wada and Wada (1975) recommended specific precautions to remove entrapped air from the structurally hollow spherules of allophane particles (50Å outside diameter and about 30Å inside diameter). Plasticity is one of the physical properties which distinguishes allophane from crystalline materials. In contrast with crystalline clays, the plasticity limits of allophane samples located far from the "A" line on a Cassagrande plot (Fig. 20) having a high liquid limit and low plastic index. This suggested the use of plastic values in classification of allophane soils (van Schuylenborgh, 1953; Gradwell and Birrell, 1954; Warkentin, 1972; and Warkentin and Maeda, 1974). The "A" line on Cassagrande's plasticity chart is an important empirical boundary within the Unified Classification system for soil mechanics and is presented by the equation (Cassagrande, 1948; Sato, 1971):

\[
\text{Plasticity index} = 0.73 \times (\text{liquid limit} - 20) \quad (1)
\]
This gives the boundary between inorganic clays which occur above the "A" line and the organic colloids and typical inorganic silt and silt clays which occur below the "A" line. The practical significance of this chart is that the "A" line together with liquid limit of 50% boundary classifies all soils largely within five categories for the purpose of soil engineering.

It has long been observed that the initially large volume of wet allophane decreased but only a limited recovery of the volume was obtained on rewetting. This volume change has been termed "irreversible." This characteristic distinguishes allophane and amorphous soils from other swelling mineral soils (Maeda, et al., 1977). It was reported that the shrinkage limit occurred between 50 and 100% (gravimetric %) for allophane soils, a much higher value than for crystalline clays (takenaka, 1965; and Soma and Maeda, 1974). Takenaka (1965) also found that the shrinkage limit of allophane soils occurred near pH 6.

Wells and Furkert (1972) attempted to investigate in more detail the extraordinary behavior of water associated with allophane materials. They proposed three different means of water bonding to allophane; namely surplus free water, single water molecules hydrogen bonded to the clay surface, and hydrogen bonded clusters of water molecules situated in micropores which represent the main structural bulk in naturally occurring allophane. The last form was
partially obtained by re-wetting allophane from its wilting point water content, but not obtained following re-wetting allophane after intensive drying. Wada and Wada (1977) studied the structure of allophanes separated from samples of weathered pumice using X-ray diffraction, infrared spectroscopy, and density measurement. They suggested a scheme for spherical, structural units of allophane. They characterized allophane particles as having 35-55Å of external diameter and 7-10Å of wall thickness containing many openings which permit passage of water molecules. They also postulated that the wall of the unit consists of imperfect, or defective kaolin-like layer structures with Al in four-fold coordination, and that the space surrounded by the wall is filled with water (10% of oven dry clay) which is strongly retained.
APPENDIX II

Particle size distribution at different soil water content (%)

<table>
<thead>
<tr>
<th>moisture content (%)</th>
<th>particle size distribution (%)</th>
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<tbody>
<tr>
<td></td>
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<table>
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<th>Kaiwiki sub-surface soil</th>
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(continued)
APPENDIX II, continued

Particle size distribution at different soil water content (%)

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<tr>
<th>moisture content (%)</th>
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<th>Hilo sub-surface soil</th>
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<td>2-53μm</td>
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## Particle size distribution at different soil water content (%)

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<tr>
<th>moisture content (%)</th>
<th>&lt;2um</th>
<th>2-53um</th>
<th>&gt;53um</th>
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APPENDIX III

Soil consistency at different soil water content (%)

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<thead>
<tr>
<th>Soil Moisture</th>
<th>Kaiwiki surface soil</th>
<th>Kaiwiki sub-surface soil</th>
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</thead>
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<tr>
<td>Liquid Limit</td>
<td>205.0 200.0 202.0 184.0 170.0 78.0 47.6</td>
<td>438.0 439.0 435.0 392.0 175.0 112.0 53.0 46.5</td>
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<td>Plastic Limit</td>
<td>138.0 129.9 133.3 139.0 132.7 no cohesion</td>
<td>320.3 319.5 321.7 304.0 96.7 45.6 no cohesion</td>
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<td>Plastic Index</td>
<td>67.0 70.1 68.7 45.0 37.3 no cohesion</td>
<td>117.7 119.5 113.3 88.0 78.3 66.4 no cohesion</td>
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</tbody>
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(continued)
Soil consistency at different soil water content (%)

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<tr>
<th></th>
<th>Hilo surface soil</th>
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</thead>
<tbody>
<tr>
<td>soil moisture</td>
<td>176.9% 132.3% 102.4% 68.0% 54.3% 36.1% 0.0%</td>
<td>166.0% 145.2% 134.2% 97.4% 79.6% 65.4% 0.0%</td>
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<tr>
<td>liquid limit</td>
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<td>149.0 150.0 150.0 138.0 117.0 90.0 45.0</td>
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<td>plastic limit</td>
<td>111.8 114.9 111.5 99.2 97.4 75.0 50.0</td>
<td>90.7 94.9 93.6 87.8 77.3 69.9 no cohesion</td>
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<tr>
<td>plastic index</td>
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<td>59.0 55.1 56.4 50.2 39.7 20.1 no cohesion</td>
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(continued)
APPENDIX III, continued

Soil consistency at different soil water content (%)

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<th>Puauulu surface soil</th>
<th></th>
<th>Puauulu sub-surface soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>soil moisture</td>
<td>147.0%   135.1%</td>
<td>107.7%  87.5%</td>
<td>71.2%  45.2%  0.0%</td>
</tr>
<tr>
<td>liquid limit</td>
<td>131.0     136.0</td>
<td>131.0  117.0</td>
<td>100.0  68.2  33.4</td>
</tr>
<tr>
<td>plastic limit</td>
<td>85.6      83.3</td>
<td>84.6  78.9</td>
<td>68.2  49.1  no cohesion</td>
</tr>
<tr>
<td>plastic index</td>
<td>45.4      45.1</td>
<td>44.8  38.1</td>
<td>31.8  18.9  no cohesion</td>
</tr>
<tr>
<td>soil moisture</td>
<td>321.2%   257.7%</td>
<td>189.5%  158.8%</td>
<td>85.7%  52.9%  21.9%  0.0%</td>
</tr>
<tr>
<td>liquid limit</td>
<td>288.0     285.0</td>
<td>259.0  230.0</td>
<td>103.0  71.0  56.0  47.3</td>
</tr>
<tr>
<td>plastic limit</td>
<td>184.5     190.5</td>
<td>170.5  148.9</td>
<td>65.1  55.8  no cohesion</td>
</tr>
<tr>
<td>plastic index</td>
<td>93.3      94.5</td>
<td>88.5  81.1</td>
<td>37.9  15.2  no cohesion</td>
</tr>
</tbody>
</table>