AN ABSTRACT OF THE THESIS OF

Gody Spycher

for the degree of Ph.D.

in Soil Science presented on August 12, 1977

Title: Fractionation and Some Properties of Water-Dispersible Soil Organic-Mineral Particles

Abstract approved: (J. L. Young)

A survey of clay-size soil organic-mineral particles (somp's) from Oregon soils representing six different soil orders was conducted. An additional andeptic surface soil sample from Japan was included. The samples were fractionated into size fractions by water-dispersion and centrifugation. The clay-size material was further fractionated by density using a newly devised surfactant-free method.

The distribution of density subfractions depended on the levels of organic matter and the nature and amounts of associated amorphous oxides. Broad density distributions were prominent in soil suborders (andepts, humults, aquods) known for their high contents of amorphous oxides and/or organic matter. The relative contents of amorphous oxides, organic matter, and microcrystalline iron oxides also accounted for the observed overall density of soils.

Specific pedogenetic conditions influenced the distribution and composition (organic carbon and nitrogen) in the granulometric fractions. The C/N ratios decreased with particle size.

Organic carbon and nitrogen decreased with increasing subfraction density; the C/N ratios narrowed sharply from the lightest to the next heavier fractions, then more gradually over the remaining fractions. The alkali extractability of organic matter followed a similar trend but
increased with subfraction density. It was concluded that the degree of humification increased with subfraction density, and that the lightest fractions included admixtures of less humified materials.

Oxidative degradation (DTA under O_2) of the high organic matter subfractions resulted in two well-defined exotherms, one above and one below 400°C. Variations in exotherm intensities and peak temperatures with subfraction density were considered in terms of strength of the organo-mineral interaction, metal-organic complexing, degree of humification, and extent of interlamellar adsorption. Evidence of interlamellar adsorption of soil organic materials was obtained.

Amounts and composition of amorphous inorganic oxides in the density subfractions were assessed using a kinetic dissolution method. Amorphous Al and Si decreased with increasing subfraction density. The final slopes of the cumulative extraction curves appeared to be related to the susceptibility of smectite and chloritic intergrades to the dissolution treatments. The molar SiO_2/Al_2O_3 ratios of the amorphous oxides ranged from 0.2 to 6.7, and reflected varying contributions of organically complexed Al, mineral composition, and weathering environments. Significant correlations between amorphous Al and organic carbon were observed.

The X-ray analysis of the density subfractions indicated gradual transitions from light, poorly defined mineral matter to heavier, more crystalline components, particularly in the case of chloritic intergrades. The major matrix mineral in Quillayute, Blacklock and Mitaka was beidellite; in Jory, Woodburn and Madras the nature of the chloritic intergrade matrix could not be definitely ascertained.

Surface areas determined by nitrogen adsorption were very low in some's and inversely correlated with organic carbon. After peroxidation the N_2-areas decreased with increasing subfraction density as did the areas determined by adsorption of water vapor before and after peroxidation. The Kelvin radii calculated from nitrogen desorption isotherms peaked within 20-24 Å.

The cation exchange capacities determined with neutral salt and at pH 8.2 also decreased with increasing subfraction density. The
differences between the two values were significantly correlated with organic carbon.

The IR spectra of some subfractions failed to indicate major differences in the organic phases. This result was attributed to high attenuation of the organic matter in KBr pellets.

Electron microscopy of selected subfractions tended to confirm the results obtained by other methods. Light particles were heavily coated with amorphous gels while heavier particles had well-defined, clean outlines.

A microaggregate model was proposed in an effort to account for the continua in composition and properties observed in studying somp subfractions. The model proposes that heavier somp's are preferentially located in the core of spherical microaggregates, while lighter somp's tend to occupy peripheral positions. The proposed model implies that, in some soils, microaggregates may be the sites and provide the conditions necessary for important pedochemical processes such as clay mineral synthesis.
Fractionation and Some Properties of Water-Dispersible Soil Organic-Mineral Particles

by

Gody Spycher

A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

June 1978
 APPROVED:

Redacted for privacy

Associate Professor of Soil Science; Chemist ARS, USDA

Redacted for privacy

Head of Soil Science

Redacted for privacy

Dean of Graduate School

Thesis presented August 12, 1977

Typed by Karla McMechan for Gody Spycher
The author wishes to express his gratitude to Dr. J. L. Young for his counsel, patience, and encouragement in conducting this study. Appreciation is also extended to Drs. M. E. Harward, K. Cromack and W. H. Slabaugh for serving on the program committee, and for providing laboratory facilities. Special thanks are due to M. Meconis, T. E. Laurent, and C. J. Choquette for assistance in laboratory work and drafting.

The author gratefully acknowledges financial support from the OSU Agricultural Experiment Station, the USDA-ARS, and the OSU Water Resources Research Institute.
# TABLE OF CONTENTS

## I. Introduction ......................................................... 1

## II. Literature review .................................................. 2
1. Introduction .................................................. 2
2. Adsorptive behavior of soil organic compounds on clay minerals ............................................... 4
   21. Adsorption isotherms ....................................... 4
   22. Effect of cation saturation .............................. 6
   23. Effect of pH ............................................. 7
   24. Effect of minerals ....................................... 8
   25. Preferential adsorption of soil organic compounds .......................... 10
4. Soil organic-mineral particles .................................. 12
   41. Methods of fractionation .................................. 13
   42. Review of results ....................................... 14
5. Soil aggregation .................................................. 16
6. Summary .......................................................... 19

## III. Materials and methods ........................................... 21
1. Soils ......................................................... 21
2. Methods ...................................................... 21
   22. Density fractionation of the less-than 2 μm somp's ............................................... 23
   23. Organic carbon, total nitrogen, extractability of organic matter ............................................... 26
   24. Oxidative degradation of somp's (DTA) .................... 26
   25. Determination of amorphous inorganic oxides ............... 27
   26. X-ray analysis, IR spectroscopy, and transmission electron microscopy ............................................... 28
   27. Determination of surface areas and porosity ............... 29
   28. Cation exchange capacity .................................. 31

## IV. Results ........................................................... 33
1. Preliminary experiments ....................................... 33
2. Distribution of density subfractions in soil clays .......... 38
3. Organic carbon and total nitrogen in granulometric soil fractions ............................................... 42
5. Oxidative degradation of the organic phase in somp subfractions ............................................... 53
6. Amorphous oxides in somp subfractions ....................... 62
7. X-ray diffraction analysis of somp subfractions ............. 72
8. Surface areas and porosity .................................... 96
9. Cation exchange capacities .................................... 103
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10. Infrared spectroscopy of selected somp subfractions</td>
<td>106</td>
</tr>
<tr>
<td>11. Electron microscopy of selected somp subfractions</td>
<td>113</td>
</tr>
<tr>
<td>V. Discussion</td>
<td>123</td>
</tr>
<tr>
<td>1. Summary of results</td>
<td>123</td>
</tr>
<tr>
<td>2. The organic and crystalline phases in somp's</td>
<td>126</td>
</tr>
<tr>
<td>3. Microaggregates in soils</td>
<td>128</td>
</tr>
<tr>
<td>4. A tentative model for the structure and function of soil microaggregates</td>
<td>129</td>
</tr>
<tr>
<td>VI. Bibliography</td>
<td>134</td>
</tr>
<tr>
<td>VII. Appendices</td>
<td>148</td>
</tr>
<tr>
<td>I. Sampling Locations and Profile Descriptions</td>
<td>148</td>
</tr>
<tr>
<td>II. X-Ray Diffraction Pattern of Soil Organic-Mineral Density Subfractions</td>
<td>160</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Classification and factors of formation of soils</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>Yield of $&lt;2 \mu m$ soil organo-mineral particles separated from different soils and subfractionated by centrifugation in heavy-density liquids</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>Organic carbon and total nitrogen in granulometric soil fractions</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>Organic carbon and total nitrogen in $&lt;2 \mu m$ organo-mineral density subfractions</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>Amorphous Si-, Al-, and Fe-oxides in clay-size organo-mineral density subfractions</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>Summary of X-ray diffraction results from somp density subfractions before and after removal of organic matter and amorphous inorganic oxides</td>
<td>73</td>
</tr>
<tr>
<td>7</td>
<td>Surface areas of clay-size somp density subfractions measured by adsorption of nitrogen gas and water vapor before and after peroxidation</td>
<td>97</td>
</tr>
<tr>
<td>8</td>
<td>Cation exchange capacities with neutral salt and at pH 8.2 of somp density subfractions</td>
<td>104</td>
</tr>
<tr>
<td>9</td>
<td>Assignments of IR adsorption bands for clay-size somp's</td>
<td>108</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>X-ray diffractograms of organo-mineral fractions separated from Jory B22 bulk clay by surfactant-aided centrifugation in a stepwise density gradient</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Selective extraction of amorphous oxides from Quillayute A bulk clay and of iron oxides from Jory B3 clay, X-ray diffractograms of Mg-saturated specimens, 54% relative humidity</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>X-ray diffractograms of clay-size organo-mineral density fractions separated from Quillayute A bulk clay</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Distribution of organo-mineral density subfractions</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Organic carbon and total nitrogen in granulometric soil fractions</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Organic carbon and nitrogen in granulometric fractions as % of total soil organic carbon and nitrogen</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Organic carbon and total nitrogen in organo-mineral clay-size density subfractions</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>DTA curves of clay-size somp density subfractions from Bashaw, Madras, and Woodburn</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>DTA curves of clay-size somp density subfractions from Blacklock</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>DTA curves of clay-size somp density subfractions from Quillayute</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>DTA curves of clay-size somp density subfractions from Mitaka</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>DTA curves of clay-size somp density subfractions from Jory, (a) untreated, (b) peroxide treated</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>13</td>
<td>Cumulative extraction curves for SiO$_3$, Al$_2$O$_3$, and Fe$_2$O$_3$ in clay-size, peroxide-treated subfractions from Quillayute and Bashaw.</td>
<td>63</td>
</tr>
<tr>
<td>14</td>
<td>Amorphous Si-, Al-, and Fe-oxides in clay-size organic-mineral density subfractions</td>
<td>67</td>
</tr>
<tr>
<td>15a</td>
<td>X-ray diffractograms of untreated Quillayute somp subfractions</td>
<td>75</td>
</tr>
<tr>
<td>15b</td>
<td>X-ray diffractograms of Quillayute somp subfractions after removal of amorphous oxides</td>
<td>76</td>
</tr>
<tr>
<td>15c</td>
<td>X-ray diffractograms of Quillayute somp subfractions after removal of amorphous oxides</td>
<td>77</td>
</tr>
<tr>
<td>16a</td>
<td>X-ray diffractograms of untreated Jory somp subfractions</td>
<td>78</td>
</tr>
<tr>
<td>16b</td>
<td>X-ray diffractograms of Jory somp subfractions after removal of amorphous oxides</td>
<td>79</td>
</tr>
<tr>
<td>17a</td>
<td>X-ray diffractograms of untreated somp subfractions from Blacklock</td>
<td>80</td>
</tr>
<tr>
<td>17b</td>
<td>X-ray diffractograms of untreated somp subfractions from Blacklock</td>
<td>81</td>
</tr>
<tr>
<td>17c</td>
<td>X-ray diffractograms of untreated somp subfractions from Blacklock</td>
<td>82</td>
</tr>
<tr>
<td>17d</td>
<td>X-ray diffractograms of somp subfractions from Blacklock after removal of amorphous oxides</td>
<td>83</td>
</tr>
<tr>
<td>17e</td>
<td>X-ray diffractograms of somp subfractions from Blacklock after removal of amorphous oxides</td>
<td>84</td>
</tr>
<tr>
<td>18a</td>
<td>X-ray diffractograms of somp subfractions from Mitaka after removal of amorphous oxides</td>
<td>85</td>
</tr>
<tr>
<td>18b</td>
<td>X-ray diffractograms of somp subfractions of Mitaka after removal of amorphous oxides</td>
<td>86</td>
</tr>
<tr>
<td>19a</td>
<td>X-ray diffractograms of untreated somp subfractions from Woodburn</td>
<td>87</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>19b</td>
<td>X-ray diffractograms of somp density fractions from Woodburn after removal of amorphous oxides</td>
<td>88</td>
</tr>
<tr>
<td>20a</td>
<td>X-ray diffractograms of untreated somp subfractions from Bashaw</td>
<td>89</td>
</tr>
<tr>
<td>20b</td>
<td>X-ray diffractograms of somp subfractions from Bashaw after removal of amorphous oxides</td>
<td>90</td>
</tr>
<tr>
<td>21a</td>
<td>X-ray diffractograms of untreated somp subfractions from Madras</td>
<td>91</td>
</tr>
<tr>
<td>21b</td>
<td>X-ray diffractograms of somp subfractions from Madras after removal of amorphous oxides</td>
<td>92</td>
</tr>
<tr>
<td>22</td>
<td>X-ray diffractograms of some density subfractions from Jory</td>
<td>93</td>
</tr>
<tr>
<td>23</td>
<td>Surface areas of clay-size somp density subfractions measured by adsorption of nitrogen gas and water vapor before and after peroxidation</td>
<td>98</td>
</tr>
<tr>
<td>24</td>
<td>Nitrogen adsorption-desorption isotherms of selected peroxide-treated somp subfractions</td>
<td>100</td>
</tr>
<tr>
<td>25</td>
<td>Pore size distributions below 100 Å of selected peroxide-treated somp subfractions</td>
<td>101</td>
</tr>
<tr>
<td>26</td>
<td>Water vapor adsorption-desorption isotherms of selected untreated and peroxide-treated somp subfractions</td>
<td>102</td>
</tr>
<tr>
<td>27</td>
<td>Cation exchange capacities of somp subfractions measured with neutral salt and at pH 8.2</td>
<td>105</td>
</tr>
<tr>
<td>28</td>
<td>IR spectra of fulvic and humic acid, bentonite, kaolinite and imogolite</td>
<td>109</td>
</tr>
<tr>
<td>29</td>
<td>IR spectra of somp subfractions and water-dispersible clay from Quillayute before and after treatment with peroxide</td>
<td>110</td>
</tr>
<tr>
<td>30</td>
<td>IR spectra of somp subfractions and water-dispersible clay from Jory before and after treatment with peroxide</td>
<td>111</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>31</td>
<td>IR spectra of individual somp subfractions from selected soils before and after treatment with peroxide</td>
<td>112</td>
</tr>
<tr>
<td>32</td>
<td>The distribution of organic, amorphous inorganic and crystalline phases in somp subfractions</td>
<td>125</td>
</tr>
</tbody>
</table>
FRACTIONATION AND SOME PROPERTIES OF WATER-DISPERSIBLE
SOIL ORGANIC-MINERAL PARTICLES

I. INTRODUCTION

Organic and inorganic colloids in soils interact to form complexes of varying composition and properties. These clay-size soil organic-mineral particles (somp's) provide the dominant surfaces for physical, chemical and biological phenomena in soils.

There remains a widespread preference to investigate organo-mineral systems with both organic and mineral phases well defined. The work on artificial systems has led to a much improved understanding of soil organo-mineral interactions, although the transfer of results to soil systems may be questionable at times. Studies concerned with natural somp's are therefore needed.

Heterogeneity in both the mineral and organic components of somp's is commonly observed. The implications of particle heterogeneity for data collection and interpretations are considerable. For this reason, many studies devote much attention to somp fractionation procedures. Research along these lines has intensified during the past decade, with emphasis frequently on the organic phase. Comprehensive studies of somp's are scarce, and attempts to relate somp heterogeneity to specific pedogenetic processes are lacking.

This study surveys clay-size organic-mineral particles as they occur in surface soils of different pedogenetic character. Specifically the objectives were

1. to devise a method of fractionation permitting the collection of more uniform separates of somp's,
2. to determine the composition and some properties of the organic and inorganic components of these separates, and
3. to relate these findings to pedologic functions of somp's.
II. LITERATURE REVIEW

1. Introduction

Inorganic and organic soil constituents cover broad ranges in molecular dimensions and chemical properties. Interactions between these components lead to an impressive array of products, including small, water-soluble metallo-organic complexes, larger clay-organic particles, and ultimately systems of higher order, such as aggregates (Deuel, 1960). This review is limited to a discussion of particles formed by the interaction of clay minerals and soil organic polymers, commonly called soil organo-mineral complexes (omc's) or soil organo-mineral particles (somp's).

Basic to the existence and understanding of somp's are the chemical and physical interactions between various types of mineral surfaces and polydisperse organic materials. The most productive approach in studying these interactions has been to utilize organic compounds of known constitution, and to infer from their known chemical properties their expected behavior with specific mineral surfaces. It is then assumed that the same functional groups, when present in soil organic materials, would exhibit similar reactivities in contact with mineral surfaces in soil. Much of what is known about soilorganic-mineral interactions has been derived from work on systems wherein both organic and inorganic phases were well defined.

Proposed bonding mechanisms between soil organic and inorganic materials have been extensively reviewed by Greenland (1965 a, b; 1971) and Mortland (1970). The various classes of bonding mechanisms may be summarized as follows.

Coulombic interactions: These include reversible anion and cation adsorption. Protonation is an important cationic reaction whereby organic bases are rendered ionic by accepting protons supplied from exchangeable hydrogen, hydration water of exchangeable metal cations, or by proton transfer from other cationic species adsorbed on the clay
surface. Metal cations linking negative mineral surface charges with negatively charged organic functional groups are termed cation bridges. Specific adsorption or pH-dependent ligand exchange (Hingston et al., 1972) refers to the penetration of the coordination shells of surface metal atoms by functional groups such as carboxyls. Cation bridges and ligand exchange may well undergo coordinative interactions, particularly when transition metals are involved.

Ion dipole and coordinative interactions: Mortland (1970) reserves this class of reactions to polar organic compounds. For example, amides will protonate on hydrated, acid (H, Al) montmorillonite surfaces (Tahoun and Mortland, 1966a), but coordination complexes result when Na, Ca or Cu are the exchangeable cations (Tahoun and Mortland, 1966b). Pi-bonding involving molecular orbital overlap between pi-electrons of unsaturated and aromatic hydrocarbons and transition metal d-orbitals may be included here.

Hydrogen bonding: Water bridges between polar organic molecules and mineral surfaces provide a common mode of linkage. Organic-organic hydrogen bonding between adsorbed species is also likely to occur. Hydrogen bonding is 10 to 20 times less energetic than coulombic interactions, but additivity may lead to stable complexes with large polymers. Hydrogen bonding between mineral surfaces and nonpolar portions of organic molecules, considered fundamental in the past, have not been confirmed by recent work according to Mortland (1970). However, Francis (1973) studying PVP-adsorption on montmorillonite again suggested the existence of such bonds.

Van der Waals forces: Greenland (1965a) suggested that these relatively weak forces are significant in soap's, although the principal interaction appears to operate between adsorbed molecules rather than at the organic-mineral interface.

Entropy effects: Positive entropy change accompanying the adsorption of a large molecule and the simultaneous desorption of several small molecules (usually water) has been suggested as a factor in the adsorption of polymers, depending on their molecular weight (Greenland

Covalent bonds: Covalent linkages between silicates and organic compounds have been formed artificially, but the extent of their occurrence in soils is unknown.

All these bonding mechanisms are likely to contribute simultaneously in soils both on the level of individual somp's and in aggregate formation. However, current analytical techniques are far from quantifying the relative contribution of each possible interaction in a given soil.

2. Adsorptive behavior of soil organic compounds on clay minerals

21. Adsorption isotherms

Adsorption isotherms help in (a) interpreting adsorption mechanisms and solute orientation at solid surfaces, (b) identifying the presence of associated solute molecules or impurities, (c) determining the specific surface areas of solids (Giles et al., 1974).

Considering humic- or fulvic acid-bentonite systems, Langmuir curves (L-type) were observed with K⁺-saturation (Evans and Russell, 1959), Ca²⁺- and Al³⁺-saturation (Inoue and Wada, 1968), while linear C-type curves were found with Ca²⁺- and H⁺-saturation (Evans and Russell, 1959). Theng and Scharpenseel (1975) reported C-type curves regardless of saturation. Maxima in the adsorption isotherms of similar systems were tentatively related to aggregate formation by Valla et al (1972). With Ca²⁺-, K⁺-, and H⁺-saturated kaolinite, humic and fulvic acid gave Langmuir curves (Evans and Russell, 1959).

Langmuir type curves are often associated with systems having few and widely spaced adsorption sites and where hydrophobic ends of molecules may lay flat on the surface. C-curves are linear over a given range of solute concentration, then show an abrupt change to zero slope (plateau) unless a new layer of solute is adsorbed. Adsorption
yielding C-type curves is interpreted (Giles et al., 1974) in terms of solute molecule penetration into substrate micropores, rendering additional adsorption sites accessible to solute molecules. The continuous creation of new sites requires an expansion of the accessible surface as adsorption progresses. In montmorillonite this can be achieved through interlayer penetration by solute molecules such as amino acids and oligopeptides (Greenland et al., 1965a, b), or, at low pH, fulvic acids (Schnitzer and Kodama, 1966) and humic acids (Martinez and Rodriguez, 1969). In the case of an allophane-alkylammonium system (Theng, 1972), C-curves resulted from entry of solute into adsorbent interstices. Because humic acids do not enter interlayer spaces of bentonite under slightly acid to neutral conditions, alternative explanations had to be found for C-curves. Theng and Scharpenseel (1975) attributed linear adsorption to penetration of intradomain pores by humic acid polymers acting as wedges. The average domain porosity in bentonite of about 100Å (Aylmore and Quirk, 1960) would be large enough to accommodate humic colloids. Saturation with polyvalent cations does not seem to affect this process.

Whether organic molecules in soils are capable of exposing new surfaces during adsorption remains a matter of speculation. Adsorption of many inorganic and small organic anions by allophanic soils yielded Langmuir curves rather than C-curves (Gebhardt and Coleman, 1974; Appelt et al., 1975).

Desorption of a marine humic acid extract previously adsorbed at pH 8 to natural sediments and various clay minerals was studied by Rashid et al. (1972). Washes with distilled water desorbed more than half of the adsorbed humic acid; recovery was lowest with illite (68%) and highest with kaolinite (86%) as adsorbents. Natural somp's extracted with cold water release but insignificant amounts of organic materials; the difficulty of inferring natural behavior from adsorption of humic extracts to clay minerals is clearly illustrated by these experiments.
22. Effect of cation saturation

The influence of exchangeable cations on the adsorption of humic compounds on clay minerals has been known empirically for a long time (Demelon and Barbier, 1929). Meyer (1935) suggested the existence of Ca-bridges between organic and inorganic soil phases.

Several studies have established that increasing valence charge of exchangeable cations increases their efficiency in binding humic preparations to smectites and kaolinites (Evans and Russell, 1959; Sen, 1964; Scharpenseel, 1966; Valla et al., 1972; Theng and Scharpenseel, 1975). Similar series were observed in experiments with kaolinite and soil polysaccharides (Saini and McLean, 1966), and in a system containing montmorillonite, humic and amino acids (Scharpenseel and Kruse, 1971). Other work by Scharpenseel (1970) with electrodialysed montmorillonite demonstrated that amino acids can assume bridging functions in the formation of clay-humic complexes.

The study of Theng and Scharpenseel (1975) with montmorillonite and \(^{14}C\)-labelled humic acid supports modern concepts about clay-organic interactions. According to these authors, adsorption is related to the ionic potential \((Z/r)\) and hydration properties of exchangeable cations. Humic acid functional groups appear to be directly associated with monovalent ions, whereas in polyvalent ion systems linkage occurs through water bridges. Positive deviations of Al and Fe from the observed relationship were attributed to supplemental ligand exchange and complexation reactions.

There are instances where these simple relationships are seemingly not applicable. For example, the intermellar adsorption of fulvic acid on smectite (Kodama and Schnitzer, 1968) resulted in a cation series whose order seems unrelated to ionic potentials, and bears little resemblance to the order of stability of fulvo-metallic complexes (Schnitzer, 1969), or to that of the Irving-Williams series (Irving and Williams, 1953). Kodama and Schnitzer (1968) concluded from DTA-experiments that cations enhancing the adsorption of fulvic acid may have less affinity
for water when situated in the clay lattice interlayer. A precise explanation of these findings is still lacking. In a humic acid-allophane system, cation saturation did not significantly affect adsorption (Inoue and Wada, 1968); whether cations affect adsorption by other amorphous materials such as hydrous oxide coatings has not been reported.

23. Effect of pH

Several reports show that adsorption of humic substances on clay minerals increases as pH is lowered (Demelon and Barbier, 1929; Evans and Russell, 1959; Schnitzer and Kodama, 1967). Interlamellar adsorption of fulvic acid (Schnitzer and Kodama, 1966) and humic acid (Martinez and Rodriguez, 1969) on montmorillonite at low pH is one of the mechanisms enhancing adsorption. However, increased adsorption of humics at low pH occurs also with non-swelling phyllosilicates (Kodama and Schnitzer, 1974). The release of Al-ions from clay lattices in acid systems can enhance adsorption if equilibration times are of the order of one day or more (Evans and Russell, 1959); but Schnitzer and Kodama (1967) found that the reaction between fulvic acid and montmorillonite was virtually complete within one hour. Positive edge charges on clay minerals potentially favor coulombic interactions between organic and inorganic phases, although, simultaneously, the dissociation of organic acid groups is suppressed. Zero or low charge on fulvic acid when sorbed on montmorillonite was inferred from DTA and IR adsorption (Schnitzer and Kodama, 1967), yet it appeared from IR spectra that carboxyl groups of fulvic acid were dissociated upon interaction at low pH with sepiolite (Kodama and Schnitzer, 1974). Certainly, pH among other factors profoundly affects the conformation (Chen and Schnitzer, 1976) and the polydispersity (Warshaw and Pinckney, 1971; Seidel and Ziechmann, 1972) of solvated humic materials. Thus, large aggregates of fulvic acid forming at low pH (Chen and Schnitzer, 1976) may be a deciding factor in its enhanced adsorption at low pH.
Higher adsorption at low pH was also observed on lepidocrocite, but bayerite and gibbsite showed the reverse behavior (Evans and Russell, 1959); no explanation was given for these findings.

24. Effect of minerals

Only a few comparative studies on the adsorption of soil organic materials on different minerals have been published. Among phyllosilicates, bentonites have been studied most frequently and are generally more adsorptive than kaolinites (Evans and Russell, 1959). Comparing non-expanding minerals (kaolinite, muscovite, sepiolite), Kodama and Schnitzer (1974) noted relatively high adsorption of fulvic acid by sepiolite, a behavior resulting from FA penetration into the structural channels of this mineral.

Amorphous oxides are commonly considered as highly efficient adsorbents of humates (Evans and Russell, 1959; Levashkevich, 1966). "Allophane" with an Si/Al ratio of less than one adsorbed nearly ten times as much humic acid at slightly alkaline pH as did bentonite (Inoue and Wada, 1968); no correlation of adsorption with extractable iron was found. Iron, usually credited with a high affinity for humic functional groups (Saini and McLean, 1966; Schnitzer, 1969; Theng and Scharpenseel, 1975), does not seem to enhance the adsorption of humics on amorphous allophanic clays. Conceivably, iron is readily incorporated into surfaces of allophanic oxides and/or its effect on adsorption may be overshadowed by the extensive surface areas of these materials.

Greenland (1971) suggests that the main mechanisms of interaction on hydrous oxide surfaces are anion and ligand exchange, as proposed by Hingston et al. (1967 and 1972) in their work on anion adsorption by goethite and gibbsite. The application of these concepts to the interaction of organic compounds with amorphous hydrous oxides existing in soil as surface coatings, edges of clay particles, and allophanic phases seems realistic since similar relationships have been observed in adsorption studies on whole soils (Obihara and Russell, 1972) including
andepts (Appelt et al., 1975). Although the mechanisms of specific adsorption (ligand exchange) have been derived from experiments with small inorganic and organic anions, humic and fulvic acids containing carboxylic groups may be expected to participate in ligand exchange reactions.

Terminal metal atoms of an oxide surface complete their coordination shells with OH-groups and/or water molecules. In aqueous suspension, $\text{H}^+$ and $\text{OH}^-$ act as potential determining ions. For pure metal oxides, the point where all surface sites are neutral, has been called the "point of zero charge" (pzc). In soils where oxides are closely associated with clay minerals having a permanent negative charge, the pzc refers to equality of negative and positive charges. At a pH below the pzc, $\text{H}^+$ is adsorbed in excess of $\text{OH}^-$, and the surface acquires a net positive charge which can be balanced by adsorption of an anion from solution, provided that the anion has no specific affinity for the metal atoms of the surface. The anion is non-specifically adsorbed and exchangeable.

The specific adsorption of an anion involves the formation of a coordination complex at an oxide surface (Hingston et al., 1972). The relationship between adsorption and pH varies with the $pK_a$ of the conjugate acid of the anion. Fully dissociated acids adsorb specifically only to the extent of the positive surface charge, i.e. not beyond the pzc. With incompletely dissociated acids, anion adsorption occurs also at pH-values more alkaline than the pzc, if the pH is in the vicinity of the $pK_a$ of the acid. The energy required to abstract a proton from the acid is at a minimum near the $pK_a$. The proton is required to remove a surface OH-group which provides the site for the anion (Hingston et al., 1972). Ligand exchange always implies either a decrease in positive charge (adsorption of fully dissociated acid), or an increase in negative charge (adsorption of incompletely dissociated acid), and hence a shift of the pzc to more acid values.

While it was suggested that similar mechanisms are operative in allophanic soils (Appelt et al., 1975), the possible influence of
tetrahedrally coordinated Al in amorphous silico-alummas (de Kimpe et al., 1961; Cloos et al., 1969) and allophane (Udagawa et al., 1969) has not been ascertained. But high surface areas together with the fact that ligand exchange does not require charged sites would help explain humus accumulation in allophanic soils.

25. Preferential adsorption of soil organic compounds

Selective adsorption of soil humic compounds by clay minerals has been reported by several workers. Optical density measurements revealed that darker components of fulvic acid and lighter components of humic acids were preferentially adsorbed by montmorillonite (Evans and Russell, 1959). Levashkevich (1966) showed decreasing adsorption by sesquioxides of chernozem humic acid, podzolic humic acid, and podzolic fulvic acid, in that order. Inoue and Wada (1968) observed preferential adsorption of a darker humic acid fraction having a higher particle weight by both montmorillonite and allophane. Similarly, photometric measurements (Beutelspacher, 1955) indicated virtually complete adsorption of humic acid by montmorillonite when readings were taken at a wavelength of 400 μm, but very low adsorption at 800 μm. The question whether this was a case of selective adsorption or one of changing dispersity (coarsening of humic particles) was left open.

The concepts proposed by Seidel and Ziechmann (1972) may be relevant in this context. According to these authors, polydisperse solvated humic colloids exhibit the property of "variable dispersity," i.e. there is a dynamic equilibrium between association and dissociation of component humic particles. Humic colloid systems may be uninhibited or inhibited with respect to dispersity. Inhibition of the equilibrium reactions may have physical (i.e. ionic strength or pH of the system; formation of micelles) or chemical (formation of covalent bonds) causes. Adsorbed humic materials in soils are considered to be strongly inhibited, but alkaline humic extracts are largely uninhibited. Parfitt and Greenland (1970) studying the adsorption of dextrans and polysaccharides
of different molecular weights on montmorillonite suggested that entropy changes arising from changes in the molecular configuration and the association of water molecules with clay surfaces and polymers are controlling factors in the adsorption of these molecules. Thus, the introduction of clay particles into solvated humic preparations is likely to shift and partially inhibit the dispersion equilibrium as humic particles of suitable conformation and size are preferentially adsorbed and minimum energy of the system is acquired.

While these considerations may help to explain reactions in artificial systems, little information is gained relative to in situ soil processes where accumulation of organic materials occurs primarily in the solid phase.

3. Catalytic effects in organic-mineral complexes

The process of soil organic matter formation is often considered as a primarily biological one (Allison, 1973). Yet recent research on organo-mineral interactions has increasingly pointed to catalytic properties of minerals as potentially powerful agents in the transformation of organic materials in soils and sediments. Most of these results have been obtained in well defined systems. Among the phenomena relevant to catalysis is for example protonation of organic compounds by clay mineral surfaces (Mortland, 1968) which is considered important for reactions requiring protons. Al at crystal edges and transition metals in higher valency states (Fe$^{3+}$) can function as electron-accepting sites; conversely, transition metals in the lower valency states may act as electron-donating sites (Solomon, 1968). Catalytic polymerization of some unsaturated organic compounds (e.g. Styrene) by clay minerals has been explained on that basis. Polymerization of benzene and phenol adsorbed on Fe(III)-or Cu(II)-montmorillonite has been reported by Mortland and Halloran (1976). Surface-catalyzed hydrolysis, e.g. parathion on kaolinite (Saltzmann et al., 1974) has also been observed.
Somewhat closer to soil systems are attempts at minerally catalyzing the synthesis of humic materials. Scheffer et al. (1959) demonstrated the synthesis of humic substances from solutions of hydroquinone using Fe-oxides as catalysts; fine-grained (amorphous) oxides exhibited increased catalytic activity over coarser, more crystalline oxides. Similar results were obtained by Ziechmann (1959) with silica as a catalyst. Kyuma and Kawaguchi (1964) incubated a substrate containing a tannin with allophanic clays which led to polymerized products similar to humic acids within short periods of time; the authors suggested that such reactions could be significant in the formation and accumulation of humus in andosols. Kumada and Kato (1970) tested several minerals relative to their effect on browning reactions of pyrogallol; allophane, amorphous and crystalline aluminous oxides were found effective, surpassed only by lepidocrocite.

Conversely, organic compounds may catalyze mineral synthesis in soils. Recently, it has been shown that fulvic acid (Linares and Huertas, 1971) and quercitin (Hem and Lind, 1974) catalyze the formation of kaolinite at room temperature in aqueous solutions of Al and Si over a wide range of pH and Si/Al ratios. It appears that the principal effect of the organic species is to complex Al and thereby slow the polymerization of polynuclear Al-hydroxy species.

4. Soil organic-mineral particles (somp's)

Most researchers of naturally occurring somp's consider such soil particles as sufficiently heterogeneous as to warrant their fractionation by some means. Another important requirement is to separate possible fractions with minimum modification of their organic and inorganic components. In the following, methods of fractionation and some results of research on organic-mineral particles are reviewed.
41. Methods of fractionation

Opinions differ widely as to what constitutes the most suitable method for fractionating somp's. This is perhaps not surprising considering that somp's have not been extensively studied and approaches are not yet standardized.

An early and original method, in tune with colloid chemical approaches to soil popular at that time, was proposed by Tyulin (1938). It entails the separation both of electronegative gels dispersible from soil by sodium chloride, and of isoelectric gels obtained after treatment of the residue with both dilute hydrochloric acid and sodium hydroxide.

Certainly the most widely used fractionation of somp's has been by particle size (Alexandrova et al., 1964; Arshad and Lowe, 1966; Posner et al., 1968; Chichester, 1969; Kyuma et al., 1969; Dudas and Pawluk, 1969; Parasher and Lowe, 1970; McKeague, 1971; Satoh and Yamanaka, 1972a; Swift and Posner, 1972). Because the separation of particles has to be carried out in the presence of organic matter and inorganic cementing substances, the means of dispersion and the completeness of separation remain a subject of some debate. Since the work of Edwards and Bremner (1967a and b) ultrasonic vibration has become a popular tool permitting the isolation of complexes that are relatively unaltered compared to those obtained by chemically aided methods (Watson, 1971). There are however dissenting voices. Gattá (1964) reported an increase in cation exchange capacity after ultrasonic treatment; and Halma (1969) has presented electron micrographic evidence of damage to clay platelets in the form of severe ruptures. Ultrasonic vibration remains poorly understood in its application to the dispersion of colloidal systems. It appears that the optimal frequency is a function of particle size, and that for clay-size particles optimal frequencies lie considerably above those of commercially available instruments (Mathieu-Sicaud and Levavasseur, 1949).
Most earlier attempts in density fractionation did not aim at clay-size smp’s per se, but at the isolation of non-complexed, partially humified organic matter from whole soil (Hénin and Turc, 1950; Monnier et al., 1962; Greenland and Ford, 1964; Ford et al., 1969). Khan (1959) reported density fractionation in Toulet solutions ($K_2MgI_4$) after removal of the less-than 1 μm fraction. Recent attempts (Halma, 1969; Francis et al., 1972) at clay mineral separation in heavy liquids have revived interest in fractionating natural smp's by similar methods. Satoh and Yamaneh (1972b) employed a bromoform/ethanol system to fractionate different particle size separates, but reported difficulties due to coagulation. Turchenek and Oades (1974) used ultrasonic dispersion, a surfactant and continuous centrifugation to fractionate smp’s by density. However, it was not possible to remove the surfactant, and as a result, organic carbon contents in the separates were 20 to 30% above natural levels. Richter et al. (1975) reported successful fractionation of whole soil in bromoform/ethanol mixtures without using surfactants.

42. Review of results

The majority of studies concerned with naturally occurring smp’s have emphasized characterization of the organic phase rather than the complexes as a whole. After separation of individual fractions traditional methods are commonly employed to investigate the particles, and few if any new approaches have been developed.

The proportion of organic matter contained in the clay-organic complex is not readily determined, since bonding mechanisms presumably range from mere physical entanglement to the formation of multiple chemical bonds. Separation of the "free" organic from combined organic-clay materials using densimetric methods was attempted by Hénin and Turc (1950), Khan (1959), Monnier et al. (1962), and Greenland and Ford (1964) who all presented evidence that the free material (the "light fraction") was in a much earlier stage of decomposition than combined organic matter. The particles in the light fraction were predominantly silt-
and sand-sized, and the inorganic material associated with it consisted largely of plant phytoliths (Khan, 1959; Greenland and Ford, 1964). Khan (1959) noted high HA/FA ratios in the light fraction. Levels of hydrolyzable sugars and amino acids exceeded those in humic acid extracted from the same soil, and the light fraction proved to be a readily available substrate for microbial attack (Greenland and Ford, 1964).

While the light fraction seldom constitutes more than a few percent by weight of whole soil, it commonly contains 20 to 30% of the total carbon in soils, except in extreme cases such as podsols with very high contents, or lateritic soils with perhaps only fractions of one percent.

Some workers (Alexandrova et al., 1964; Chichester, 1969; Kyuma et al., 1969; Satoh and Yamaneh, 1972a) report a more or less uniform decrease of organic carbon as particle sizes increase from clay to sand; others have found maximum levels of organic carbon in fractions other than clay (Posner et al., 1968; McKeague, 1971; Swift and Posner, 1972).

Carbon/nitrogen ratios are commonly reported to decrease with particle size, but there are exceptions, particularly in subfractions of clay-size particles (Arshad and Lowe, 1966; Dudas and Pawluk, 1969). Extractability of organic matter often tends to increase with decreasing particle size (Posner et al., 1968; Kyuma et al., 1969), an effect that may be related more to the exposed surface area than to differences in either the chemical properties of organic matter or the nature of the organic-mineral interaction. Surface area effects together with narrower C/N ratios may be involved in Chichester's (1969) finding of increasing nitrogen mineralization with decreasing particle size; N-mineralization was also positively correlated with nitrogen extractable by hot water. Similarly, nitrogen in the clay fraction was more hydrolyzable than in the coarser fractions (Kyuma et al., 1969). According to Swift and Posner (1972) nitrogenous compounds are preferentially extracted by alkaline reagents leaving residual humins relatively low in nitrogen; in contrast, Arshad and Lowe (1966) found maximum N-contents in "residual HA" obtained from previously alkaline extracted soil.
material by extensive HCl/HF treatments and removal of the released humin with Na-pyrophosphate.

Infrared absorption patterns of extracted HA's together with the yields of humic and fulvic acids suggested that the state of HA oxidation increased with comminution (Posner et al., 1968). Aliphatic structures were more common in humic acid derived from fine clay than in those from coarse clay; aromatic structures increased with decreasing extractability of humic acids (Arshad and Lowe, 1966), indicating a higher degree of humification in the residual humic acids.

Interlamellar adsorption of organic materials was suggested to occur in gleysolic soils (Lowe and Parasher, 1971), and a natural intercalated montmorillonite complex (17 Å) in India has been reported (Moura et al., 1973). Other workers (Dudas and Pawluk, 1969; Arshad and Lowe, 1966) based on IR and X-ray data found no evidence for interlamellar adsorption in soils. However, X-ray and IR may not be suitable tools for detection of interlamellar adsorption. Kodama and Schnitzer (1971) proposed the presence of a slight exothermic peak or a strongly reduced endothermic peak in the 600°C region of DTA-curves of somp's as a useful criterion for interlamellar adsorption.

Three recent reports have described densimetric fractionation of somp's or whole soils. Turchenek and Oades (1974) and Satoh and Yamaneh (1972b) reported decreasing organic contents with decreasing density. An inverse trend was found in densimetric fractions of whole soils by Richter et al. (1975).

5. Soil Aggregation

Soil aggregates as defined by Martin et al. (1955) are naturally occurring clusters or groups of soil particles in which the forces holding the particles together are much stronger than the forces between adjacent aggregates. The many facets of soil aggregates are extremely complex, and our knowledge about aggregation is rather unsatisfactory. There are serious shortcomings in many of the published studies, such as
1) the presence of organic matter in soil material prior to the initiation of aggregation studies, 2) the prevalence of comparatively short term studies, and 3) wide use of the wet-sieve method which is generally recognized as often giving unsatisfactory results (Allison, 1968).

An early hypothetical model of the arrangement of organic and inorganic phases in a soil aggregate was given by Emerson (1959). Four types of linkages were proposed: 1) coarse particles (quartz) linked directly by organic matter, 2) organic matter linking clay domains and quartz, 3) clay domains connected by organic matter, and 4) electrostatic attraction between clay domains. Sesquioxide coatings were thought to enhance clay-quartz interactions, and lime if present in the profile was given credit as a stabilizing agent.

A somewhat updated list of aggregating mechanisms has been presented by Harris et al. (1966): 1) linkage of clay particles by water dipoles, 2) coulombic interactions between oriented clay platelets, 3) irreversibly dehydrated colloids (silicates, sesquioxides, humates) coating soil particles, 4) aggregate stabilization against water entry by the presence of hydrophobic organic materials, 5) interparticle linkage by organic polymers forming bonds through their functional groups with the surface of two or more clay particles.

A microaggregate model was presented by Edwards and Bremner (1967a) based on detailed studies of soil dispersion by sonic and ultrasonic vibration. It proposes that the difficultly dispersible particles in soils are fine silt- and sand-size aggregates (less than 250 µm in diameter) consisting largely of clay and humified organic material linked by polyvalent ions. Application of mechanical energy disrupts intra-aggregate bonds; unfortunately, the energy input whether by shaking or ultrasonic vibration is not readily standardized and cannot be expressed in conventional physical units.

There is usually some correlation between the level of organic carbon and water-stable aggregation in soils (Chesters et al., 1957; Greenland et al., 1962). However, organic matter is not the sole stabilizing agent in aggregates. Hydrous oxides (Chesters et al., 1957;
Arca and Weed, 1966; Deshpande et al., 1968; El-Swaify and Emerson, 1975), carbonates (Stefanson, 1968), and clay skins (Allison, 1968) are effective in strengthening aggregates. Instances of significant correlations between "free iron oxides" and aggregates stability have been reported (Chesters et al., 1957; Arca and Weed, 1966). In contrast, other workers (Deshpande et al., 1964 and 1968; El-Swaify and Emerson, 1975) maintain that iron oxides are of secondary importance and inferior to Al-oxides as cementing agents (see also IV.6).

Various types of organic matter have received the most attention in relation to aggregate stability. According to Allison (1968) large humic acid molecules are poor aggregating agents because they are too large, spherical instead of linear, and have only a limited number of functional groups able to attach themselves to clay particles. Greenland (1965b) espouses the same view, arguing that negatively charged polyanions (HA, FA) tend to disperse clays, although the process is concentration dependent and negative organic charges are likely to be neutralized by metal cations and/or protonation at mineral surfaces. These views are based on data derived from extracted and solvated humic preparations expected to have uninhibited polydispersity and denatured molecular conformations (Seidel and Ziechmann, 1972; Chen and Schnitzer, 1976); revised concepts may emerge as new data become available.

Aggregate stabilization from additions of polysaccharides has been reported by Clapp et al. (1962), Rennie et al. (1954), Martin et al. (1965). In addition, loss of stability after treatment of natural aggregates with dilute periodate, a polysaccharide oxidant (Greenland et al., 1962; Clapp and Emerson, 1965; Stefanson, 1971), have led to the conclusion that linear polysaccharides of microbial origin play an important role in aggregate stabilization. Soil organic matter commonly contains 5 to 30% polysaccharides composed of many sugars (Mehta et al., 1961). The persistence of polysaccharides in soils may be due to inherent resistance of some compounds against decomposition, increased resistance from metal complexing, bonding to clay minerals, particularly inside clay lattices, and protection against microbial attack when located
inside aggregates (Allison, 1968). That organic matter components other than polysaccharides improve stability has been suspected by many authors (Mehta et al., 1960; Greenland, 1965b; Allison, 1968; Stefanson, 1968 and 1971).

Free energy considerations led Edwards and Bremner (1967a) to conclude that stable microaggregates would be roughly spherical; component particles were thought to be so tightly bonded as to render the organic matter inside the aggregates inaccessible to microorganisms. That soil microorganisms are confined to spaces between stable aggregates was also postulated by Emerson (1959). Allison (1968) took the persistence of proteins and polysaccharides in soil aggregates and clay lattices as evidence for their inaccessibility to microorganisms. Aylmore and Quirk (1967) estimated that 75% of the total porosity (0.19 g/cc) in natural aggregates from the B horizon of an Australian soil was due to "pores" less than 100 Å in diameter; hence, even the smallest bacteria (2000 Å) would be excluded from these intraaggregate voids. This implies that organic matter transformations if they occur within stable aggregates would largely follow auto- and surface-catalyzed pathways, exoenzymes being the only biological agent possibly participating in intraaggregate reactions.

The question of how long a given stable microaggregate persists in soil before radical reorganisation by external agents is of considerable interest in the context of somp's. Sufficiently long lifetimes of microaggregates should result in heterogeneous component particles (e.g. external vs. internal). Although seasonal variations in the relative stability of soil aggregates have been detected (Stefanson, 1971), nothing is known about the long-term stability of soil aggregates.

6. Summary

Extensive research on interactions of defined organic and mineral systems has yielded a framework for perceiving complex soil organo-mineral systems. This framework consists mainly of a list of possible
bonding mechanisms, but the relative importance of each in soils is still in question.

Adsorption of dissolved humic materials by clay suspensions gives mostly L-type isotherms, though C-type curves have been observed. Cation saturation of phyllosilicates and pH both influence the adsorption of humic substances from solution. Many aspects of these reactions remain obscure, particularly the state of dissociation of organic functional groups when near mineral surfaces; the change in molecular structure, conformation, and dispersity of humic and fulvic acids by ionic conditions in solution; and concomitant effects, such as preferential adsorption of certain molecular weight portions of humic solutions. Among phyllosilicates, smectites are the most efficient adsorbents of humic materials. However, amorphous oxides, particularly allophanes, exceed the adsorptive capacity of phyllosilicates by a wide margin; ligand exchange appears to be a dominant bonding mechanism in these systems. The results obtained in adsorption of organic matter from solution are of questionable value relative to in situ soil processes. Soil somp's are dynamic systems evolving in a chemical environment where reactions in solution and in the solid phase coexist and overlap.

Fractionation by particle size is commonly used to minimize the heterogeneity of somp's prior to characterization by chemical and physical methods. To date, research has focused predominantly on the organic phase, yielding results on the distribution of "free" organic matter in soils, on the distribution of organic matter in particle-size fractions of somp's, on the degree of humification, and on other properties. With few exceptions, concurrent descriptions or characterization of the inorganic portions of somp's have been omitted.

Viewing aggregation in surface soils in terms of organic-mineral interactions offers promise, though many other factors are involved. Current aggregation models are limited in scope in that they are almost exclusively concerned with bonding mechanisms.
III. MATERIALS AND METHODS

1. Soils

Diversity in pedogenic character was the main criterion in selecting soils for this study. The variety of climatic conditions, parent materials, and vegetative covers in the Pacific northwest region have produced a multitude of soil types. The current U.S. soil classification system (SCS Staff, 1975) recognizes ten different soil orders, the highest category of classification in that system. With the exception of subtropical and tropical oxisols, all of these soil orders are represented within the state of Oregon.

For this study representative surface and subsurface horizons from six of these soil orders were sampled at type locations (except Madras). Table 1 summarizes soil forming factors, land use, and classification (great groups) for each soil. Precise sampling locations, formal profile descriptions, and source references are assembled in Appendix I.

An additional allophanic surface soil sample (Mitaka) collected near Tokyo, Japan, was provided by Dr. Yoshinaga (Ehime University, Matsuyama, Japan). The parent material is volcanic ash. Mitaka is regarded as an ando soil, and almost certainly qualifies as an andept in the U.S. classification system.

2. Methods

21. Dispersion and bulk separation of water-dispersible, clay-size soil organic-mineral particles

The separation of minimally altered clay-size somp's precludes the use of chemicals that remove cementing agents and aid dispersion. Ultrasonic vibration was avoided in view of relatively high levels of amorphous hydrous oxides in important PNW soils. Amorphous materials are likely to be sensitive to high-energy disaggregation and possibly
<table>
<thead>
<tr>
<th>Soil Type/ Classification</th>
<th>Location</th>
<th>MAT (°C)</th>
<th>MAP (cm)</th>
<th>Parent Material</th>
<th>Topography/ Drainage</th>
<th>Vegetation</th>
<th>Land Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quillayute silt loam</td>
<td>Tillamook Co., OR</td>
<td>10</td>
<td>230</td>
<td>alluvium from mixed igneous &amp; sedimentary rocks</td>
<td>level stream terraces/ well drained</td>
<td>brackenfern brush grasses</td>
<td>pasture hay urban</td>
</tr>
<tr>
<td>Dystrandept</td>
<td>Benton Co., OR</td>
<td>12</td>
<td>140</td>
<td>colluvium from sedimentary &amp; basic igneous rocks</td>
<td>rolling uplands/ well drained</td>
<td>Douglas fir grand fir white oak poison oak grasses, ferns</td>
<td>small grain grass seed hay, timber recreation water supply</td>
</tr>
<tr>
<td>Jory clay loam</td>
<td>Benton Co., OR</td>
<td>11</td>
<td>135</td>
<td>marine beach sands, aeolian deposits, organic matter</td>
<td>level to concave marine terrace/ very poorly drained</td>
<td>huckleberry rhododendron red cedar shore pine madrone</td>
<td>brush wildlife homestites</td>
</tr>
<tr>
<td>Haplohumult</td>
<td>Coos Co., OR</td>
<td>11</td>
<td>110</td>
<td>silty alluvium</td>
<td>broad terraces above floodplain/ moderately well drained</td>
<td>grasses hazelnut poison oak blackberry Douglas fir white oak</td>
<td>pasture, hay small grain vegetables orchards grass seed berries</td>
</tr>
<tr>
<td>Blacklock fine sandy loam</td>
<td>Benton Co., OR</td>
<td>11</td>
<td>110</td>
<td>recent alluvium</td>
<td>level on alluvial bottomlands/ poorly drained</td>
<td>ash, white oak wild rose poison oak rushes, grasses sedges</td>
<td>spring grain hay pasture wildlife</td>
</tr>
<tr>
<td>Sideraquad</td>
<td>Benton Co., OR</td>
<td>19</td>
<td>20</td>
<td>residuum from pumiceous and tuffaceous sandstone &amp; conglomerate</td>
<td>level to rolling upland plains/ moderately well drained</td>
<td>sagebrush bunchgrasses rabbitbrush annual grasses juniper</td>
<td>alfalfa potatoes oats, barley wheat (irrigated)</td>
</tr>
</tbody>
</table>

(1) MAT = Mean annual temperature  
MAP = Mean annual precipitation
subject to redistribution in the separation process. Therefore a low-energy approach was chosen to separate water-dispersible, smaller than 2 μm components from soil. As a result, the yield of these particles is generally lower than those obtained in routine particle size analyses (Kilmer and Alexander, 1949). Some clay-size particles obviously remained in silt- and sand-size agglomerates. The separated material provided samples more representative of the somp surfaces with which plant root hairs and microorganisms interface than particles obtained by usual techniques required for complete dispersion.

The 2 μm and smaller particles were dispersed and separated from surface soil by repeated shaking and centrifugation. Air dry, less than 2 mm surface soil was first shaken contiously for ten hours on a reciproc al shaker at 200 cycles/min using a 1:10 solid:liquid ratio. The suspension was centrifuged to sediment 2 μm particles. Following centrifugation the supernatant clay suspension was filtered through a 300 mesh sieve to remove small amounts of floating, non-humified plant fragments. Additional water-dispersible, less than 2 μm material was separated from the residue by alternate 30 minute shaking and centrifugation until the supernatant was essentially clear. Soils with high levels of amorphous oxides required a higher number of extraction cycles (75 in Quillayute) than did less amorphous soils to satisfactorily remove somp's.

The clay-size particles were washed three times in absolute ethanol, and stored under refrigeration in ethanolic suspension of known solid concentration (30 to 60 mg/ml) pending subsequent assays.

Residual sand- and silt-size particles were separated by wet sieving (300 mesh), oven-dried for 24 hours at 110°C, and weighed.

22. Density fractionation of the less than 2 μm somp's

We could find no suitable published procedure for fractionating somp's by density that avoided using organic surfactants which irreversibly contaminate the organic phase. Considerable effort was invested
in developing such a procedure, taking as a base the method proposed by Francis et al. (1972) for phyllosilicates and OM-free soil clays.

In preliminary experiments using subsoil clays, the method of Francis et al. (1972) which employs linear density gradients formed with 1,1,2,2 tetrabromoethane (TBA; 2.96 g/cc) and absolute ethanol, and polyvinylpyrrolidone as a surfactant (PVP K-30, molecular weight of 40000; 0.82 g/cc) was duplicated, but stepwise rather than linear gradients were prepared.

Solutions of desired density were prepared by mixing appropriate proportions of TBA and EtOH. The densities of the mixtures were adjusted with the aid of a refractometer (American Optical, Model Spencer 2291, refractive index scale ranging from 1.450 to 1.840). Alternatively, density liquids may also be adjusted gravimetrically.

Stepwise gradients of about 6 cm length were prepared in 50 ml Tefzel or nylon centrifuge tubes by layering equal volumes of TBA/EtOH solutions in density increments of 0.1 g/cc on top of each other. The gradient densities ranged from 1.6 to 2.9 g/cc. Up to 200 mg of clay previously washed in the lightest solution of the gradient were dispersed in the lightest solution containing 10% (weight) of PVP, layered on top of the preformed gradient, and centrifuged for 18 hours at 23500 g's (Sorvall RC2-B centrifuge, HB-4 rotor). Density bands were reproducible. After centrifugation the bands were removed manually using a syringe with a needle perpendicularly bent at the tip. During band removal the density at different depths was measured via the refractive index.

These experiments (see Section VI.1) demonstrated the potential of density fractionation for clay particles from local soils, but the gradient approach had several important disadvantages: 1) time-consuming manual preparation of density gradients; 2) limited capacity (less than 200 mg clay/tube) to process clay; 3) surfactants are essential in long gradients to maintain dispersion and assure complete fractionation. Surfactants cannot be used in connection with somp's because of
irreversible adsorption to clay minerals (Francis, 1973) and soil somp's (Turchenek and Oades, 1974).

The method eventually adopted to fractionate soil omc's without surfactants involves exhaustive extraction and purification of particles in short liquid columns of a given density (Spycher and Young, 1977). In essence it entailed the following. Aliquots containing 400-500 mg of somp's in ethanolic suspension were dispensed into 50 ml Tefzel or nylon centrifuge tubes equipped with tight-fitting polyethylene lids. The suspensions were centrifuged, and the clear ethanol supernatant discarded. The sediment was redispersed by brief rapid stirring (15 to 20 seconds at about 5000 rpm) with a 1 cm diameter X 4 cm Teflon pestle in 10 ml of desired density liquid. The suspensions were immediately centrifuged in a swinging bucket Sorvall HB-4 rotor at 23000 g. The density liquids were kept at 20°C at all times during the fractionation by thermostating in a water bath and centrifuging in a temperature controllable unit (Sorvall RC2-B). Clear separation into a top band and a bottom sediment was generally achieved within 10 to 15 minutes. The sediment was resuspended and recentrifuged up to eight times, or until negligible amounts of that density somp's remained as a top band. Each top band in its supernatant liquid was collected in a second set of tubes, restirred and centrifuged to remove any small quantities of entrapped heavier particles. The latter were added back to the sediment for the next incremental density separation. Fractionations were begun at the low density end and continued in steps of 0.1 g/cc; one to four density cuts were found appropriate to cover the density ranges of the soil clays while maintaining practical yields (greater than 5 to 10% of the total water-dispersible clay) within individual density fractions. Ethanol added to the combined suspended soil omc's from each density cut decreased liquid density, permitting recovery of particles by centrifugation. These somp density fractions were washed three times in ethanol, twice in water, then freeze-dried, and stored in dessicators.
23. Organic carbon, total nitrogen, extractability of organic matter

Organic carbon was determined in duplicate samples of freeze-dried somp's using a Leco W 12 Automatic Carbon Analyzer (Courtesy OSU School of Oceanography). Total nitrogen was measured in duplicate samples by a semi-micro Kjeldahl method (analyses performed by E. Holcombe, U.S. Forest Service Laboratory, Corvallis, Oregon).

Extractability of organic matter was estimated by extracting duplicate samples of 100 to 150 mg of freeze-dried somp's in 0.5 N NaOH for eight hours. The residue was washed once in 0.1 N NaOH, three times in water, and freeze-dried. Organic carbon in the somp's was determined before and after the alkaline extraction using a Leco W 12 Automatic Carbon Analyzer.

24. Oxidative degradation of somp's (DTA)

DTA under an oxygen atmosphere was selected as a further means to characterize the organic phase of the density separates. The interpretation of thermal decomposition curves of organic matter is difficult in the absence of supplemental spectroscopic methods. However, DTA has been sufficiently studied in connection with soil organic matter (Turner and Schnitzer, 1962; Scharpenseel et al., 1964; Schnitzer and Hoffman, 1965; Wershaw and Bohner, 1969; Dupuis et al., 1970; Kodama and Schnitzer, 1970; Shurygina et al., 1971; Lutwick, 1972), with organometallic complexes (Schnitzer and Hoffman, 1967), and with somp's (Kodama and Schnitzer, 1969 and 1971; Dupuis et al., 1970; Lutwick, 1972) to make its use in this study worthwhile.

DTA curves were recorded with a Dupont 1200 thermal analyzer equipped with a 1200° DTA cell. The analyses were made on 5 to 10 mg samples of freeze-dried somp density fractions or whole clays, using calcined Al$_2$O$_3$ as a thermal reference, a flowing oxygen atmosphere (0.91 l/min), and a heating rate of 20°C/min (produced better separation of exothermic peaks than at 10°C/min).
Determination of amorphous inorganic oxides

The literature concerning the quantitative estimation of amorphous clay constituents has been reviewed by Mitchell et al. (1964), and more recently by Wada and Harward (1974).

Numerous solvents for amorphous inorganic oxides have been proposed: acid ammonium oxalate for amorphous iron oxides (Schwertmann, 1964), dithionite-citrate for "free" iron oxides (Mehra and Jackson, 1960), boiling 0.5 N NaOH for amorphous alumino-silicates (Hashimoto and Jackson, 1960), among others. More recently, acid ammonium oxalate was claimed to be superior to alkaline reagents for the removal of amorphous alumino-silicates (Fey and LeRoux, 1975). Some workers have used these reagents in sequence, often in attempts to quantify various phases of amorphous clay constituents (McKeague and Day, 1966; Bascomb, 1968; Blume and Schwertmann, 1969; Wada and Greenland, 1970; Dudas and Harward, 1971).

Kinetic approaches to selective dissolution of amorphous oxides have been proposed as an alternative. Gastuche et al. (1960) and Gastuche and Vielvoye (1960) have studied the kinetics of dissolution of well-defined materials (kaolinite, hydargillite, Al-gels) in hydrochloric acid, and have provided a mathematical treatment yielding kinetic parameters for these heterogeneous reactions. Follet et al. (1965) investigated the removal of amorphous phases in soil by successive extractions with alkaline reagents. Ségalen (1968) proposed a kinetic method using NaOH and HCl in alternation to include iron oxides insoluble in alkaline reagents. In this procedure the steady state portion of the dissolution-time curve is taken to indicate limited attack on crystalline matrix minerals. McKyes et al. (1974) used this technique in a modified form to estimate amorphous constituents in a lake-deposited clay.

A kinetic approach (McKyes et al., 1974) was selected in this study, as it promised to afford better control over the course of the dissolution, and perhaps also give indications about the stability of the crystalline phase towards the solvents. However this choice does not
imply that "true" values for amorphous constituents would be obtained. Amorphous and crystalline clay phases merely differ in their rates of dissolution in a given solvent, and the data obtained commonly depend on experimental conditions (Pawluk, 1972). Comparisons with other methods were not made in this study because of limited amounts of somp fractions available for assay.

Duplicate samples of 200-300 mg of freeze-dried, peroxide-treated somp density fractions were transferred into 50 ml polypropylene centrifuge tubes. The clay was suspended in 25 ml of 8.0 N HCl and shaken at room temperature for 30 min on a reciprocal shaker. The suspensions were centrifuged, and the clear supernatant decanted into 100 ml Nalgene volumetric flasks. The residue was dispersed in 25 ml of distilled water, centrifuged, and the supernatant decanted into the volumetric flask; this step was added to reduce the amount of residual acid in the sediment. The sediment was then dispersed in 25 ml of 0.5 N NaOH, shaken for 30 min at room temperature, and centrifuged. The supernatant was added to the volumetric flask, which was then filled to the mark with distilled water. This cycle was repeated eight times on each sample. The solutions were analyzed for Al, Si, and Fe using a Perkin Elmer 306 Atomic Absorption Spectrophotometer.

Linear equations were fitted to the last four points of the cumulative time-dissolution curve, and the calculated intercepts were taken as the amounts of amorphous Al-, Si-, or Fe-oxides in the samples.

26. X-ray analyses, IR spectroscopy, and transmission electron microscopy

Mg- and K-saturated samples of omc density fractions were applied on petrographic slides using the paste method of Theisen and Harward (1962). The Mg-saturated specimens were equilibrated over Mg(NO₃)₂·6H₂O (54% R.H.), or solvated by condensation of glycerol vapor (Brown and Farrow, 1956), or solvated by condensation of ethylene glycol vapor (Kunze, 1955). X-ray diffractograms were recorded with all three
treatments in an atmosphere controlled at 54% R.H. The treatments with K-saturated omc's included drying at 105°C, equilibration over Mg(NO₃)₂₆H₂O after drying at 105°C, and heating at 300 and 500°C. These slides were analyzed in a dry air atmosphere with a Phillips Norelco X-ray diffractometer using Cu Kα radiation.

IR spectra were recorded on a Beckmann IR-4 spectrometer (Courtesy Dr. R. F. Keeler, ARS Poisonous Plant Laboratory, Logan, Utah). Pellets were pressed under vacuum using 3 mg of selected samples of freeze-dried somp subfractions per 300 mg of KBr. The disks were dried for 60 hours at 100°C prior to scanning.

Transmission electron microscope copper grids were coated with Formvar and reinforced with a carbon film. Aqueous suspensions containing about 0.1% solids were prepared with selected samples of freeze-dried somp subfractions. Particles were deposited on the coated grids either by atomizing the suspensions (holding the grid in the fog) or by air-drying a drop of the suspensions applied with a syringe on the grids. Carbon-shadowed carbon replicas were prepared for a few specimens. The grids were viewed with a Phillips EM 300 operated at 60 or 80 KV and 15-20 micro-amps beam current. Interpretations were made by examination of photographs (3 to 5 plates per sample).

27. Determination of surface areas and porosity

Adsorption and desorption isotherms with N₂ at -196°C and water vapor at room temperature were obtained by means of an adsorption balance described by Slabaugh and Stump (1964). Selected samples of freeze-dried organic-mineral density fractions were outgassed for 48 hours at 70°C in a temperature-controllable vacuum desiccator connected to a vacuum pump. Duplicate samples of approximately 200 mg were weighed into tin buckets and outgassed at low pressure (≥ 10⁻⁴ torr) at room temperature in the adsorption columns. The loss in weight due to outgassing was subtracted from the original sample weight. Adsorption isotherms were determined with N₂ allowing 15 min between each step for
equilibration. Full adsorption-desorption isotherms were run only on peroxide treated samples because of the extremely low nitrogen adsorption by somp's.

Outgassing at room temperature following the nitrogen runs resulted in complete desorption of the adsorbed nitrogen as determined by the weight loss. Hence, adsorption-desorption isotherms with water vapor were obtained on the same samples without removing them from the adsorption columns. Equilibration times for water vapor runs were 30 min at each step.

The linear form of the BET-equation was used to calculate the surface areas:

\[
P / M(P - P_p) = 1/M_{m}C + (C - 1)P / M_{m}P_0
\]

Where
- \( M \) = weight of the adsorbed gas per gram of adsorbent at pressure \( P \)
- \( M_{m} \) = weight of the adsorbed gas per gram of adsorbent at monolayer coverage
- \( P_0 \) = saturation pressure of the gas
- \( C \) = constant related to the heat of adsorption of the first adsorbed layer and to the heat of liquefaction of the adsorbing gas.

Since \( 1/M_{m}C + (C - 1)/M_{m}C = 1/M_{m} \), it follows that

\[
M_{m} = 1/(\text{slope} - \text{intercept})
\]

Linear regression equations were fitted to the adsorption data at relative pressures between 0.05 and 0.35; linear regression coefficients were generally between 0.98 and 1.00 indicating excellent linearity.

Pore size distributions in the range of 19 to 300 Å were calculated from the nitrogen desorption isotherms of peroxide treated samples by the method developed by Pierce (1953) and modified by Orr and Dallavalle.
Pore size distributions were not calculated from water desorption isotherms as water vapor penetration into interlayers of clay minerals makes the calculation invalid (Slabaugh and Stump, 1964); furthermore, no data on probable values of contact angles needed in the calculation with the Kelvin equation were found in the literature for clay-water systems.

28. Cation exchange capacity

Errors in the determination of cation exchange capacities arising from salt retention and hydrolysis have been pointed out by several authors (Ensminger, 1944; Schofield, 1949; Okazaki et al., 1962; Frink, 1964). Wada and Harada (1969) showed that these effects occur most markedly in allophane and imogolite with low Al/Si ratios, while unexplained minor effects were observed with montmorillonite. Although Frink (1964) questioned the reality of hydrolysis which he tentatively attributed to sample loss, most authors agree that washes with distilled water to remove excess saturating cations should be replaced by washing the samples in dilute solutions of the index cation, and a correction for the gravimetrically measured volume of the occluded solution applied.

Analogous studies on somp's are lacking, and it is nearly impossible to make inferences from work on soil organic matter in view of the widespread disagreement on methods used in studying exchange properties of these materials (e.g. MacCarthy and Mark, 1976). To establish the relationships governing the exchange behavior of organic functional groups in somp's would require intensive study. Complicating factors, such as organic complexation of mono- to polymeric Al- and Fe-hydroxides, blockage of inorganic exchange sites by soil organics, and changes induced by the introduction of extraneous solutions would have to be considered.

Conventional methods, widely tested and adequate for soil minerals are therefore expected to yield somewhat arbitrary results when applied to somp's. However, because of time restraints and limited amounts of
available sample, a simple conventional method was chosen in this study.

Neutral salt CEC: Duplicate clay samples of 100 to 150 mg each were weighed into 30 ml Pyrex centrifuge tubes and dispersed by rapid stirring (Teflon rod, ≥ 3000 rpm) in 25 ml of 1 N MgCl₂. The suspensions were left standing for 30 min, then centrifuged. Three more washes with 1 N MgCl₂ were applied; a fifth wash was left to equilibrate overnight. Excess salt was removed with two washes in distilled water, and three washes in absolute ethanol. Adsorbed Mg was extracted with five washes of 25 ml 1 N NaCl adjusted to pH 8.2 with NaOH. The last wash was left to equilibrate overnight.

pH-dependent CEC: The samples were washed, saturated and extracted as above, except that the saturating (1 N MgCl₂) and exchanging solutions were adjusted to pH 8.2 with NaOH. In general, the pH of the suspensions was stable at 8.2 following overnight equilibration in the 1 N NaCl solutions of the extracting step in the neutral salt procedure. Mg in the extracts was determined by atomic absorption spectrophotometry (Perkin Elmer, Model 306).
IV. RESULTS

1. Preliminary experiments

This section describes some results of several series of preliminary experiments designed to explore the potential application of density centrifugation to natural clay-size particles. X-ray diffraction was used to monitor the nature of the separates.

In a first set of experiments the method of Francis et al. (1972) was applied to bulk clay separated from the B horizons of several soils selected for thesis work. However, stepwise, rather than linear gradients were used. A typical result is shown in Figure 1 for clay separated from a sample of the Jory B22 horizon. The light density band (1.75-2.01 g/cc) contained largely X-ray amorphous material. Two bands with well defined peaks followed, the first of which (2.01-2.31 g/cc) contained the bulk of the clay in the gradient. Phyllosilicate peaks were weak again in the heavy density fractions because of low contents and masking due to microcrystalline iron oxides (see sections VI.6, VI.7 and VI.11).

The results suggested the possibility of separating specific monomineralic fractions from soil clays. In a second set of experiments attempts were made to selectively extract amorphous materials at 1.78 g/cc from clay of Quillayute A, and iron oxides at 2.96 g/cc from clay of Jory B3. Since yields were to be determined quantitatively, PVP was not added to the density liquids. Instead, clay samples were repeatedly (six times) extracted in short liquid columns (2 cm long) of uniform density. Figure 2 shows that the lighter than 1.78 g/cc fraction of Quillayute was not free of phyllosilicates. In contrast in the heavier than 2.96 g/cc fraction of Jory peaks for phyllosilicates were not observed; the peaks in the diffractogram were ascribed to microcrystalline iron oxides (see sections VI.6 and VI.7). The yield was 10.4% by weight, sufficient to indicate the potential of the method for this type of application.
Figure 1: X-ray diffractograms (Mg-saturated, 54% relative humidity) of organo-mineral fractions separated from Jory B22 bulk clay by surfactant-aided centrifugation in a stepwise density gradient.
Figure 2: Selective extraction of amorphous oxides from Quillayute A bulk clay and of iron oxides from Jory B3 clay; X-ray diffractograms of Mg-saturated specimens, 54% relative humidity.
The next step was to apply the surfactant-free approach to somp's and to cover the complete density range of a given soil bulk clay in steps of 0.1 g/cc. The result for Quillayute is shown in Figure 3. A very gradual transition from poorly crystalline material to well defined chloritic minerals was seen, with micaceous clays appearing in fractions heavier than 1.9 g/cc. A parallel transition in color with increasing density from black to light brown suggested significant differences in the contents of organic matter. The yields in the heaviest and the two lightest fractions were less than 5% of the starting material. This procedure was adopted for larger scale fractionations of surface soil clays. However, to get sufficient material for further analyses, cuts at the low and high density ends were chosen so as to yield at least ten percent of the starting material.
Figure 3: X-ray diffractograms of clay-size organo-mineral density fractions separated from Quillayute A bulk clay (Mg-saturated, 54% relative humidity).
2. Distribution of density subfractions in soil clays

The distributions of density fractions of clay-size somp's from surface horizons of six soils and the Bh horizon of a seventh soil are shown in Figure 4 (Table 2). The observed ranges of different density materials depended both on the kind of mineral phase and the amount of organic matter present. Thus, Jory, though high in organic matter, owes its overall greater density to the presence of adsorbed heavier iron oxides (see VI.7). Intermediate and narrow density ranges were found in the clay-size materials from Woodburn, Madras, and Bashaw; all contained low levels of organic matter and low to intermediate amounts of amorphous oxides (see sections VI.4 and VI.6). Broad density ranges (Quillayute, Jory, Blacklock) were associated with high contents of amorphous materials and/or (Blacklock) organic matter. Amorphous oxides and organic matter also accounted for the lower overall density (median of 1.8 g/cc) in Quillayute, Mitaka, and Blacklock.

Published data against which to compare these density ranges are very scarce. Surfactant-aided density centrifugation of reference clay minerals (Francis et al., 1972) gave bands at densities somewhat below those listed by Dana (1955), presumably as a result of adsorbed surfactant. Cuts at a density of 2.0 g/cc to remove free organic matter from whole soil (Monnier et al., 1962; Greenland and Ford, 1964; Ford et al., 1969) appear reasonable for non-amorphous soils, but would greatly overestimate free organic matter in more amorphous soils such as Andepts. The study of Turchenek and Oades (1974) dealt with size subfractions of clay from a red-brown earth like Jory, and yielded particles within similar density ranges (2.25 to 2.60 g/cc; surfactant aided). Similarly, Satoh and Yamaneh (1972) separated organo-mineral fractions having densities of less than 1.8 g/cc from the fine clay of an acidic volcanic ash soil, probably an Andept like Quillayute and Mitaka. The density ranges of clay-size somp's obtained in this study are therefore in agreement with those found in the literature. However the observed
ranges do not necessarily represent absolute values which would be difficult to establish for multicomponent systems such as soil omp's.

Published studies showing the reproducibility of smp density fractionations are lacking. In this study, maximum deviations of ± 3% from the mean were set initially for acceptance of the separated frac-

tions. Fractionations were performed by three different operators at different times (separated by up to six months) on bulk clay suspensions kept under refrigerated storage. Deviations in subfraction yields remained within the ± 3% limit in separations performed by a given operator. Taking all fractionations (Table 2), the limit was exceeded in six out of twenty-five cases. These larger deviations occurred after extended storage, and involved in all cases the heavier density fractions of clays with broad density ranges (Quillayute, Jory, Blacklock). They are attributed in part to a further breakdown of microaggregates during redispersion (overnight shaking) of the ethanolic bulk clay suspensions prior to density fractionation. Brief ultrasonic vibration, in spite of its disadvantages, might be useful to minimize deviations in yield of subfractions between replicate separation runs. Total yields from sub-

fractions (Table 2, last column) approached complete recovery, except in Blacklock and Madras.
Table 2: Yield of <2 μm soil organo-mineral particles separated from different soils and sub-fractionated by centrifugation in heavy-density liquids.

<table>
<thead>
<tr>
<th>Soil/Suborder</th>
<th>Liquid density (g/cc)</th>
<th>Number of separate subfractionations</th>
<th>Subfraction as weight % of w.d. clay (1)</th>
<th>Range (%)</th>
<th>Standard deviation (%)</th>
<th>Range of yields (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quillayute Alp</td>
<td>&lt;1.7</td>
<td>8</td>
<td>13.0</td>
<td>10.7-14.7</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Andept</td>
<td>1.7-1.8</td>
<td>8</td>
<td>32.4</td>
<td>28.6-34.0</td>
<td>1.8</td>
<td>97-100</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>8</td>
<td>29.2</td>
<td>23.2-36.3</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;1.9</td>
<td>8</td>
<td>25.3</td>
<td>20.7-30.0</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Mitaka Al</td>
<td>&lt;1.8</td>
<td>4</td>
<td>28.7</td>
<td>25.9-31.3</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Andept</td>
<td>1.8-1.9</td>
<td>4</td>
<td>40.2</td>
<td>36.5-43.0</td>
<td>2.9</td>
<td>98-100</td>
</tr>
<tr>
<td></td>
<td>1.9-2.0</td>
<td>4</td>
<td>15.6</td>
<td>15.3-16.2</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;2.0</td>
<td>4</td>
<td>15.4</td>
<td>14.9-16.0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Jory Al</td>
<td>&lt;2.0</td>
<td>8</td>
<td>14.2</td>
<td>13.6-16.4</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Humult</td>
<td>2.0-2.1</td>
<td>8</td>
<td>20.2</td>
<td>17.7-24.0</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.1-2.2</td>
<td>8</td>
<td>23.0</td>
<td>18.9-28.5</td>
<td>3.6</td>
<td>96-99</td>
</tr>
<tr>
<td></td>
<td>2.2-2.3</td>
<td>8</td>
<td>24.8</td>
<td>16.4-32.4</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;2.3</td>
<td>8</td>
<td>21.5</td>
<td>16.5-27.3</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>Blacklock Al</td>
<td>&lt;1.6</td>
<td>8</td>
<td>14.3</td>
<td>11.9-16.9</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Aquod</td>
<td>1.6-1.7</td>
<td>8</td>
<td>22.7</td>
<td>19.0-25.5</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.7-1.8</td>
<td>8</td>
<td>22.1</td>
<td>20.9-24.8</td>
<td>1.3</td>
<td>88-91</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>8</td>
<td>15.5</td>
<td>9.7-21.5</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;1.9</td>
<td>8</td>
<td>21.8</td>
<td>19.5-24.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Woodburn Ap</td>
<td>&lt;2.1</td>
<td>7</td>
<td>12.5</td>
<td>9.9-15.1</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Xerelt</td>
<td>2.1-2.2</td>
<td>7</td>
<td>82.7</td>
<td>79.2-86.5</td>
<td>2.5</td>
<td>94-100</td>
</tr>
<tr>
<td></td>
<td>&gt;2.2</td>
<td>7</td>
<td>4.6</td>
<td>3.5-5.8</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Bashaw Ap</td>
<td>&lt;1.95</td>
<td>4</td>
<td>63.1</td>
<td>61.8-64.2</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Xerert</td>
<td>&gt;1.95</td>
<td>4</td>
<td>36.9</td>
<td>35.8-38.2</td>
<td>1.0</td>
<td>96-98</td>
</tr>
<tr>
<td>Madras Ap</td>
<td>&lt;1.95</td>
<td>5</td>
<td>66.9</td>
<td>63.8-70.9</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Argid</td>
<td>&gt;1.95</td>
<td>5</td>
<td>33.1</td>
<td>29.1-36.2</td>
<td>2.7</td>
<td>82-87</td>
</tr>
</tbody>
</table>

(1) w.d. clay = water dispersible bulk clay. Average of all separate fractionations
(2) Recovery of clay in fractionations as weight % of starting material
Figure 4: Distribution of organo-mineral density subfractions (subfraction as weight % of water-dispersible clay).
3. **Organic carbon and total nitrogen in granulometric soil fractions**

Previously published generalizations regarding the organic carbon and nitrogen distribution in granulometric fractions need modification in view of the results of this study. Several independent factors influence the distribution of the organic phase, including (1) the adsorptive capacity of the fraction, a function of particle size distribution, mineralogy, and the degree of weathering, and (2) the degree of humification and particle size distribution of the partially and non-humified organic material, both dependent on climatic, vegetational and biological (comminution and decomposition chains) factors.

Increased contents of organic matter with decreased particle size, as previously reported in the literature (Alexandrova et al., 1964; Chichester, 1969; Kyuma et al., 1969; Satoh and Yamaneh, 1972), occurred in four out of seven soils used in this study (Quillayute, Mitaka, Blacklock, Madras; Table 3, Figure 5). Particular conditions account for the different results in the other cases. In Jory, a forest soil, the organic carbon in the sand-size fraction exceeded that in both silt and clay, and it occurred mainly in the form of coarse, non-humified plant remains (C/N = 39). The sand-size fraction of Bashaw, a Pelloxerert, consisted largely of Mn-concretions which can be observed microscopically, and which can be recognized qualitatively by their vigorous reaction with hydrogen peroxide. As would be expected from transition metal oxides, these nodules sorb and incorporate high amounts of organic matter resulting in maximum carbon and nitrogen contents in the sand fraction of this soil. The distinct minimum in concentration of organic carbon and nitrogen in the silt fraction of Woodburn appears to reflect old humic-sesquioxidic coatings on silt particles; the coatings on the silt evolved in a more arid environment (Palouse formation, Eastern Washington) and may have persisted through wind- and water-transport to the Willamette Valley in a more or less unaltered state (Dr. J. A. Norgren, personal communication).
Table 3. Organic carbon and total nitrogen in granulometric soil fractions.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Fraction</th>
<th>Fraction as wt % of total soil</th>
<th>Organic Carbon: as wt % of as % of soil total O.C.</th>
<th>Total Nitrogen: as wt % of as % of soil total N</th>
<th>Organic C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quillayute</td>
<td>Sand 27</td>
<td>11.0</td>
<td>22.1</td>
<td>0.68</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td>Silt 57</td>
<td>13.5</td>
<td>56.6</td>
<td>0.74</td>
<td>51.9</td>
</tr>
<tr>
<td></td>
<td>Clay 16</td>
<td>18.2</td>
<td>21.3</td>
<td>1.33</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>Sum (1)</td>
<td>13.6</td>
<td>.</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soil (2)</td>
<td>14.2</td>
<td>.</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Mitaka</td>
<td>Sand 29</td>
<td>6.0</td>
<td>20.0</td>
<td>0.34</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>Silt 53</td>
<td>8.6</td>
<td>54.1</td>
<td>0.52</td>
<td>51.9</td>
</tr>
<tr>
<td></td>
<td>Clay 18</td>
<td>12.2</td>
<td>25.9</td>
<td>0.87</td>
<td>29.6</td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td>8.5</td>
<td>.</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soil n.d. (3)</td>
<td>.</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Jory</td>
<td>Sand 23</td>
<td>6.6</td>
<td>28.3</td>
<td>0.17</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>Silt 44</td>
<td>4.8</td>
<td>39.6</td>
<td>0.16</td>
<td>29.2</td>
</tr>
<tr>
<td></td>
<td>Clay 33</td>
<td>5.0</td>
<td>32.1</td>
<td>0.40</td>
<td>54.2</td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td>5.3</td>
<td>.</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soil</td>
<td>5.4</td>
<td>.</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Blacklock</td>
<td>Sand 82</td>
<td>3.7</td>
<td>48.4</td>
<td>0.09</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>Silt 10</td>
<td>15.6</td>
<td>25.8</td>
<td>0.59</td>
<td>37.5</td>
</tr>
<tr>
<td></td>
<td>Clay 8</td>
<td>20.0</td>
<td>25.8</td>
<td>9.88</td>
<td>43.7</td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td>6.2</td>
<td>.</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soil</td>
<td>8.4</td>
<td>.</td>
<td>0.17</td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
Table 3: Continued

<table>
<thead>
<tr>
<th>Soil</th>
<th>Fraction</th>
<th>Fraction as wt % of total soil</th>
<th>Organic Carbon: as wt % of fraction total O.C.</th>
<th>Total Nitrogen: as wt % of fraction total N</th>
<th>Organic C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woodburn</td>
<td>Sand</td>
<td>12</td>
<td>1.2</td>
<td>0.07</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>Silt</td>
<td>70</td>
<td>0.4</td>
<td>0.04</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>Clay</td>
<td>18</td>
<td>1.2</td>
<td>0.10</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td>Sum (1)</td>
<td></td>
<td>0.6</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soil (2)</td>
<td></td>
<td>0.6</td>
<td>0.06</td>
<td>10.0</td>
</tr>
<tr>
<td>Bashaw</td>
<td>Sand</td>
<td>3</td>
<td>3.6</td>
<td>0.22</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>Silt</td>
<td>52</td>
<td>1.4</td>
<td>0.09</td>
<td>45.4</td>
</tr>
<tr>
<td></td>
<td>Clay</td>
<td>45</td>
<td>1.7</td>
<td>0.12</td>
<td>45.5</td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td></td>
<td>1.6</td>
<td>0.11</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>Soil</td>
<td></td>
<td>1.6</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Madras</td>
<td>Sand</td>
<td>48</td>
<td>0.7</td>
<td>0.08</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>Silt</td>
<td>35</td>
<td>1.1</td>
<td>0.09</td>
<td>27.3</td>
</tr>
<tr>
<td></td>
<td>Clay</td>
<td>17</td>
<td>2.4</td>
<td>0.24</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>Sum</td>
<td></td>
<td>1.1</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soil</td>
<td></td>
<td>1.0</td>
<td>0.09</td>
<td>11.1</td>
</tr>
</tbody>
</table>

(1) From sum of (organic C or total N X fraction wt %)
(2) From separate analysis of bulk soil before fractionation.
(3) n.d. = not determined
Figure 5: Organic carbon (O.C.) and total nitrogen (N) in granulometric soil fractions.
Carbon/nitrogen ratios decreased with particle size reflecting increased humification with comminution. The only exception was Quillayute, arising most likely from a preferential accumulation of partially humified material in the silt fraction of this coastal soil under pasture. Forested soils (Jory, Blacklock) have higher C/N ratios in the coarser fractions, and the ratios decrease more sharply with particle size than in cultivated or grassland soils.

Organic carbon and nitrogen in size fractions expressed as percentages of total soil carbon and nitrogen may be termed reservoirs (Table 3, Figure 6). Any of the granulometric fractions may contain the biggest share of soil carbon or nitrogen depending on particle size distribution, degree of humification, and total adsorptive capacity. Particle size distribution is the dominant factor in Woodburn where silt, though containing lower concentrations of O.C. and N than in sand and clay, contains half of the total soil O.C. and N. The role of humification can be seen in Jory, where sand and clay hold similar amounts of carbon, but nitrogen is heavily concentrated in the clay fraction; Blacklock represents a similar case. The C/N ratios of the two andepts (Quillayute, Mitaka) do not differ by more than four to five units among size fractions; the distributions of particle sizes and those of organic carbon and nitrogen in the size fractions are quite similar, indicating that the materials in the sand and silt fractions are able to hold appreciable amounts of organic matter; however, it should be stressed that some clay-size material remained agglomerated in the silt and sand fractions during the fractionation of these andeptic soils.

Comparisons of the organic carbon and nitrogen contents of unfractionated soils with the sums calculated from the contents in the size fractions shows that a little organic matter, mostly free-floating, non-humified plant remains, was lost during the fractionation in Quillayute and Blacklock.
Figure 6: Organic carbon (O.C.) and nitrogen (N) in granulometric fractions as % of total soil organic carbon and nitrogen.

Increasing levels of organic matter with decreasing fraction density have been reported for whole soils (Hénin and Turc, 1950; Khan, 1959; Monnier et al., 1962). The same trend was observed by Turchenek and Oades (1974) in clay-size organo-mineral density fractions, although included in their figures are excesses of twenty to thirty percent of organic carbon due to adsorption of surfactant used in their separation procedure. Satoh and Yamanek (1972) also found increasing organic matter contents with decreasing density.

In all but one fraction (Woodburn, 2.1-2.2 g/cc) both organic carbon and nitrogen decrease uniformly with increasing density of the subfraction separates (Table 4, Figure 7). The trend for the C/N ratios is a sharp narrowing, by up to four units, from the lightest to the next heavier fraction, then a more gradual decrease of up to two units over the remaining fractions. The lightest fractions evidently contain a higher proportion of less humified material; Greenland and Ford (1964) determined that the light fraction (less than 2 g/cc) of whole soils had contents of hydrolysable carbohydrates intermediate between those of undecomposed plant material and humic acid. The observations made on the density subfractions in this study may have analogous causes; insufficient material and resources precluded further characterization of the less-humified organic matter. The fact that organic materials with a high C/N ratio are associated with all subfractions of Blacklock is taken to indicate adsorption of the partially humified soil organics to mineral surfaces although the interaction may be relatively loose and of predominantly physical character.

The extractability of organic carbon, where determined, parallels the C/N ratios in that it increases steeply from the lightest to the next heavier fraction, and then rises more gradually over the remaining fractions. It has been pointed out (Chichester, 1969) that the extractability of organic materials from soil particles may be related to the
Table 4: Organic carbon (O.C.) and total nitrogen (N) in < 2 μm organo-mineral density subfractions.

<table>
<thead>
<tr>
<th>Soil clay</th>
<th>Density (g/cc)</th>
<th>Fraction as wt % of bulk w.d. clay</th>
<th>Organic carbon: as wt % of total soil O.C.</th>
<th>Total nitrogen: as wt % of total soil N</th>
<th>Organic C/N</th>
<th>Extractable O.C. (1) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quillayute</td>
<td>&lt; 1.7</td>
<td>12.8</td>
<td>33.8</td>
<td>23.6</td>
<td>2.34</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>1.7-1.8</td>
<td>31.6</td>
<td>20.7</td>
<td>35.7</td>
<td>1.69</td>
<td>36.8</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>33.5</td>
<td>16.2</td>
<td>29.7</td>
<td>1.35</td>
<td>31.3</td>
</tr>
<tr>
<td></td>
<td>&gt; 1.9</td>
<td>22.2</td>
<td>8.8</td>
<td>11.0</td>
<td>0.76</td>
<td>11.8</td>
</tr>
<tr>
<td>Sum (2)</td>
<td></td>
<td></td>
<td>18.2</td>
<td>1.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>w.d. clay (3)</td>
<td></td>
<td>18.2</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mitaka</td>
<td>&lt; 1.8</td>
<td>28.7</td>
<td>16.0</td>
<td>41.8</td>
<td>1.13</td>
<td>36.8</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>40.2</td>
<td>11.3</td>
<td>40.9</td>
<td>0.93</td>
<td>42.5</td>
</tr>
<tr>
<td></td>
<td>1.9-2.0</td>
<td>15.6</td>
<td>4.5</td>
<td>6.4</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>&gt; 2.0</td>
<td>15.4</td>
<td>4.5</td>
<td>6.4</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td>11.0</td>
<td>0.87</td>
<td></td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>w.d. clay</td>
<td></td>
<td>12.2</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Woodburn</td>
<td>&lt; 2.1</td>
<td>14.7</td>
<td>2.4</td>
<td>26.7</td>
<td>0.17</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>2.1-2.2</td>
<td>80.7</td>
<td>1.2</td>
<td>66.7</td>
<td>0.12</td>
<td>76.9</td>
</tr>
<tr>
<td></td>
<td>&gt; 2.2</td>
<td>4.6</td>
<td>1.3</td>
<td>6.7</td>
<td>0.13</td>
<td>7.7</td>
</tr>
<tr>
<td>Sum (2)</td>
<td></td>
<td></td>
<td>1.5</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>w.d. clay</td>
<td></td>
<td>1.2</td>
<td>0.10</td>
<td></td>
<td>12.0</td>
</tr>
<tr>
<td>Bashaw</td>
<td>&lt; 1.95</td>
<td>63.5</td>
<td>1.8</td>
<td>68.8</td>
<td>0.15</td>
<td>71.4</td>
</tr>
<tr>
<td></td>
<td>&gt; 1.95</td>
<td>36.5</td>
<td>1.3</td>
<td>31.2</td>
<td>0.11</td>
<td>28.6</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td>1.6</td>
<td>0.14</td>
<td></td>
<td>14.2</td>
</tr>
</tbody>
</table>
Table 4: Continued

<table>
<thead>
<tr>
<th>Soil clay</th>
<th>Density (g/cc)</th>
<th>Fraction as wt % of bulk w.d. clay</th>
<th>Organic carbon: as wt % of sub-fraction</th>
<th>Total nitrogen: as % of sub-fraction</th>
<th>Organic C/N</th>
<th>Extractable O.C. (1) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jory</td>
<td>&lt; 2.0</td>
<td>13.9</td>
<td>9.4</td>
<td>25.5</td>
<td>0.58</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td>2.0-2.1</td>
<td>21.8</td>
<td>5.8</td>
<td>25.5</td>
<td>0.48</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>2.1-2.2</td>
<td>20.5</td>
<td>5.3</td>
<td>21.6</td>
<td>0.44</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>2.2-2.3</td>
<td>17.7</td>
<td>3.9</td>
<td>13.7</td>
<td>0.34</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>&gt; 2.3</td>
<td>26.1</td>
<td>2.6</td>
<td>13.7</td>
<td>0.25</td>
<td>10.4</td>
</tr>
<tr>
<td>Sum w.d. clay</td>
<td></td>
<td>5.1</td>
<td>0.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blacklock</td>
<td>&lt; 1.6</td>
<td>16.2</td>
<td>36.7</td>
<td>30.5</td>
<td>1.59</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td>1.6-1.7</td>
<td>23.2</td>
<td>26.3</td>
<td>31.0</td>
<td>1.39</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>1.7-1.8</td>
<td>24.5</td>
<td>19.5</td>
<td>24.4</td>
<td>1.12</td>
<td>17.4</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>11.3</td>
<td>16.4</td>
<td>9.6</td>
<td>0.97</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>&gt; 1.9</td>
<td>23.9</td>
<td>3.7</td>
<td>4.5</td>
<td>0.21</td>
<td>17.6</td>
</tr>
<tr>
<td>Sum w.d. clay</td>
<td></td>
<td>19.7</td>
<td>1.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Madras</td>
<td>&lt; 1.95</td>
<td>68.4</td>
<td>3.1</td>
<td>80.8</td>
<td>0.32</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>&gt; 1.95</td>
<td>31.6</td>
<td>1.6</td>
<td>19.2</td>
<td>0.21</td>
<td>7.6</td>
</tr>
<tr>
<td>Sum w.d. clay</td>
<td></td>
<td>2.6</td>
<td>0.29</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Organic carbon extracted in an eight-hour treatment with 0.5 N NaOH (in % of O.C. in subfraction)
(2) From Sum of (O.C. or total N x fraction wt %)
(3) From bulk soil sample's before subfractionation.
(4) n.d. = not determined
Figure 7: Organic carbon and total nitrogen in organo-mineral clay-size density subfrations (in weight % of subfrations)
magnitude of the surface areas rather than to differences in the chemical properties of organic matter. In some density subfractions particle sizes tend to increase with density (Satoh and Yamaneh, 1972; Turchenek and Oades, 1974). If anything, OM extractability would therefore be favored in the lightest fractions. Thus, C/N ratios and extractability of organic carbon are taken as qualitative indications of increasing humification as particle density increases. This agrees with findings of Arshad and Lowe (1966) who determined that aliphatic structures in clay-adsorbed humic acids became more prominent with decreasing particle size (i.e. probably lighter density).

Correspondence between the organic carbon content of water-dispersible clay and the sum calculated from density subfraction contents are satisfactory, except for a 1.2% deviation in Mitaka. The sums of nitrogen are often higher than the contents of whole water-dispersible clays, possibly as a result of experimental error since no nitrogenous substances were used in the fractionation procedure. It is assumed that the organic phase remained largely unaltered by the density subfractionation. Waxes and resins may be partially dissolved by the heavy liquids, but these substances constitute only a small part of the organic phase, and are expected to appear predominantly in coarser non-humified organic fragments.

In summary, it can be stated that the organic phase shows a uniform pattern of distribution and composition in clay-size organo-mineral particles subfractionated by density. A discussion of possible mechanisms leading to these patterns is deferred to a later section. As a premise to that discussion it is stressed at this point that the density fractions are considered to be minimally altered, "natural" separates. Experimental procedures were designed to avoid the creation of artifacts; no evidence has arisen from which to conclude that major physical or chemical modifications have occurred.
5. Oxidative degradation of the organic phase in sump subfractions (DTA)

DTA under an oxygen atmosphere was selected as a further tool to characterize the organic phase of the density separates. The interpretation of the thermal decomposition curves is difficult for several reasons. The methods employed by various workers differ relative to atmosphere (N₂, O₂, air, vacuum) and sample pretreatment. The bulk of the literature reports on thermal analysis of humic acids, metal-complexed humic acids, and artificially prepared clay-humic samples. As pointed out earlier, considerable differences exist between natural and artificially prepared omc's that affect the thermal stability of the organic phase and catalytic effects during degradation in still poorly understood ways.

The prominent decomposition reactions of the organic phase in DTA under O₂-gas occur between 200 and 500°C, a range relatively free of mineral thermal reactions. Analyses of humic substances under N₂-gas fail to produce clear decomposition peaks and require higher temperatures for degradation (Schnitzer and Hoffmann, 1965).

From thermoanalytic investigations of model substances it is known that aromatic rings and heteroatoms (particularly oxygen) decrease the thermostability of aliphatics. The course of the thermal decomposition of non-uniform substances, such as humic materials, depends on the relative contents of their various chemical moieties, and reactions will tend to overlap each other (Flaig et al., 1975).

The main reactions in the pyrolysis in air of extracted soil organic materials are: dehydrogenation (up to 200°C); a combination of decarboxylation and dehydroxylation (200-250°C); continued dehydroxylation (up to 400°C); decomposition of the residual, poorly condensed aromatic "nucleus" of humic materials (major peak above 400°C; Schnitzer and Hoffmann, 1964; Kodama and Schnitzer, 1970). Methoxyl groups are predominantly cleaved between 250°C and 300°C (Flaig et al., 1975). Filip et al. (1976) showed that most of the aliphatic portions and oxygen
containing functional groups of humic substances analyzed in air are lost at temperatures less than 400°C.

DTA studies of fulvic acid salts and complexes were conducted by Schnitzer and Hoffmann (1967) and Schnitzer and Kodama (1972) in static air. The major peak (≈430°C) tended to shift to higher temperatures in monovalent cation-FA complexes, and to significantly lower temperatures in polyvalent cation-FA complexes. Trivalent iron was particularly effective in shifting the major exotherm to lower temperatures. For transition metal-FA complexes the main exotherm temperatures were inversely proportional to the ionization potential of the metal ions, conceivably a catalytic effect related to electron donator/acceptor properties of transition metals (Solomon, 1968). However, Dupuis et al. (1970) did not report any significant influence of trivalent iron on the position of the high temperature exotherm (HTE, above 400°C), but noted a downward shift of the low temperature exotherms (LTE, below 400°C).

The DTA curve in air of an FA-montmorillonite complex showed a major exotherm near 670°C indicative of interlamellar adsorption (Kodama and Schnitzer, 1969). These workers inferred catalytic activity of the clay surface from a downward shift of the 460°C FA-exotherm by about 50°C in both physical FA-montmorillonite mixtures and FA-montmorillonite complexes (prepared at low pH). Dupuis et al. (1970) noted an amplification of the LTE (≈340°C) but no shift in the HTE (450°C) of an HA-montmorillonite complex compared to purified HA (analyses in O₂).

In a study of the less-than 0.2 um clay-organic particles from a podzol A horizon (Kodama and Schnitzer, 1971), the presence of a weak exotherm at 540°C in untreated samples, and the presence of a weak endotherm in peroxide treated samples at the same approximate temperature was taken as evidence for naturally occurring interlamellar adsorption.

The only more extensive study on DTA (DTG) of organic-mineral particles was published by Lutwick (1972); unfortunately, he performed his analyses under reduced pressure which hampers comparison with more common practices (air or oxygen). The thermograms of the clay-organic particles and alkali-extracted organic materials were similar and lacked
an HTE. Dry mixed FA-montmorillonite, silts, and residual roots gave thermograms with an LTE and an HTE. Lutwick (1972) also reported that acid pretreatments of both somp's and alkali extracts induce changes in their decomposition properties.

In the following discussion it is assumed that mineral surfaces and organically complexed Al and Fe catalyze the thermal degradation of the adsorbed organic phase; this results in downward shifts of the HTE's and LTE's, and perhaps also in deamplification of the HTE. Implicit in this assumption is the possibility that the type of association between organic and inorganic phases (chemisorption vs. looser physical adsorption) affects the thermograms; i.e. "loose" adsorption of humic material of a given composition would amplify the HTE and shift it to higher temperatures. A low degree of humification (high C/N ratio) most likely reduces the thermostability of soil organics (Flaig et al., 1975).

The thermograms of low organic matter density subfractions (Woodburn, Madras, Bashaw; Figure 8) show broad, ill-defined exotherms in the 250 to 350°C region, and differences between density subfractions are hardly detectable. The high organic matter subfractions (Blacklock, Quillayute, Mitaka, Jory; Figures 9-12) have well expressed LTE's and HTE's. The LTE's in the Blacklock subfractions are consistently more intense than the HTE's. In Quillayute, Mitaka and Jory the HTE's change gradually from dominance in the lightest fractions to a shoulder in the heaviest fractions.

A coherent interpretation of the results from the high OM samples is difficult to give. In considering the results from Blacklock (Figure 9), it must be remembered (see Appendix I) that at least part of its organic matter is translocated from the overlying A horizon into the Bh horizon, and this material would tend to be of fulvic character, i.e. low molecular weight, oxygen-rich, perhaps low in aromatics, and thus inherently less thermostable. Another, probably more massive contribution of organic matter comes directly from the root mat located in the Bh horizon just above the hard impenetrable ortstein (B22ir). Extremely acidic conditions (pH 4.4) and poor drainage in the Bh restrict microbial
Figure 8: DTA curves of clay-size sample density subfractions from Bashaw, Madras, and Woodburn.
Figure 9: DTA curves of clay-size somp density subfractions from Blacklock.
Figure 10: DTA curves of clay-size sOMP density subfractions from Quillayute.
Figure 11: DTA curves of clay-size somp density subfractions from Mitaka.
Figure 12: DTA curves of clay-size omp density subfractions from Jory, (a) untreated, (b) peroxide-treated.
activity and therefore rapid humification, a condition reflected in the
high C/N ratios of the organic phase. Thus the organic materials of
this horizon have an inherently low overall thermostability which may
have caused the dominance of the LTE's.

The fact that the HTE's in Blacklock are all well defined (except
for the shoulder in the heaviest subfraction) might indicate a loose
organic-mineral association resulting in a minimal surface catalytic
activity. Weak organo-mineral bonding in this soil would be expected in
view of (1) a high organic matter level occurring together with very
moderate amounts of amorphous oxides, and (2) the presence of quartz
(low adsorptive capacity for OM) in all subfractions (see section VI.7).
The peak temperatures of both LTE's and HTE's barely differ (within
10°C) among subfractions, perhaps another indication of low catalytic
activity by mineral surfaces.

The HTE's in the lightest fractions of Quillayute, Mitaka and Jory
are more intense than the LTE's. This could arise from relatively loose
adsorption, a higher degree of aromaticity, and lesser metal-organic
complexing. The intensities of the HTE's decline in the heavier frac-
tions, presumably because the organo-mineral interaction becomes more
intimate, and metal complexing increases.

Variations in the degree of aromaticity could result from prefer-
ential exposure of the lightest particles to microenvironments (e.g.
periphery of soil aggregates) where microbially produced aromatics
abound. The catalytic activity of mineral surfaces during the degrada-
tion reactions appears to be reflected in downward shifts of peak
temperatures as subfraction density increases. This is particularly
obvious in Quillayute with gradual shifts adding up to about 30°C for
LTE's and to about 20°C for HTE's. Similar trends occur in Mitaka and
Jory, but are obscured because of poor peak expression and composite
peaks.

Composite peaks are most evident in the Mitaka subfractions.
However, it is impossible to unravel the meaning of LTE component peaks
and shoulders without further investigation.
Finally, endotherms in the 500°C region and above (mineral OH-loss) are weak or absent in the somp subfractions of Jory (Figure 12a). In contrast, these endotherms occur consistently in the peroxide treated subfractions of the same soil (Figure 12b) and become more intense as subfraction density increases. In concurrence with Kodama and Schnitzer (1971) this is taken as evidence for interlamellar adsorption of soil organic materials. Since none of the density subfractions (including those of the smectitic Bashaw) exhibit clear endotherms in that region, it would appear that interlamellar adsorption commonly occurs in soils.

Interlamellar adsorption is expected to increase with particle density, as a result of lower levels of amorphous oxides (Section VI.6) and greater crystallinity and expansibility of the chloritic intergrades (Section VI.7) in the heavier fractions. Therefore retarded decomposition of increasing amounts of organic matter may contribute to the intensity decline of the HTE's in heavier subfractions.

6. Amorphous oxides in somp subfractions

Cumulative extraction curves of peroxide treated light and heavy density subfractions from Quillayute and Bashaw (Figure 13) are first discussed to illustrate the nature of the results obtained by the kinetic method to determine amorphous oxides. The extraction curves for Si, Al and Fe in the two Quillayute subfractions are representative for the majority of cases. The curves are resolved into a rapid initial release of components (amorphous oxides) followed by a nearly linear portion (final slope) interpreted as uniformly progressing dissolution of crystalline material (Segalen, 1968; McKyes et al. (1974)). In contrast, the extraction curves for Bashaw typify a non-amorphous smectitic clay fraction sensitive to the dissolution treatment. Bashaw clay yields high amounts of "amorphous" material (≥ 60%) when analyzed by the conventional weight loss method of Hashimoto and Jackson (1960) (D.H. McNabb, personal communication). Although appreciable quantities of oxides are extracted from this clay by the kinetic method, the yields per cycle
Figure 13: Cumulative extraction curves for SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ in clay-size, peroxide-treated somp subfractions from Quillayute and Bashaw (oxides in weight % of peroxide-treated freeze-dried subfractions).
remain constant, and extrapolation gives low values, i.e. less than two percent.

When carefully executed, the method gave well reproducible results. The errors listed below are standard deviations calculated from the means of the differences in percent oxides between duplicate determinations. The bulk of the amorphous materials generally appears during the first two extraction cycles; for these two points the standard errors were 0.6% for Fe$_2$O$_3$, 0.3% for Al$_2$O$_3$, and 1.1% for SiO$_2$. The errors for the last four points of the curves were 0.1% for Fe$_2$O$_3$ and Al$_2$O$_3$, and 0.25% for SiO$_2$. Finally the standard deviations for the extrapolated amorphous oxides were 0.6% for Fe$_2$O$_3$, 0.4% for Al$_2$O$_3$, and 0.8% for SiO$_2$.

The results for all fractions are summarized in Table 5 and Figure 14. In general, the final slopes calculated by fitting linear regression equations to the last four points of the extraction curves, remain within narrow limits for the subfractions of a given soil clay. Slopes of 0.1 to 0.4% per cycle are the rule for Fe$_2$O$_3$, except in Bashaw (up to 0.7% per cycle) most likely because lattice Fe is liberated from smectite. The slopes for Al$_2$O$_3$ and SiO$_2$ are low (Al$_2$O$_3$: 0.0-0.4%; SiO$_2$: 0.0-0.7%) in Mitaka, Quillayute and Blacklock; the subfractions of all the other soils have significantly higher slopes (Al$_2$O$_3$: 0.4-1.0%; SiO$_2$: 0.9-2.9%). Invariably, X-ray diffraction patterns (see Section VI.7) of samples with low Si- and Al-slopes show enhanced peak intensity and sharpness at 14 Å (chloritic intergrades, chlorites), while reduced 14 Å intensities are associated with high slopes. Differences in the final slopes therefore seem indicative of varying susceptibility of certain minerals, particularly smectites and chloritic intergrades, to the dissolution treatment.

Significant discrepancies in the Si-slopes were observed within the subfractions of Quillayute. The slope in the lightest fraction of this soil was roughly twice as steep as in the heavier subfractions. The lightest fraction is obviously less stable against dissolution as well as less ordered, and probably consists of smaller particles, yet because
Table 5: Amorphous Si-, Al-, and Fe-oxides in clay-size, organo-mineral density subfractions.

<table>
<thead>
<tr>
<th>Soil clay</th>
<th>Density</th>
<th>Amorphous oxides (1)</th>
<th>Molar SiO$_2$/Al$_2$O$_3$</th>
<th>Sum of amorphous oxides</th>
<th>Final slopes (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe$_2$O$_3$</td>
<td>Al$_2$O$_3$</td>
<td>SiO$_2$</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Mitaka</td>
<td>&lt;1.8</td>
<td>14.8</td>
<td>28.7</td>
<td>17.2</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>18.2</td>
<td>24.7</td>
<td>17.8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>1.9-2.0</td>
<td>17.2</td>
<td>21.6</td>
<td>15.6</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>&gt;2.0</td>
<td>16.8</td>
<td>13.5</td>
<td>11.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Sum w.d. clay (3)</td>
<td>16.7</td>
<td>23.8</td>
<td>16.3</td>
<td>1.2</td>
<td>43.9</td>
</tr>
</tbody>
</table>

Quillayute | <1.7    | 13.4       | 20.4      | 7.4     | 0.6       | 27.8       | 21.2     | 0.2       | 0.4       | 1.5       |
|           | 1.7-1.8 | 15.1       | 16.0      | 8.4     | 0.9       | 24.4       | 39.5     | 0.1       | 0.2       | 0.7       |
|           | 1.8-1.9 | 17.7       | 8.4       | 8.7     | 1.7       | 17.2       | 34.3     | 0.2       | 0.3       | 0.7       |
|           | >1.9    | 12.1       | 6.1       | 7.9     | 2.2       | 14.0       | 26.1     | 0.2       | 0.3       | 0.7       |
| Sum w.d. clay | 14.8 | 11.9 | 8.2 | 1.4 | 18.5 | 33.8 | 0.1 | 0.3 | 0.6 |

Jory      | <2.0    | 13.9       | 8.4       | 12.6    | 2.6       | 21.0       | 34.9     | 0.2       | 0.8       | 1.3       |
|           | 2.0-2.1 | 15.6       | 7.1       | 10.9    | 2.6       | 18.0       | 33.6     | 0.3       | 1.0       | 1.4       |
|           | 2.1-2.2 | 16.8       | 7.2       | 10.0    | 2.4       | 17.2       | 34.0     | 0.2       | 0.8       | 1.9       |
|           | 2.2-2.3 | 13.1       | 6.6       | 8.4     | 2.2       | 15.0       | 28.1     | 0.2       | 0.7       | 1.4       |
|           | >2.3    | 23.6       | 6.6       | 5.6     | 1.4       | 12.2       | 35.8     | 0.2       | 0.7       | 0.9       |
| Sum w.d. clay | 17.3 | 7.3 | 9.6 | 2.2 | 18.3 | 37.9 | 0.3 | 0.7 | 1.2 |

Woodburn | 2.1     | 5.2        | 5.8       | 9.1     | 2.7       | 14.9       | 20.7     | 0.3       | 0.4       | 1.4       |
<p>|           | 2.1-2.2 | 5.8        | 4.8       | 6.1     | 2.2       | 10.9       | 16.7     | 0.4       | 0.7       | 1.5       |
| w.d. clay | 5.2     | 4.2        | 7.2       | 1.9     | 11.4      | 16.6      | 0.3      | 0.8      | 1.8       |</p>
<table>
<thead>
<tr>
<th>Soil clay</th>
<th>Density</th>
<th>Amorphous oxides (1)</th>
<th>Molar SiO₂&lt;sub&gt;2&lt;/sub&gt; Al₂O₃ SiO₂</th>
<th>Sum of amorphous oxides</th>
<th>Final slopes (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe₂O₃</td>
<td>Al₂O₃</td>
<td>SiO₂</td>
<td>SiO₂&lt;sub&gt;2&lt;/sub&gt; Al₂O₃</td>
</tr>
<tr>
<td>Blacklock</td>
<td>&lt;1.6</td>
<td>0.9</td>
<td>7.0</td>
<td>3.4</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1.6-1.7</td>
<td>0.5</td>
<td>5.5</td>
<td>1.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>1.7-1.8</td>
<td>0.2</td>
<td>3.2</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>0.3</td>
<td>3.0</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>&gt;1.9</td>
<td>0.2</td>
<td>1.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Sum w.d. clay</td>
<td>0.4</td>
<td>3.8</td>
<td>1.1</td>
<td>0.1</td>
<td>6.2</td>
</tr>
<tr>
<td>Bashaw</td>
<td>&lt;1.95</td>
<td>0.8</td>
<td>1.9</td>
<td>2.0</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>&gt;1.95</td>
<td>1.3</td>
<td>1.4</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Sum w.d. clay</td>
<td>1.0</td>
<td>1.7</td>
<td>1.6</td>
<td>2.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Madras</td>
<td>&lt;1.95</td>
<td>3.1</td>
<td>3.1</td>
<td>11.1</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>&gt;1.95</td>
<td>2.4</td>
<td>2.3</td>
<td>9.3</td>
<td>6.7</td>
</tr>
<tr>
<td>Sum w.d. clay</td>
<td>2.9</td>
<td>2.8</td>
<td>10.5</td>
<td>6.3</td>
<td>12.3</td>
</tr>
</tbody>
</table>

(1) As weight % of freeze-dried, peroxide-treated density subfractions
(2) Slope of the linear regression fitted to the last four points of the cumulative extraction curve
(3) w.d. clay = water-dispersible clay
(4) n.d. = not determined
Figure 14: Amorphous Si-, Al-, and Fe-oxides in clay-size organic-mineral density subfractions (in weight % of freeze-dried, peroxidized material)
of the steep slope, extrapolation yields less amorphous silica than all the other subfractions of Quillayute.

Gastuche et al. (1960) and Gastuche and Vielvoye (1960) have provided a kinetic model for heterogeneous reactions such as dissolution of uniformly sized kaolinite in hydrochloric acid. The data, supplemented by electron microscopic observations, led to the conclusion that the attack of kaolinite particles by hydrochloric acid proceeds uniformly on the surface of the crystallites. However, the model cannot be applied to the results of this study because of non-uniform particle size distributions and the use of two reagents in the dissolution procedure. The cumulative curves obtained by the density subfractions can be very accurately described by power curves of the type \( y = ax^b \), but the resulting coefficients are purely empirical and void of any physical meaning.

Amorphous Al (Table 5) decreases with increasing density in all subfractions. Silica behaves similarly, except in the lightest fraction of Quillayute where amorphous silica is underestimated because of the slope discrepancies mentioned above. Increasing but unknown quantities of organically complexed Al are expected to contribute to the amounts of amorphous alumina, perhaps resulting in slight relative depression of amorphous silica in the lighter subfractions. The particle size distribution is another factor to be considered. The particle size is expected to increase with density (Turchenek and Oades, 1974); that, in itself, contributes to higher levels of "amorphous oxides" in the lighter fractions.

The sums of amorphous alumina plus silica decrease with increasing density as do the sums of silica plus alumina plus iron oxides except in the heaviest fraction of Jory.

Observed molar \( \text{SiO}_2 / \text{Al}_2\text{O}_3 \) ratios range from 0.2 to 6.7. Caution is needed in interpreting these ratios as they are influenced by contributions of organically complexed Al and by slope discrepancies. Both factors are expected to depress the \( \text{SiO}_2 / \text{Al}_2\text{O}_3 \) ratios, particularly in the light fractions.
The ratios in the two andepts correspond to a range (1 to 2) now generally accepted as characteristic for allophanic clays (Yoshinaga, 1966; Wada and Harward, 1975). The rather low ratios in the two lightest fractions of Quillayute and in all of the Blacklock subfractions (less than 1) most likely are due to significant contributions of organically complexed Al liberated during peroxidation. The ratios in Jory and Woodburn are somewhat higher (2.2 to 2.7) presumably because of the relative instability against dissolution of the chloritic intergrade components in these soils as stated above. The extrapolated amorphous oxides in Bashaw are too close to the error margins, hence the SiO₂/Al₂O₃ ratios are unreliable.

In Madras, a slightly alkaline desert soil (Argid), the amorphous mineral materials are highly siliceous (SiO₂/Al₂O₃ greater than 6). A weakly developed chloritic intergrade is the dominant mineral in this soil (see Section VI.7). The dissolution and X-ray data show this mineral to be relatively sensitive to the treatment to remove amorphous oxides. Assuming a smectitic composition with contents of 20% Al₂O₃ and 50% SiO₂, the complete dissolution would result in a SiO₂/Al₂O₃ ratio of 4.3. It therefore seems that silica is preferentially released over alumina in the slightly alkaline environment of this soil, and it remains in the profile in the absence of strong leaching. This condition may be an important factor in the crusting tendency of this soil.

The elemental Al/(Al + Si) ratios (not shown in Table 5) range from 0.4 to 0.8 in all subfractions except those of Madras (less than 0.2) and Blacklock (greater than 0.8). The structural model for synthetic amorphous silica-aluminas of Cloos et al. (1969) associates the 0.4 to 0.8 range with a core of tetrahedrally linked Al and Si coated by polymerized hydroxy aluminum. A ratio below 0.2 would correspond to a similar core but with incomplete or absent coating of aluminum. Demixing of crystalline aluminum phases occurs above 0.8. These concepts cannot readily be applied to some's as the presence of the organic phase undoubtedly modifies the formation and transformation of the inorganic amorphous phase in yet unknown ways.
Amorphous iron does not show any obvious trends. The nature of these materials in soils is still somewhat obscure. Some iron presumably exists as a minor constituent in amorphous alumino-silicates. However, iron often appears to form discrete particles, at least in "oxidic" soils such as laterites, ultisols, and spodosols (Deshpande et al., 1968; Greenland et al., 1968). Individual particles are roughly spherical with diameters of 50-100 Å, and, at times, form larger, irregular aggregates ("blackberries"; Greenland et al., 1968). Similar structures were observed in the heavier than 2.96 g/cc subfraction from the Jory B3 coating clay mineral platelets (Plate 2).

According to Greenland et al. (1968) it is unlikely that continuous films of iron hydroxide are formed on kaolinite and halloysite in soils. This was inferred from electron microscopic observations and studies showing that iron oxides in soils are present as negatively charged particles (Deshpande et al., 1964). Since freshly precipitated pure iron oxides have an isoelectric point above 7, the difference, based on the findings of Hingston et al. (1972), was attributed to the adsorption of phosphate, silicate and organic anions at the surfaces of iron oxides in soils. The apparent preference of iron oxides to form globular particles rather than continuous films (as Al-oxides do) on the clay minerals appears to be the principal reason for the comparatively poor aggregating effect of iron oxides in "oxidic" soils (El-Swaify and Emerson, 1975).

Chukhrov et al. (1972) presented detailed diffraction and IR-absorption data on a natural ferric hydroxide from the USSR. They proposed ferrihydrate as a new name for ferric hydroxide showing five broad X-ray and electron diffraction lines indicative of a defect hematite structure; less well organized forms, considered as precursors to ferrihydrate, were called protoferrihydrate.

Schwertmann and Fischer (1973) examined amorphous ferric hydroxides from precipitates deposited from soil-borne waters. Most of these samples contained less than 6% organic carbon. Electron microscopy revealed particles of about 100 Å in diameter. X-ray diffraction
patterns showed lines characteristic of ferrihydrate. Both Schwertmann and Fischer (1973) and Chukhrov et al. (1975) concluded that ferrihydrate formation is largely linked to microbial decomposition of soluble iron-organic complexes. Transformation experiments (Schwertmann and Fischer, 1973) suggested that aging under conditions corresponding to a humid temperate climate causes conversion to goethite. The aging process is greatly retarded by organic compounds (Schwertmann et al., 1968) and other compounds retained by the hydroxide.

Evidence was obtained (Section VI.7) that ferrihydrates perhaps along with microcrystalline goethite and hematite (subhorizon) occur in Jory, and that, at least in the subhorizon, these materials form discrete granules of about 100 µ in diameter (Section VI.11). The question was not further pursued however, and it is estimated that iron occurs in less crystalline forms (protoferrihydrates, mixed amorphous oxides) in the surface horizons of the other soils.

The main objective of these experiments was to assess the levels of amorphous oxides in density subfractions. The method used for this purpose is rather harsh and not designed to investigate the suspected relationship between amorphous mineral materials and organic matter accumulation. Nonetheless, linear regressions of organic carbon and total nitrogen on amorphous oxides were calculated, but the meaning of good correlations should not be overestimated. For example, amorphous Al$_2$O$_3$ and organic carbon in Quillayute and Blacklock are linearly correlated at the 1% level (F-test); the organic carbon contents of the two soils are similar, but Quillayute is two to three times higher in amorphous oxides.

Good correlations ($r^2$ greater than 0.9) between organic carbon and amorphous Al were consistent in all soils with broad density subfraction distributions (Quillayute, Mitaka, Blacklock, Jory). Regression of total N on amorphous Al gave somewhat lower coefficients (0.80 to 0.92). The coefficients from the regression of organic carbon on silica dropped below 0.8; organic carbon with silica plus alumina resulted in $r^2$-values
of 0.86 to 0.96. Amorphous iron, though often available in large quantities does not seem to affect organic matter levels.

7. X-ray diffraction analysis of somp subfractions

The main features of the X-ray diffraction patterns from somp density subfractions are shown in part in figures 15-22 and described in Table 6. Complete sets of x-ray diffraction patterns for all density subfractions are assembled in Appendix 2.

The X-ray analysis of the somp density subfractions clearly indicates gradual transitions from poorly defined mineral matter in the light fractions to heavier, more crystalline components approaching the behavior of end-member minerals when subjected to standard identification treatments. These transitions are particularly well expressed with chloritic intergrades, frequently the dominant mineral component, and in the subfractions from soils with broad density distributions. The subfractions from Jory (Figure 16) are an exception in that phyllosilicates are best expressed in the intermediate density fractions because of increased incrustation with iron oxides in the heavier fractions. Again, particle size must be taken into account; the smaller particle size in the light fractions contributes to the decline in peak intensity with subfraction density.

Chloritic intergrades in the clays of untreated subfractions (before removal of OM and amorphous oxides) show partial to complete (Bashaw, Figure 20a) expansion after solvation with glycerol (G1) and ethylene glycol (EG). In Blacklock (Figure 17b) and to a lesser extent in Quillayute (Figure 15a) expansion with G1 and EG ranges from slight in the light fractions to nearly complete in the heavier fractions. Solvation with glycerol in Jory (Figure 16a) only led to reduced intensities at 14 Å. Broad shoulders in the 16-17 Å range were obtained with G1 and EG Woodburn (Figure 19a) and Madras (Figure 21a). The smectite in Bashaw (Figure 20a) formed complete duo- inter-layers with both G1 and EG. Considerable resistance to collapse with K-saturation/heat treatments is
Table 6: Summary of X-ray diffraction results from sopp density subfractions before and after removal of organic matter and amorphous inorganic oxides (1)

<table>
<thead>
<tr>
<th>Soil</th>
<th>Mineral</th>
<th>Untreated (2)</th>
<th>Treated (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quillayute</td>
<td>Chloritic intergrade</td>
<td>Peak intensity and sharpness increasing with density; partial expansion with EG and Gl; partial collapse with K/105 treatments.</td>
<td>Improved peak intensity and sharpness; expansion with Gl only in the two lighter fractions; expansion with EG partial to almost complete in the lighter fractions.</td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td>Invariant 14 Å reflections only in &gt;1.9 g/cc fraction.</td>
<td>Chlorite also present in the 1.8-1.9 g/cc fraction.</td>
</tr>
<tr>
<td></td>
<td>Micaceous</td>
<td>Minor admixture in &gt;1.9 g/cc fraction</td>
<td>Minor amounts apparent in all fractions.</td>
</tr>
<tr>
<td>Jory</td>
<td>Chloritic intergrade</td>
<td>Reflections best defined in intermediate subfractions; partial expansion with EG, very slight with Gl, similar in all subfractions; partial collapse with K/105, almost complete with K/550.</td>
<td>Similar behavior, but reduced peak intensities; peak intensity and sharpness increasing with density.</td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>Best defined in intermediate subfractions.</td>
<td>Somewhat sharper reflections, particularly with K/heat treatments.</td>
</tr>
<tr>
<td></td>
<td>Micaceous</td>
<td></td>
<td>Minor admixture in the heaviest fraction.</td>
</tr>
<tr>
<td>Iron oxides</td>
<td>(goethite, hematite) in the heaviest subfractions (see Figure 22).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blacklock</td>
<td>Chloritic intergrade</td>
<td>Peak sharpness increasing with density; partial expansion with EG and Gl increasing with density; collapse with K/105 partial to almost complete in the heavier fractions.</td>
<td>Expansion only with EG; collapse with K/105 strong in all fractions.</td>
</tr>
<tr>
<td></td>
<td>Micaceous</td>
<td>Accessory in the &gt;1.9 g/cc.</td>
<td>Slightly enhanced.</td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>Present in all fractions.</td>
<td>Enhanced peak intensity.</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>Present in all fractions.</td>
<td>Unchanged.</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Soil</th>
<th>Mineral</th>
<th>Untreated (2)</th>
<th>Treated (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mitaka</td>
<td>Chloritic</td>
<td>n.d. (4)</td>
<td>Peak intensity and sharpness increasing with density; partial expansion with EG; partial collapse with K/treatments.</td>
</tr>
<tr>
<td></td>
<td>intergrade</td>
<td></td>
<td>Minor amounts probably present in all fractions.</td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td>n.d.</td>
<td>Accessory in the heaviest fraction.</td>
</tr>
<tr>
<td></td>
<td>Micaceous</td>
<td>n.d.</td>
<td>Nearly ideal behavior, including reexpansion with K/54 after K/105.</td>
</tr>
<tr>
<td>Bashaw</td>
<td>Montmorillonite</td>
<td>Nearly ideal behavior, including reexpansion with K/54 after K/105.</td>
<td>Broader peaks; expansion with G1 sluggish; appearance of strong reflections near 7 Å.</td>
</tr>
<tr>
<td>Woodburn</td>
<td>Chloritic</td>
<td>Partial expansion with EG and G1; collapse nearly complete after K/105.</td>
<td>Strongly reduced peak intensity.</td>
</tr>
<tr>
<td></td>
<td>intergrade</td>
<td></td>
<td>Enhanced peak intensity.</td>
</tr>
<tr>
<td></td>
<td>Micaceous</td>
<td>Present in both fractions.</td>
<td>Enhanced peak intensity.</td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>Present in both fractions.</td>
<td>Enhanced peak intensity.</td>
</tr>
<tr>
<td>Madras</td>
<td>Chloritic</td>
<td>Partial expansion with EG and G1; nearly complete collapse after K/105.</td>
<td>Peak intensity and sharpness reduced.</td>
</tr>
<tr>
<td></td>
<td>intergrade</td>
<td></td>
<td>Enhanced peak intensity.</td>
</tr>
<tr>
<td></td>
<td>Micaceous</td>
<td>Present in both fractions.</td>
<td>Enhanced peak intensity.</td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>Present in both fractions.</td>
<td>Enhanced peak intensity.</td>
</tr>
</tbody>
</table>

(1) Abbreviations used in table:
EG = Mg-saturated specimens solvated with ethylene glycol; G1 = Mg-saturated specimens solvated with glycerol K/105 (550) = K-saturated specimens heated at 105(550)°C K/54 = K-saturated specimens equilibrated at 54% relative humidity after drying at 105°C.

(2) Somp's subjected only to standard characterization treatments (saturation, solvation, heating) used in X-ray diffraction of clay minerals.

(3) After removal of organic matter and amorphous oxides.

(4) n.d. = not determined.
Figure 15a: X-ray diffractograms of untreated Quillayute smp subfractions.
Figure 15b: X-ray diffractograms of Quillayute sump subfractions after removal of amorphous oxides.
Figure 15c: X-ray diffractograms of Quillayute smp subfractions after removal of amorphous oxides
Figure 16a: X-ray diffractograms of untreated Jory sump subfractions.
Figure 16b: X-ray diffractograms of Jory sOMP subfractions after removal of amorphous oxides.
Mg-saturated, 54% relative humidity

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1.6</td>
<td>29</td>
</tr>
<tr>
<td>1.6-1.7</td>
<td>25</td>
</tr>
<tr>
<td>1.7-1.8</td>
<td>20</td>
</tr>
<tr>
<td>1.8-1.9</td>
<td>15</td>
</tr>
<tr>
<td>&gt;1.9</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 17a: X-ray diffractograms of untreated somp subfractions from Blacklock.
Mg-saturated
54% rel. humidity

Density (g/cc)
< 1.6
1.6-1.7
1.7-1.8
1.8-1.9
>1.9

d(Å) 7 10 14

Figure 17b: X-ray diffractograms of untreated smp subfractions from Blacklock.
Figure 17c: X-ray diffractograms of untreated somp subfractions from Blacklock.
Mg-saturated, 54% relative humidity

Mg-saturated, Glycerol

Figure 17d: X-ray diffractograms of smp subfractions from Blacklock after removal of amorphous oxides.
Figure 17e: X-ray diffractograms of smp subfractions from Blacklock after removal of amorphous oxides.
Figure 18a: X-ray diffractograms of smp subfractions from Mitaka after removal of amorphous oxides.
Figure 18b: X-ray diffractograms of somp subfractions of Mitaka after removal of amorphous oxides.
Mg-saturated, 54% relative humidity

Density (g/cc)
- <2.1
- 2.1-2.2

K-saturated, 105°C

Density (g/cc)
- <2.1
- 2.1-2.2

K-saturated, 550°C

Density (g/cc)
- <2.1

Figure 19a: X-ray diffractograms of untreated somep subfractions from Woodburn.
Figure 19b: X-ray diffractograms of somp density fractions from Woodburn after removal of amorphous oxides.
Mg-saturated, 54% rel. humidity

Density (g/cc)
< 1.95
> 1.95

d(Å)
7 10 14

K-saturated, 54% rel. humidity

Density (g/cc)
< 1.95
> 1.95

d(Å)
7 10 14

Mg-saturated, Glycerol

Density (g/cc)
< 1.95
> 1.95

d(Å)
7 10 14

K-saturated, 550°C

Density (g/cc)
< 1.95
> 1.95

d(Å)
7 10 14

Figure 20a: X-ray diffractograms of untreated somp subfractions from Bashaw.
Mg-saturated, 54% rel. humidity

Density (g/cc)
<1.95
>1.95

K-saturated, 100°C

Density (g/cc)
<1.95
>1.95

Mg-saturated, Glycerol

Density (g/cc)
<1.95
>1.95

K-saturated, 550°C

Density (g/cc)
<1.95
>1.95

Figure 20b: X-ray diffractograms of somp subfrations from Bashaw after removal of amorphous oxides.
Figure 21a: X-ray diffractograms of untreated sump subfractions from Madras.
Figure 21b: X-ray diffractograms of somp subfractions from Madras after removal of amorphous oxides.
Figure 22: X-ray diffractograms of some density subtractions from Jory (figures in parentheses are relative peak intensities of iron oxides according to Chukrov et al., 1975).

Spacings in Å

- 1.66 goethite (10)
- 1.69 goethite (10)
- hematite (80)
- 1.72 goethite (20)
- ferrihydrate (30)
- 1.99 ferrihydrate (50)
- ferrihydrate (70)
- 2.20 goethite (20)
- protoferrihydrate ferrihydrate (100)
- 2.52 hematite (80)
- 2.69 goethite (30)
- hematite (100)
- 4.18 goethite (100)
- 4.98 goethite (15)
evident in all fractions. The collapse is generally partial at 105°C, and improves at higher temperatures. Reexpansion after the 105°C treatment and rehydration at 54% relative humidity was observed only in Bashaw (Figure 20a).

The diffraction patterns recorded after removal of organic matter and amorphous oxides should give some indication about the nature of the chloritic intergrade matrix minerals, although the dissolution treatment was not specifically designed to remove interlayers.

In Blacklock (Figure 17 d, e) and Quillayute (Figure 15 b, c) the dissolution treatments clearly produced improved diffractograms. Expansion with glycerol was absent in all Blacklock subfractions and in the two heavier subfractions of Quillayute; ethylene glycol solvation gave strong reflections in the 16-17 Å region. This indicates beidellite as a matrix mineral, and confirms Singleton's (1966) results in a comparable coastal soil. Collapse to 10 Å with heat treatments was improved, but reexpansion after rehydration at 54% r.h. was incipient at best.

Partial expansion with glycerol in the Blacklock subfractions only before removal of amorphous oxides might occur because of the presence of patchy interlayer material facilitating the penetration of glycerol; the interlayer material appears to have been completely removed by the dissolution treatment. Alternatively, a matrix component (perhaps smectite) largely destroyed during the dissolution treatment could be present. In the two lightest fractions of Quillayute the persistence of expansion with glycerol suggest smectite in addition to beidellite as a matrix mineral. Beidellite also appears to serve as a matrix in the intergrades of Mitaka (Figure 18).

The chloritic intergrades of Jory, Woodburn and Madras are considered as a separate group because of their response to the dissolution treatment and other similarities. The 14 Å reflections of the Mg-saturated untreated subfractions at 54% r.h. are not well defined.
Partial expansion occurs upon solvation with Gl and EG, although in Jory glycerol solvation merely reduces the 14 Å peak intensity. The collapse following the heat treatment is sluggish with some concomitant enhancement of 10 Å reflections in Woodburn and Madras, but not in Jory. After removal of amorphous oxides, the 14 Å reflections at 54% r.h. (Mg-sat.) show reduced intensities, particularly in Jory. Some expansion after the solvation treatments does occur, but it is too diffuse to allow identification of the matrix minerals. The subfractions from this group of soils all yielded significantly higher final slopes during the dissolution treatment (Table 5) than did those of Quillayute, Mitaka and Blacklock. Other component minerals in the subfractions of these soils (e.g. micaceous minerals in Woodburn and Madras) were enhanced following the dissolution treatment. It therefore appears that the chloritic intergrades of this group are considerably less stable towards the dissolution treatment. Unexpectedly high yields of amorphous oxides in Woodburn and Madras (15-20%, Table 5) may be regarded as supporting evidence for these conclusions.

In contrast to beidellite, the smectitic clay from Bashaw is highly susceptible to damage during the removal of amorphous oxides. A smectitic matrix of the intergrades in Jory, Woodburn and Madras could account in part for the instability towards selective dissolution.

It is difficult to account for the differences between the chloritic intergrades in the two groups of soils (Quillayute, Mitaka, Blacklock versus Jory, Woodburn, Madras). Climatic conditions are rather similar for both groups, except for Quillayute (high rainfall, Table 1) and Madras (low rainfall). However, age may be a factor, at least in Jory where kaolinite and iron oxides appear to evolve at the expense of intergrades and perhaps other minerals. Kaolinite also appears to occur in Woodburn and Madras, but is absent in Quillayute and Mitaka.

Some indications of the possible forms of iron in Jory are given in Figure 22. The diffractogram of the heavy separate from Jory B33 serves as a baseline since this material is free of phyllosilicates (see Figure 2); it contains goethite, hematite and ferrihydrates. The same forms
appear to occur in the >2.3 g/cc subfraction, and, to a lesser extent, in the <2.0 g/cc subfraction of the Jory surface horizon.

Published material against which to compare the results of the diffraction analyses are lacking. Dudas and Pawluk (1969) examined the mineralogy of the clay-size organo-mineral particles from a black chernozem, but reported generally similar behavior and composition among their granulometric subfractions.

8. Surface areas and porosity

The surface areas of selected density subfractions before and after peroxidation measured by adsorption of nitrogen gas and water vapor are listed in Table 7 and plotted in Figure 23. The mean and standard errors calculated from the deviations between duplicate determinations were 2.8 m$^2$/g and 2.3 m$^2$/g for N$_2$-surface areas, 2.7 m$^2$/g and 2.2 m$^2$/g for H$_2$O vapor-surface areas.

Considering surface areas from nitrogen adsorption first, surprisingly small areas were found on untreated subfractions. In Quillayute and Jory the areas decreased with subfraction density. Nitrogen appears to have a low affinity for soil organo-mineral surfaces; the linear regression of the organic carbon contents on N$_2$-areas of the nine subfractions has a negative slope and is significant at 1%. Similarly low areas, decreasing with increasing retention of alkyl-ammonium, were reported by Slabaugh (1971) for hydrophobic organo-bentonites (alkyl-ammonium retention equivalent to 20-50% organic carbon).

After peroxidation the N$_2$-areas decrease as subfraction density increases. The linear regression of the contents of amorphous silica and alumina on the N$_2$-areas (after peroxidation) of the nine subfractions is positive and significant at 5%. Particle sizes (presumably smaller in light subfractions) also contribute to the decrease in surface area. The N$_2$-areas of the peroxide-treated subfractions of Quillayute and Jory are much larger than before peroxidation and of similar magnitude as those determined by Chichester (1967) on the clay fractions of soils.
Table 7:  Surface areas of clay-size somp density subfractions measured by adsorption of nitrogen gas and water vapor before and after peroxidation.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Density subfraction (g/cc)</th>
<th>Surface area before peroxidation</th>
<th>Surface area after peroxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$N_2$-gas ($m^2/g$)</td>
<td>$H_2O$-vapor ($m^2/g$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_2$-gas ($m^2/g$)</td>
<td>$H_2O$-vapor ($m^2/g$)</td>
</tr>
<tr>
<td>Quillayute</td>
<td>1.7-1.8</td>
<td>7</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td></td>
<td>136</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>&gt;1.9</td>
<td>14</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93</td>
<td>103</td>
</tr>
<tr>
<td>Jory</td>
<td>&lt;2.0</td>
<td>27</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>107</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>42</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>&gt;2.3</td>
<td>48</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>86</td>
<td>50</td>
</tr>
<tr>
<td>Woodburn</td>
<td>&lt;1.95</td>
<td>54</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>123</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>&gt;1.95</td>
<td>42</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>67</td>
</tr>
</tbody>
</table>

formed from Mazama pumice. In Woodburn the nitrogen areas of treated and untreated subfractions are very similar.

The water vapor surface areas of untreated fractions greatly exceed the corresponding $N_2$-areas, but do not differ much among soils. The decrease of the areas with increasing subfraction density is probably related to levels of both organic carbon and amorphous oxides and increasing particle size; since these phases are both hydrophilic, it is difficult to recognize relative contributions.

In peroxide treated fractions the water vapor areas exceed the $N_2$-areas by 15-40% in Quillayute, 60-68% in Woodburn, but differ insignificantly in Jory. Surface areas measured by water vapor adsorption on allophanic clays (Amine and Otsuka, 1968) were reported to be up to four times as extensive as $N_2$-areas, a phenomenon ascribed to the fine spherical particles of allophane forming aggregates whose interstices are inaccessible to nitrogen gas. Although Quillayute is not a strictly allophanic soil, it appears that the observed water vapor surface areas are relatively small. In Woodburn and Jory the water vapor areas drop
Figure 23: Surface areas of clay-size sump density subfractions measured by adsorption of nitrogen gas and water vapor before and after peroxidation.
by up to 50% following peroxidation. These observations are unexpected
and suggest the possibility that peroxidation releases sufficient
amounts of organically complexed metals to block access to fine pores
and interlayer spaces. Chichester (1967) found that surface areas ($N_2$)
of peroxide-treated clay samples increased strongly with profile depth
(OM decreases); the fact that amorphous components as determined by the
weight loss method did not significantly increase with depth also points
to peroxide-induced surface alterations. The similarity of $N_2$- and $H_2O$-
areas in peroxide-treated Jory subfractions is ascribed in part to the
same condition and in part also to the mineralogy of the clay fraction
(high in kaolinite).

Full nitrogen adsorption-desorption isotherms for selected peroxide-
treated samples are shown in Figure 24. Desorption hysteresis occurs
mostly at relative pressures above 0.45. The pore size distributions
calculated from such isotherms are shown in Figure 25. Pore radii of
less than 50 Å are dominant. The pore volume per increment of pore
radius ($\Delta V/\Delta r$) peaks in the range of 20-24 Å, and peak values show only
minor deviations among subfractions and soils. These results are in
close agreement with those reported by Slabaugh and Stump (1964) for
marine sediments, and by Aylmore and Quirk (1960 and 1967) for various
clays. The latter authors interpreted the Kelvin cylindrical radii as a
measure of intraaggregate porosity, i.e. slit- or wedge-shaped pores
resulting from the interleaving of crystal-units of several elementary
sheets in thickness. This interpretation is tentatively adopted for the
results of this study, with the reservation that amorphous oxides
undoubtedly contribute to the porosity, but more detailed studies would
be required to make definitive differentiations.

The water vapor adsorption-desorption isotherms of untreated and
peroxide-treated subfractions (Figure 26) exhibit strong continuous
hysteresis over the whole pressure range; an abrupt change occurred only
in the peroxide-treated Quillayute subfractions at a relative pressure
of about 0.4. Desorption hysteresis decreased with increasing subfrac-
tion density in both treated and untreated fractions. A concise
Figure 24: Nitrogen adsorption-desorption isotherms of selected peroxide-treated sump subfractions.
Figure 25: Pore size distributions below 100 Å of selected peroxide-treated somp subfractions.
Figure 26: Water vapor adsorption-desorption isotherms of selected untreated and peroxide-treated smp subfractions.
interpretation of these isotherms is difficult because of the retention of water around charged sites and exchangeable ions as well as interlayer adsorption.

9. Cation exchange capacities

The results obtained in the determination of CEC's with neutral salt and at pH 8.2 are shown in Table 8 and plotted in Figure 27. The mean and standard errors calculated from the deviations between duplicate determinations were 0.6 and 0.7 meq/100 g for neutral salt CEC's, 1.1 and 1.5 meq/100 g for CEC's at pH 8.2. Higher errors for the latter CEC's result from greater probable sample loss and slight dissolution of organic matter at pH 8.2; yellowish extracts were obtained in the Quillayute and Jory subfractions, and brownish extracts in the Blacklock subfractions. Dudas and Pawluk (1969) reported no losses of organic matter in the course of CEC determinations at pH 3.5 and 10 on less than 2 μm organo-clay subfractions from Black Chernozems. Partial organic matter dissolution may also account for some of the larger discrepancies observed between the CEC values measured on water-dispersible bulk clays and the values obtained by summing up the CEC's of the subfractions.

The general magnitude of the subfraction CEC's are low compared to those reported by Sahwney et al. (1970) for clay-size organo-mineral separates from northeastern Bt spodosol horizons, but similar to those determined by Dudas and Pawluk (1969) on clay-size granulometric subfractions from A horizons of black chernozems. It was stressed earlier that methods realistically applicable to study the exchange behavior of somp's have not been evaluated in detail; the data in Table 8 are therefore discussed more in terms of relative variations and trends.

Exchange sites in somp's arise from three major sources: interlayer sites of phyllosilicates (pH independent), sites of inorganic amorphous oxides and sites of the organic phase (both pH dependent).
<table>
<thead>
<tr>
<th>Soil</th>
<th>Density subfraction</th>
<th>CEC neutral salt</th>
<th>CEC pH 8.2</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/cc</td>
<td>meq/100 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quillayute</td>
<td>&lt;1.7</td>
<td>32.0</td>
<td>98.7</td>
<td>66.7</td>
</tr>
<tr>
<td></td>
<td>1.7-1.8</td>
<td>27.4</td>
<td>73.4</td>
<td>46.0</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>27.4</td>
<td>67.1</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td>&gt;1.9</td>
<td>24.9</td>
<td>47.2</td>
<td>22.3</td>
</tr>
<tr>
<td>Sum (1)</td>
<td></td>
<td>27.3</td>
<td>68.2</td>
<td>40.8</td>
</tr>
<tr>
<td>Bulk w.d. clay (2)</td>
<td>29.2</td>
<td>77.0</td>
<td>48.5</td>
<td></td>
</tr>
<tr>
<td>Mitaka</td>
<td>&lt;1.8</td>
<td>31.5</td>
<td>81.3</td>
<td>49.8</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>23.4</td>
<td>67.4</td>
<td>44.0</td>
</tr>
<tr>
<td></td>
<td>1.9-2.0</td>
<td>21.4</td>
<td>60.3</td>
<td>38.9</td>
</tr>
<tr>
<td></td>
<td>&gt;2.0</td>
<td>17.8</td>
<td>45.4</td>
<td>27.6</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>24.9</td>
<td>66.8</td>
<td>42.2</td>
</tr>
<tr>
<td>Bulk w.d. clay</td>
<td></td>
<td>29.4</td>
<td>66.8</td>
<td>37.4</td>
</tr>
<tr>
<td>Blacklock</td>
<td>&lt;1.6</td>
<td>48.0</td>
<td>111.8</td>
<td>63.8</td>
</tr>
<tr>
<td></td>
<td>1.6-1.7</td>
<td>46.0</td>
<td>93.9</td>
<td>48.9</td>
</tr>
<tr>
<td></td>
<td>1.7-1.8</td>
<td>42.0</td>
<td>70.3</td>
<td>28.3</td>
</tr>
<tr>
<td></td>
<td>1.8-1.9</td>
<td>40.1</td>
<td>58.9</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>&gt;1.9</td>
<td>14.8</td>
<td>23.6</td>
<td>8.8</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>35.8</td>
<td>67.1</td>
<td>31.3</td>
</tr>
<tr>
<td>Bulk w.d. clay</td>
<td></td>
<td>39.8</td>
<td>76.8</td>
<td>37.0</td>
</tr>
<tr>
<td>Jory</td>
<td>&lt;2.0</td>
<td>31.1</td>
<td>47.5</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>2.0-2.1</td>
<td>28.5</td>
<td>41.8</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>2.1-2.2</td>
<td>29.0</td>
<td>40.9</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>2.2-2.3</td>
<td>27.6</td>
<td>38.5</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>&gt;2.3</td>
<td>23.1</td>
<td>32.1</td>
<td>9.0</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>28.7</td>
<td>41.0</td>
<td>12.4</td>
</tr>
<tr>
<td>Bulk w.d. clay</td>
<td></td>
<td>28.8</td>
<td>38.4</td>
<td>9.6</td>
</tr>
<tr>
<td>Woodburn</td>
<td>&lt;2.1</td>
<td>33.2</td>
<td>42.6</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>2.1-2.2</td>
<td>24.9</td>
<td>33.1</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>&gt;2.2</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Bulk w.d. clay</td>
<td></td>
<td>32.9</td>
<td>40.6</td>
<td>8.5</td>
</tr>
<tr>
<td>Bashaw</td>
<td>&lt;1.95</td>
<td>48.3</td>
<td>58.2</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>&gt;1.95</td>
<td>46.4</td>
<td>57.6</td>
<td>11.2</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>47.6</td>
<td>57.9</td>
<td>10.3</td>
</tr>
<tr>
<td>Bulk w.d. clay</td>
<td></td>
<td>50.1</td>
<td>58.9</td>
<td>8.8</td>
</tr>
<tr>
<td>Madras</td>
<td>&lt;1.95</td>
<td>36.5</td>
<td>44.3</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>&gt;1.95</td>
<td>33.8</td>
<td>41.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>35.8</td>
<td>43.4</td>
<td>7.8</td>
</tr>
<tr>
<td>Bulk w.d. clay</td>
<td></td>
<td>37.4</td>
<td>43.9</td>
<td>6.5</td>
</tr>
</tbody>
</table>

(1) From sum of (CEC x subfraction wt %)
(2) CEC's of <2 μm somp's before subfractionation
(3) n.d. = not determined
Figure 27: Cation exchange capacities of somp subfractions measured with neutral salt (NS) and at pH 8.2 (figures in bars indicate subfraction density in g/cc).
In addition, each of the three major components (crystalline, inorganic amorphous, organic) may modify the exchange properties of the others. Permanent interlayer sites may be occupied by gibbsitic interlayer material or inaccessible because of exterior amorphous coatings. Active sites of amorphous inorganic materials are affected by both permanent phyllosilicate charges and interactions with the organic phase (e.g. ligand exchange). Organic functional groups capable of exchange reactions suffer modifications from interactions with inorganic surfaces and cation species in solution. Finally, the whole system is sensitive to changes in pH, ionic strength, and type of introduced ion species.

The NS (neutral salt)-CEC's decrease moderately with increasing subfraction density. The sharply lower NS-CEC in the heaviest fraction of Blacklock results from high amounts of quartz and low contents of organic matter in that fraction. The generally moderate decrease of the NS-CEC's over the density subfractions is attributed to decreasing levels of organic matter and amorphous oxides counteracted by increasing access to interlayer exchange positions. The NS-CEC's of the water-dispersible bulk clays may reflect contents of amorphous oxides occupying or blocking access to interlayer positions. Thus, Jory, Quillayute and Mitaka have low NS-CEC's; Woodburn and Madras occupy an intermediate position followed by Bashaw and Blacklock with comparatively high CEC's.

The difference between NS-CEC's and CEC's at pH 8.2, as expected, are significantly correlated with organic carbon. The correlations for Quillayute, Jory, Blacklock, and all the density subfractions taken together are significant at 1%, for Mitaka at 5%. However, further experiments would be required to assess the relative contributions of the various somp components to the CEC as the pH is raised.

10. **Infrared spectroscopy of selected somp subfractions**

IR spectra were recorded (Courtesy Dr. R. F. Keeler, ARS Poisonous Plant Laboratory, Logan, Utah) primarily in the hope of detecting differences in major organic components (e.g. aromatic structures vs.
carbohydrates) among the subfractions of a given soil. However, successful IR spectroscopy of clay-humic complexes is intrinsically hindered by similar positions of major adsorption bands of clay minerals and humic matter, notably in the regions 3400-3750 cm\(^{-1}\), 1600-1720 cm\(^{-1}\), and 960-1250 cm\(^{-1}\); other organic band positions occur, but are weak, as the organic component of somp's in KBr pellets suffers high attenuation (Arshad and Lowe, 1966; Scharpenseel, 1967). Implicitly, comparisons of band intensities between samples differing greatly in organic matter contents cannot be made. IR spectroscopy of extracted humic materials, functional group analysis, determination of the relative age of the organic carbon in the various density subfractions, or mass spectroscopy would appear more promising in evaluating the organic phase, but limited sample amounts and resources precluded these determinations.

The band assignments (Table 9) used in the following discussion were assembled from several authoritative sources (Goh and Stevenson, 1971; Scharpenseel, 1967; Farmer, 1974; Flaig et al., 1975; Beutelspacher and van der Marel, 1976).

The spectra of fulvic and humic acid (Figure 28) are fairly typical compared to published ones (Beutelspacher and van der Marel, 1976). The shoulders at 2350 cm\(^{-1}\) might arise from amino groups. The 1600 cm\(^{-1}\) (aromatic vC=C) and 1235 cm\(^{-1}\) (vC-O) bands are better expressed in humic acid.

The spectrum for imogolite (Figure 28) is very similar to that reported by Yoshinaga and Aomine (1962) for that mineral; the physical basis for the shoulder at 1400 cm\(^{-1}\) is uncertain. Similarly, the spectra for bentonite and kaolinite are typical, except for the strong band at 1170 cm\(^{-1}\), the cause of which is unknown.

Adsorption in the 3400-3700 cm\(^{-1}\) region of the untreated subfractions produced one broad band in Quillayute and Woodburn, while separate bands can be recognized in the other subfractions. Following treatment with peroxide the higher frequency portion of these bands (structural vOH) become sharper and at times more intense.
Table 9: Assignments of IR adsorption bands for clay-size sopa's (1).

<table>
<thead>
<tr>
<th>$\tilde{\nu}$ (cm$^{-1}$)</th>
<th>Organic phase</th>
<th>Mineral phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>3750-3400</td>
<td>structural $v$OH</td>
<td></td>
</tr>
<tr>
<td>3620-3400</td>
<td>$OH$-vibration in $H$-bonds between interlayer water and surface oxygens, and in $H$-bonds between water molecules.</td>
<td></td>
</tr>
<tr>
<td>3450-3100</td>
<td>$v$OH, $H$-bonded $OH$, intermolecular bonded $OH$</td>
<td></td>
</tr>
<tr>
<td>3100-3030</td>
<td>aromatic $vC$-$H$</td>
<td></td>
</tr>
<tr>
<td>2950-2850</td>
<td>aliphatic $vC$-$H$</td>
<td></td>
</tr>
<tr>
<td>2850-2500</td>
<td>$v$OH of $-COOH$</td>
<td></td>
</tr>
<tr>
<td>2315</td>
<td>amines, amino acids</td>
<td></td>
</tr>
<tr>
<td>1725-1640</td>
<td>$vC=O$ of carboxyls, aldehydes, ketones, quinones</td>
<td></td>
</tr>
<tr>
<td>1640-1585</td>
<td>$vC=C$</td>
<td>$dOH$ of adsorbed water</td>
</tr>
<tr>
<td>1630</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1575</td>
<td>metallo-carbonyls</td>
<td></td>
</tr>
<tr>
<td>1515</td>
<td>$vC=C$, aromatic, sec. amines</td>
<td></td>
</tr>
<tr>
<td>1470-1420</td>
<td>aliphatic $dC$-$H$</td>
<td></td>
</tr>
<tr>
<td>1280-1050</td>
<td>$vC$-$O$ of esters, ethers, phenols</td>
<td></td>
</tr>
<tr>
<td>1200-700</td>
<td></td>
<td>$vSi-O$</td>
</tr>
<tr>
<td>950-700</td>
<td></td>
<td>$dOH$, structural $OH$, vibrations of the silicate framework, (R-OH)</td>
</tr>
<tr>
<td>772</td>
<td>$COO^-$-scissoring</td>
<td></td>
</tr>
</tbody>
</table>

(1) In the table the prefix $v$ refers to stretching vibrations, $d$ to bending deformations.
Figure 23: IR spectra of fulvic and humic acid, bentonite, kaolinite and imogolite.
Figure 29: IR spectra of smp subfractions and water-dispersible (w.d.) clay from Quillayute before (a) and after (b) treatment with peroxide.
Figure 30: IR spectra of some subfractions and water-dispersible (w.d.) clay from Jory before (a) and after (b) treatment with peroxide.
Figure 31: IR spectra of individual somp subfractions from selected soils before (a) and after (b) treatment with peroxide.
Weak bands in the 2950-2850 cm\(^{-1}\) region (aliphatic vC-H) are present in all subfractions. In Jory, this band is notably stronger in the lighter fraction, and is absent in whole clay. These bands should largely disappear after peroxidation, yet improved sharpness and intensity was observed in most samples. It is conceivable that these bands arise from oxidation products of aliphatic character similar to those reported by Goh and Stevenson (1971).

The shoulders in the 2300-2600 cm\(^{-1}\) region are too indistinct to attempt any correlations.

Adsorption is strong and increasing with subfraction density (Quillayute, Jory) in the 1725-1620 cm\(^{-1}\) region (vC=O). The band intensity decreased after peroxidation, but remained comparatively strong because of adsorbed water (dOH at 1630 cm\(^{-1}\)) and possibly contributions from unoxidized organic materials.

Aromatic vC=C (1640-1585 cm\(^{-1}\)) did not produce distinct bands or shoulders. Aliphatic dC-H at 1400-1470 cm\(^{-1}\) gave distinct bands in Quillayute and Jory subsamples, broad shoulders in the subfractions of the other soils. Remnants of these bands persisted after peroxidation.

Slight shoulders around 1240 cm\(^{-1}\) vC-O) which disappear upon peroxidation are visible in all fractions except Jory >2.3 g/cc, Woodburn and Madras subfractions. Differences in intensities are attributed to varying organic matter contents.

The bands below 1000 cm\(^{-1}\) remain largely unchanged following peroxidation, and are due to dOH and vibrations of the silicate framework. Conspicuously strong adsorption at 803, 782, and 698 cm\(^{-1}\) indicative of quartz occurred in the heaviest fraction of Blacklock.

11. Electron microscopy of selected somp subfractions

Greatly differing electron densities of the organic and inorganic phases in somp's limits the usefulness of transmission electron microscopy in studying the morphology of somp's. In general, the organic phase cannot be clearly distinguished from mineral components (Chen and
Schnitzer, 1976), therefore the electron micrographs presented below are intended mainly to provide an overall impression of smp morphology.

The water-dispersible clay from Bashaw (Plate 1) reveals superimposed, crumpled membranes typical of smectites. Electron-dense particles (Plate 2) up to about 100 Å in diameter occur as clusters and seemingly also as surficial coatings on phyllosilicate particles in the >2.97 g/cc fraction of Jory B3. Particles of the same size and morphology have been reported by Greenland et al. (1968) in the clay fraction of Australian red earth soils. It is probable that these particles are microcrystalline goethite and hematite while the smaller subparticles in less electron-dense areas may represent less crystalline ferrihydritic phases (see also Figure 22).

The less than 1.7 g/cc subfraction of Quillayute (Plates 4 and 5) shows an abundance of amorphous gel coatings forming "bridges" between individual particles. Similar features have been reported for the clay fraction of Hawaiian soils (Jones and Uehara, 1973). In contrast, the >1.9 g/cc subfraction (Plate 6) of this soil is "cleaner" in appearance though not entirely free of amorphous coatings.

Particle coatings and interparticle bonding are also evident in the lightest Blacklock subfraction (Plates 7 and 8). The fibrous substructure of the coatings is ascribed to the organic phase (the fraction contains less than 12% of amorphous oxides, but 36% organic carbon). The organic matter to a large extent appears to be sorbed on mineral particles, though this may not be representative of its original condition in soil. As in Quillayute, the heaviest subfraction of Blacklock (Plate 10) consists of remarkably clean particles with well defined outlines and more crystalline in appearance. Plate 10 (carbon shadowed carbon replica) shows quartz particles after removal of organic matter and amorphous oxides; the dissolution treatment merely seems to have rounded the edges of clay-size quartz particles.
Plate 1: Electron micrographs of Bashaw, water-dispersible clay.
Plate 2: Electron micrograph of clay from Jory B3, >2.96 g/cc.

Plate 3: Electron micrograph of the >2.3 g/cc subfraction from Jory Al.
Plate 4: Electron micrographs of the <1.7 g/cc subfraction from Quillayute.
Plate 5: Electron micrograph of the <1.7 g/cc subfraction from Quillayute.
Plate 6: Electron micrographs of the >1.9 g/cc subfraction from Quillayute.
Plate 7: Electron micrographs of the <1.6 g/cc subfraction from Blacklock.
Plate 8: Electron micrograph of the <1.6 g/cc subfraction from Blacklock.

Plate 9: Electron micrograph of the >1.9 g/cc subfraction from Blacklock, amorphous oxides removed.
Plate 10: Electron micrographs of the >1.9 g/cc subfraction from Blacklock.
IV. DISCUSSION

1. Summary of results

Samples from surface and subsurface horizons of seven soils representing six different soil orders were fractionated by particle size (water-dispersible sand, silt and clay), and the clay-size organic-mineral particles (somp's) were further subfractionated by density using a newly devised surfactant-free method.

The distribution of somp density subfractions depended on the levels of organic matter and the nature and amounts of associated amorphous oxides. Broad density distributions were prominent in soil suborders (andepts, humult, aquod) known for their high contents of amorphous oxides and/or organic matter. The relative contents of amorphous oxides, organic matter, and microcrystalline Fe-oxides (ferrihydrates) also accounted for the observed overall densities (heavy in humult, light in andepts, intermediate in the others).

Specific pedogenetic conditions (e.g. vegetation, parent material, concretions) influenced the distribution and composition (organic carbon and nitrogen) of the organic matter in the granulometric fractions. The C/N ratios decreased with particle size.

Organic carbon and nitrogen decreased with increasing somp subfraction density; the C/N ratios narrowed somewhat sharply from the lightest to the next heavier fractions, then more gradually over the remaining subfractions. The alkali extractability of organic matter followed a trend similar to that of the C/N ratios, but increased with subfraction density. It was concluded that humification increased with subfraction density, and that the lightest fractions included admixtures of less humified material assumed to be sorbed rather than free although bonding may be relatively loose, perhaps predominantly physical.

Oxidative degradation (DTA under O₂) of the high organic matter subfractions resulted in two well-defined exotherms, one above (HTE) and one below (LTE, composite) 400°C. Variations in exotherm intensities
and peak temperatures with subfraction density were considered in terms of strength of organo-mineral bonding, metal-organic complexing, degree of humification and extent of interlamellar adsorption. Evidence of interlamellar adsorption of soil organic materials was obtained.

Amounts and composition of amorphous inorganic oxides in the density subfractions were assessed using a kinetic dissolution method. Amorphous Al and Si decreased with increasing subfraction density. The final slopes of the cumulative extraction curves appeared to be related to the susceptibility of smectite and chloritic intergrades to the dissolution treatment. The molar SiO$_2$/Al$_2$O$_3$ ratios of the amorphous oxides extracted from the subfractions ranged from 0.2 to 6.7, and reflected varying contributions of organically complexed Al, mineral composition, and weathering environment. Significant correlations between amorphous Al and organic carbon were observed.

The X-ray analysis of the somp density subfractions revealed gradual transitions from light poorly defined mineral matter to heavier more crystalline components. These transitions were particularly evident in the case of chloritic intergrades, frequently the dominant mineral component in the subfractions. The major matrix mineral in Quillayute, Blacklock and Mitaka was beidellite; in Jory, Woodburn and Madras the nature of the chloritic intergrade matrix could not be definitely ascertained, but smectite was suggested on the basis of stability towards selective dissolution.

Figure 32 summarizes the distribution of organic, amorphous inorganic and crystalline phases in somp subfractions.

Surface areas determined by nitrogen adsorption were very low in somp's and inversely correlated with organic carbon. After peroxidation the N$_2$-areas decrease with increasing subfraction density as do the areas determined by adsorption of water vapor before and after peroxidation. It was suspected that peroxidation modifies mineral surfaces by the release and adsorption of metals (Al, Fe) previously complexed by the organic phase. The Kelvin radii below 300 Å, calculated from nitrogen desorption isotherms, peaked within 20-24 Å.
Figure 32: The distribution of organic, amorphous inorganic and crystalline phases in smp subfractions.
The cation exchange capacities determined with neutral salt and at pH 8.2 also decreased with increasing subfraction density. The differences between the two values were significantly correlated with organic carbon.

The IR spectra of some subfractions failed to indicate major differences in the organic phases. This result was attributed to high attenuation of the somp organic matter in KBr pellets and to differing contents of organic carbon.

Electron microscopy of selected somp subfractions tended to confirm the results obtained by other methods. Light particles were heavily coated with amorphous gels, while heavier particles had well-defined clean outlines.

2. The organic and crystalline phases in somp's

For the purposes of this discussion it is immaterial whether the lightest subfractions contain admixtures of free partially humified organic matter. The removal of this component would merely straighten the low density end of the organic matter curves in Figure 32, but the variations of various properties (C/N ratios, extractability, OM-content) with subfraction density would remain. The "degree of humification" is a poorly defined term. Low C/N ratios, low apparent oxygen content, and more aromatic than aliphatic features are sometimes associated with a high degree of humification (Arshad and Lowe, 1966). The C/N ratios are useful indices in that they reflect the state of the organic phase reached through biological and perhaps abiological transformation of high C/N ratio plant material. Whether the variations of the C/N ratios in the subfractions represent continua in the degree of humification or increasing admixtures of less humified materials to a uniformly humified organic phase cannot be answered with certainty.

Inoue and Wada (1968) determined that allophane compared to montmorillonite preferentially adsorbed "darker" (higher molecular weight) components from extracts of humified clover. Thus in hypothetical
systems in which a mixture of humified (e.g. HA) and non-humified (e.g. polysaccharides) were allowed to react with clean smectite or amorphous oxides, two things are expected to occur: (1) the amorphous oxide would adsorb significantly greater amounts of organic carbon than smectite, and (2) the non-humified component would not be preferentially adsorbed by the amorphous oxide. In other words, given a soil with equally accessible mineral surfaces of varying crystallinity (such as in smp subfractions) preferential adsorption of less humified organic components by less crystalline mineral surfaces is not expected. Hence, the wider C/N ratios in lighter subfractions appear to arise from particular spatial relationships and existence of different microenvironments as outlined in Section IV.4.

It was not the objective of this study to explain clay mineral assemblies in the soils under consideration; additional data (parent material, composition of the soil solution, etc.) would be required for that purpose. However, the chloritic intergrades occurring in all soils except Bashaw present an interesting case. Thermodynamically, a single mineral occupies a certain stability niche which varies as a function of pH, drainage and other factors (Rai and Lindsay, 1975). If the point-to-point environment in a given soil horizon were uniform, wide variations in the properties of a single mineral would not be expected. The relatively continuous variation in the properties of chloritic intergrades is reminiscent of those exhibited by the organic and amorphous inorganic phases, and again seems to point to the existence of specific microenvironments.

In the case of minerals, the argument is complicated by additions of mineral matter from varying sources in the course of time, particularly through floods in alluvial soils (e.g. Quillayute). The question then arises whether the added materials are significantly different from those originally in the soil, and whether there was sufficient time to reach equilibrium in the new environment. This is an extremely complex problem; little is known about the rate of mineral formation and transformation in soils. However, since the same continua in the properties
of minerals were observed in Jory (formed from colluvium of a uniform source) and Blacklock (from marine beach sands), it is assumed that these variations indeed result from evolution in specific soil micro-environments.

3. Microaggregates in soils

The term microaggregates (MA) is used in accordance with Edwards and Bremner (1967), i.e. difficultly dispersible, roughly spherical particles, up to 250 μm in diameter, "consisting largely of clay and humified organic matter." Particles in that size range are also called microcrumbs or granules, and are considered as subunits of larger (up to 10 mm) soil crumbs (Russell, 1973).

The mean residence time of natural aggregates in soils before suffering severe disruption and reorganisation is not known. In soils providing a favorable environment for earthworms up to 5 mm of soil (in part derived from subsoils) may be deposited on the soil surface per year (Russell, 1973). Assuming that earthworms disrupt MA's (prior to reaggregation in casts), the minimum mean residence time of an MA in a surface horizon 20 cm thick would be 40 years. Wetting of dry aggregates and freezing must also be taken into account. Freezing is relatively rare in western Oregon; while freezing probably disrupts crumbs, it may not affect MA's. Wetting of dry crumbs in general leads to more or less slaking (i.e. MA-separation from the crumbs), but not dispersion (complete loss of structure) except in soils with a high Na-saturation (Emerson, 1967). Wetting may therefore not seriously affect the integrity of MA's in many soils.

The mean residence time of the organic phase in soils varies widely, ranging for example from 25 years for HA-hydrolysates (6N HCl) to about 1200 years for humins (Campbell et al., 1967). However, factors other than accessibility to microorganisms affect the $^{14}$C-ages of these materials, therefore aggregate mean residence times cannot be estimated from $^{14}$C-ages.
The available evidence, scant as it may be, points to an MA mean residence time of at least several decades, a period of time seemingly long enough to allow the organic, and probably also the inorganic phase, to achieve relative equilibrium within their microenvironments. Superimposed seasonal cycles provide the "raw material" and the driving force for these reactions and longer term aggregation-disaggregation processes in soils.

Studies on the porosity of natural aggregates (Quirk and Panabokke, 1962; Aylmore and Quirk, 1967) show that pores appear to be concentrated in three ranges: one at 20-50 Å (from interleaving of crystal units several unit layers thick; intradomain voids), another at 200 Å (also considered as intradomain space, Russell, 1973), and one around 1000 Å and above (interdomain porosity). About 70% of the total porosity in natural B horizon aggregates was due to pores less than 100 Å in diameter. Microorganisms are therefore excluded from spaces within MA's, while enzymes (longest dimension up to 150 Å; Lehninger, 1970) would appear to have partial access.

4. A tentative model for the structure and function of soil microaggregates

A microaggregate model is proposed in this section in an effort to account for the continua in composition and properties observed in some density subfractions. Following Edwards and Bremner (1967), the average diameter of such an aggregate would be about 250 μm or less. Microaggregates (MA's), arising from inherent aggregating forces of component particles, may represent stable, minimum-energy formations with upper limits in size dictated by physical-chemical and perhaps biological constraints. The model applies only to virgin, non-saline and non-alkaline surface material with a stable structure. The poorly aggregated Bh horizon of Blacklock, though it shows similar continua, is excluded at this point. Also excluded are soils such as Bashaw with special pedogentic processes (self-churning) affecting "normal" aggregation
processes. Cultivated soils are excluded because of possible aggregate
disruption from application of machinery, loss of organic matter (e.g. 
up to 40% less N in cultivated soils than in their virgin counterparts; 
Keeney and Bremner, 1964), and disruption of microbial and faunal ecology 
from the application of pesticides. However, it is estimated that 
microaggregate structures as described below are at least residually 
present in cultivated soils.

For convenience, the model considers only isolated spherical MA's. 
It should be kept in mind, however, that aggregating interactions of 
microaggregates and coarser silt- and sand-size particles provide for 
endless configurative and microenvironmental variations.

The model simply proposes that heavier somp's are preferentially 
located in the core of spherical microaggregates, while lighter somp's 
tend to occupy peripheral positions. A component particle may have a 
history of surface exposure and core protection, but it is assumed 
that in general relocations are sufficiently apart in time to allow 
the particle to assume the properties characteristic of its location.

The model appears to account for the continua observed in the data 
of this study. A peripheral particle, continually exposed to the 
activity of the soil biosphere, quite likely accumulates an organic phase 
with a high C/N ratio. The organic materials are subject to both 
biological and surface catalysed transformations. The mineral component 
of peripheral particles absorbs the major impact of biologically 
produced weathering agents (protons, short chain organic acids, chelates), 
here particles would tend to be small, and their lattice integrity would 
suffer. Lattice disintegration together with the release of metal 
cations (Fe, Al) from microbially decomposed metal-organic complexes 
would precipitate maximum amounts of amorphous oxides in peripheral areas. 
In short, typical low density somp's would evolve at the periphery.

In contrast, the core microenvironment of an MA is comparatively 
sheltered. Exoenzymes may reach and transform parts of the organic 
phase of a core particle. If significant transformations of the organic 
phase do occur, it is probable that reactions catalyzed by mineral
surfaces play an important role; the nature and extent of such reactions in soils is largely unknown (see Section 1.3). It is unlikely that significant amounts of larger, partially humified organic materials ever reach the interior of stable, undisturbed MA's.

The effects of peripheral biological activity reach the interior in a modified and deamplified way. An important and complex question arises, namely what kind of intra-aggregate transfers of material are likely to occur and in what direction? The types of the transfers are expected to differ depending on the nature of drainage, i.e. the average annual frequency distribution of water saturation states.

Transfers and gradients undoubtedly occur. For example, the hydrogen ion activity may be lower in the interior, as the core generates limited amounts of acidity, if any. Metal ions and silica in the interior may be less subject to loss by leaching. There may be transfers of metal ions from the periphery to the core via chelates. During periods of strong leaching, losses from the interior would preferentially affect the amorphous inorganic phase. Phenomena of this kind could be conducive to the neoformation of phyllosilicates.

Unfortunately, the variability of short term soil conditions (e.g. OM decomposition "flushes" after wetting of dry soil, water saturation, ionic strength of the soil solution, pH, plant uptake, etc.) makes the inference of predominant intra-aggregate transport processes sketchy. But, eventually a given MA would be disrupted by some external agent and its component particles would randomly re-aggregate. A larger heavy particle from the core (a secondary clay mineral) may then occupy a peripheral position where, in time, it would suffer lattice disintegration and a decrease in size; it would adsorb additional organic matter (high C/N ratio) and accumulate amorphous oxides as stated above.

Conversely, an originally peripheral particle may end up in the "core" of a newly formed MA. Compared to its former position, addition/production of organic matter is now limited to smaller molecules able to reach the interior by diffusion. Among these molecules are probably exoenzymes of microbial origin which would tend to diminish easily
decomposable organic components such as carbohydrates. In the absence of strong organic matter turnover, minerally catalyzed reactions are expected to contribute to the transformation of the organic phase. From all accounts, such reactions do occur in soil, but little, if anything, is known in detail; hence it is difficult to infer with any degree of certainty the main effects on the organic phase.

Enlargement and improvement of crystallinity of smaller, previously peripheral particles, and even formation of new clay mineral platelets using existing mineral surfaces as templates, is more plausible in the light of recent findings on kaolinite synthesis (Linares and Huertas, 1971; Hem and Lind, 1974). In fact, the presence of the organic phase and of small metal-organic complexes in solution may be essential for these reactions.

The implications of the proposed MA-structure concern first of all soil aggregation. If MA's are indeed stable and persistent for relatively long periods of time, the properties of MA-surfaces would be crucial in determining the stability of larger aggregates such as crumbs. Similarly, plant-soil interactions would tend to be dominated by the properties of MA-surfaces. Little can be said at this point on the effects of MA's on organic matter transformation and turnover. However, microaggregates may have a significant influence on mineral transformations as proposed in the following hypothesis. The equilibrium between amorphous and crystalline inorganic phases may shift depending on location within a microaggregate (toward crystalline particles in the interior, and toward amorphous phases at the periphery), perhaps with the soil biosphere providing the weathering agents and the organic phase controlling to some extent crystallization. If, in addition, longer term aggregation-disaggregation cycles are superimposed over the mineral equilibria, a mechanism through which the soil rejuvenates its mineral phase and prevents the rapid degradation of permanent charge into variable charge, is provided.

It appears that a good test for the structure of MA's as proposed in this section would be to embed soil MA's in an N-free resin, grind
the blocks to expose cross-sections, and examine the cross-section with an electron microprobe (i.e. distribution of Al, Si, Fe, N). Possibly, such preparations could also be etched by various reagents and then viewed in a scanning electron microscope.

Alternatively, MA's could be prepared with well-defined clay minerals and subjected to weathering cycles through additions of organic materials, microorganisms and variations in temperature and water saturation.

As a rule, soil structure is considered for purposes of soil classification and genesis and soil physics (transmission of water and gases, consistency, plasticity, etc.). The proposed model implies that MA's, in some soils, may be the sites and provide the conditions necessary for important pedochemical processes.
BIBLIOGRAPHY


Ségalen, P. Note sur une méthode de détermination des produits minéraux amorphes dans certains sols à hydroxides tropicaux. Cah. ORSTOM, Série pédol. 1:105-126. 1968.


APPENDIX I

SAMPLING LOCATIONS AND PROFILE DESCRIPTIONS
Quillayute Silt Loam

Location: SW 1/4, NW 1/4, Sec. 13, T. 1S., R. 10 W., 110' north of farm road, 100' east of point where road joins Wilson River.


Climate: Mean annual temperature (MAT) 10°C; mean annual precipitation (MAP) 230 cm.

Parent material: Old alluvium from mixed igneous and sedimentary rocks.

Topography: Nearly level stream terraces.

Vegetation: Brackenfern, bursh, grasses.

Drainage: Well-drained.

Land use: Improved pasture, hay, urban.

Classification: Hydric Dystrandept; Thixotropic, mesic.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alp</td>
<td>0-20</td>
<td>Black (10YR2/1) silt loam; moderate fine and very fine subangular blocky structure that breaks to strong, very fine granular structure; friable, slightly sticky, slightly plastic; many roots, many very fine tubular and interstitial pores; medium acid (pH 5.6); clear smooth boundary.</td>
</tr>
<tr>
<td>A12</td>
<td>20-48</td>
<td>Black (10YR2/1) silt loam; weak fine and very fine subangular blocky structure that breaks to strong very fine granular structure; friable, slightly sticky, slightly plastic; many roots; many fine tubular and interstitial pores; very strongly acid (pH 5.0); clear wavy boundary.</td>
</tr>
<tr>
<td>A31</td>
<td>48-63</td>
<td>Black (10YR2/1) silty clay loam; weak fine and very fine subangular blocky structure that breaks to strong very fine granular structure; friable, sticky, plastic; many roots; many very fine tubular pores; strongly acid (pH 5.2); gradual smooth boundary.</td>
</tr>
</tbody>
</table>
Quillayute Silt Loam (Continued)

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A32</td>
<td>63-83</td>
<td>Very dark grayish brown (10YR3/2) silty clay loam; weak very fine subangular blocky structure; friable, sticky, plastic; common roots; many very fine tubular pores; strongly acid (pH 5.2); clear wavy boundary.</td>
</tr>
<tr>
<td>B2</td>
<td>83-110+</td>
<td>Dark yellowish brown (10YR4/4) silty clay loam; moderate very fine and weak fine subangular blocky structure; friable, sticky, plastic; few roots; many very fine tubular pores; strongly acid (pH 5.4).</td>
</tr>
</tbody>
</table>
Jory Clay Loam

Location: Benton County, Oregon. SE corner of Sec. 4, T. 11 S., R. 5 W. in the McDonald Forest, about 300 feet SE of the road intersection at Lewisberg Saddle.


Description by E. G. Knox.

Climate: MAT 12°C; MAP 140 cm.

Parent material: Colluvium from sedimentary and basic igneous rocks.

Topography: Higher rolling uplands bordering steeper mountainous areas. Elevation: 400-1200 ft.

Vegetation: Douglas fir, grand fir, Oregon white oak, poison oak, snowberry grasses and ferns.

Drainage: Well-drained.

Land use: Small grain, grass seed, hay, timber production, recreation, water supply, wildlife habitat.

Classification: Xeric Haplohumult; clayey, mixed, mesic.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0-10</td>
<td>Dark reddish brown (5YR3/3 dry, 5YR2/2 moist), clay loam; strong medium to very fine granular structure; very friable, slightly sticky, slightly plastic; common fine spherical pellets (shot) in the top inch, few below; abundant roots; pH 6.0 (Chlorphenol red); lower boundary smooth and clear.</td>
</tr>
<tr>
<td>A3</td>
<td>10-22</td>
<td>Dark reddish brown (5YR3/2 dry, 5YR2/2 moist) clay loam; strong medium subangular blocky breaking to moderate fine and very fine subangular blocky breaking to moderate fine granular structure; friable, slightly sticky, slightly plastic; few fine spherical pellets; abundant roots; lower boundary smooth and clear.</td>
</tr>
<tr>
<td>Horizon</td>
<td>Depth (cm)</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>B21</td>
<td>35-51</td>
<td>Reddish brown (2.5YR4/4 dry), dark reddish brown (2.5YR3/4 moist) clay; moderate fine and very fine angular blocky structure; friable, plastic, sticky; thin continuous clay flows, roots common; pH 5.6 (chlorphenol red); lower boundary smooth and gradual.</td>
</tr>
<tr>
<td>B22</td>
<td>51-72</td>
<td>Reddish brown (2.5YR 4/4 dry), dark reddish brown (2.5YR3/4 moist) clay; moderate fine angular blocky structure; friable, sticky, plastic; thin continuous clay flows; common roots; pH 5.4 (chlorphenol red); lower boundary smooth and gradual.</td>
</tr>
<tr>
<td>B3</td>
<td>72-110</td>
<td>Red (2.5YR4/6 dry), dark reddish brown (2.5YR3/4 moist) clay; moderate medium and fine angular blocky structure; friable, sticky, plastic, thin continous clay flows; few black (MnO₂) splotches; few basalt fragments; few roots; pH 5.4 (chlorphenol red); lower boundary smooth and gradual.</td>
</tr>
<tr>
<td>B3 Dr</td>
<td>110-130</td>
<td>Red (2.5YR4/8 dry), dark red (2.5YR3/6 moist) clay; moderate medium and fine angular blocky structure; friable, slightly plastic, slightly sticky; common thin patchy clay flows; abundant basalt fragments (about 50% by volume) pH 5.4 (chlorphenol red).</td>
</tr>
</tbody>
</table>
Blacklock Fine Sandy Loam

Location: Coos County, Oregon. About 8 km (5 miles) north of Bandon, Oregon; 33 m (100 feet) north, 570 m (1750 feet) east of the southwest corner, Section 33, T. 27 S., R. 14 W., W.M. About 10 m (30 feet) west of the paved edge of Seven Devils Road, west of U.S. 101, Lot 7 of Pacific Riviera No. 2. Photo COB-4HH-68.


Climate: MAT 11°C; MAP 135 cm.

Parent material: Marine beach sands, aeolian deposits, organic matter.

Topography: Level to concave marine terrace; elevation: 160 ft.

Vegetation: Huckleberry, rhododendron, western red cedar, shore pine, madrone.

Drainage: Very poorly drained.

Land use: Formerly brush and wildlife; presently homesites.

Classification: Typic Sideraquod; sandy, ortstein, mixed, mesic.

Source: Personal communication, R. J. Kienzle, SCS, Bandon, Oregon.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>3-0</td>
<td>Litter of leaves, twigs, decomposed material, root mat, and moss; abrupt, smooth boundary.</td>
</tr>
<tr>
<td>A1</td>
<td>0-8</td>
<td>Black (10YR2/1) fine sandy loam, dark gray (10YR 4/1) when dry; massive; soft, very friable, non-sticky and nonplastic; many, very fine and fine roots; common, very fine and fine, tubular pores; extremely acid (pH 4.4); abrupt, smooth boundary.</td>
</tr>
<tr>
<td>A21</td>
<td>8-23</td>
<td>Very dark gray (10YR3/1) fine sandy loam, gray (10YR6/1) when dry; massive; hard, friable, non-sticky and nonplastic; many, very fine to medium roots; few, very fine and fine, tubular pores; extremely acid (pH 4.4); abrupt, wavy boundary.</td>
</tr>
<tr>
<td>Horizon</td>
<td>Depth (cm)</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>A22</td>
<td>23-33</td>
<td>Gray (10YR6/1) fine sandy loam, white (N 8/ ) when dry, with dark grayish-brown (10YR4/2) exped staining, gray (10YR6/1) when dry; massive; hard, friable, nonsticky and nonplastic; many, very fine to medium roots; few, very fine and fine, tubular pores; very strongly acid (pH 4.6); abrupt, wavy boundary.</td>
</tr>
<tr>
<td>B21h</td>
<td>33-38</td>
<td>Black (5YR2.5/1) organic loam, dark reddish gray (5YR4/2) when dry; massive; slightly hard, friable, nonsticky and nonplastic; many, very fine to coarse roots; common, very fine and fine, tubular pores; extremely acid (pH 4.4); abrupt, wavy boundary.</td>
</tr>
<tr>
<td>B22ir</td>
<td>38-53</td>
<td>Strong brown (7.5YR5/6) strongly cemented sands, yellowish brown (10YR5/6) when dry; massive; extremely hard, extremely firm, nonsticky and nonplastic; very few, very fine, flattened roots; very few, very fine, tubular pores; medium acid (pH 5.6); clear, wavy boundary.</td>
</tr>
<tr>
<td>B23ir</td>
<td>53-84</td>
<td>Yellowish-brown (10YR5/4) strongly cemented sands, yellowish brown (10YR5/6) when dry, reddish-brown (5YR4/4) and dark red (2.5YR3/6) stains and seams in the hardpan, brown (7.5YR4/4) and yellowish red (5YR5/6) when dry; massive; extremely hard, extremely firm, nonsticky and nonplastic; very few, very fine roots in horizontal root mats; very few, very fine, tubular pores; medium acid (pH 5.6); clear, wavy boundary.</td>
</tr>
<tr>
<td>B3ir</td>
<td>84-132</td>
<td>Yellowish-brown (10YR5/6) strongly cemented sands, very pale brown (10YR7/4) when dry, with strong brown (7.5YR5/6) streaks; massive; very hard, very firm, nonsticky and nonplastic; very few, very fine roots in horizontal root mats; very few, very fine, tubular pores; medium acid (pH 5.8); clear, wavy boundary.</td>
</tr>
<tr>
<td>C1</td>
<td>132-178</td>
<td>Light, olive brown (2.5YR5/6) sand with red (2.5 YR4/6) stains or lenses; massive, friable (sort of brittle); nonsticky and nonplastic; medium acid (pH 5.8); gradual, wavy boundary.</td>
</tr>
<tr>
<td>C2</td>
<td>178-190</td>
<td>Variegated sand averaging light, olive brown (2.5Y 5/4) with few, fine, distinct brown (7.5YR4/4) stains; massive; very friable (sort of brittle), nonsticky and nonplastic; medium acid (pH 5.8).</td>
</tr>
</tbody>
</table>
Woodburn Silt Loam

Location: NW 1/4, NW 1/4, Sec. 9, T. 11 S., R. 4W., Hyslop Agronomy Experimental Farm.


Parent material: Silty alluvium.

Topography: Broad terraces above Willamette River floodplain; elevation: 200-300 ft.

Vegetation: Grasses, hazelnut, poison oak, blackberry, Douglas fir, Oregon white oak.

Drainage: Moderately well-drained.

Land use: Pasture, hay, small grain, vegetable crops, orchards, grass seed, berries, wildlife, recreation.

Classification: Aquultic Argixeroll; fine-silty, mixed, mesic.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ap</td>
<td>0-24</td>
<td>Very dark brown (10YR2/2) silt loam; moderate very fine subangular blocky structure; friable, slightly sticky, slightly plastic; many roots; many very fine and few medium and coarse tubular pores; slightly acid; abrupt smooth boundary.</td>
</tr>
<tr>
<td>Al2</td>
<td>24-42</td>
<td>Dark brown (10YR2/2) silty clay loam; moderate fine and very fine subangular blocky structure; friable, sticky, plastic; many roots; many very fine and few medium tubular pores; slightly acid; clear smooth boundary.</td>
</tr>
<tr>
<td>Bl</td>
<td>42-62</td>
<td>Dark brown (10YR3/3) silty clay loam; moderate fine subangular blocky structure that parts to weak very fine subangular blocky structure; friable, sticky, plastic common roots; many very fine and few medium and coarse tubular pores; few mottles; few scattered thin clay skins; slightly acid; clear smooth boundary.</td>
</tr>
<tr>
<td>Horizon</td>
<td>Depth (cm)</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>B2t</td>
<td>62-95</td>
<td>Dark yellowish brown (10YR4/4) silty clay loam; moderate very coarse prismatic structure that parts to moderate coarse subangular blocky structure; firm, sticky, plastic; common roots; few medium tubular pores; common very fine tubular pores; prominent medium clay skins; common medium distinct mottles, dark yellowish brown (10YR3/4) when moist; slightly acid; gradual smooth boundary.</td>
</tr>
<tr>
<td>B35</td>
<td>95-125</td>
<td>Yellowish brown (10YR5/4) silty clay; weak very coarse prismatic structure that breaks to weak very coarse subangular blocky structure; firm, sticky, plastic; few roots; few medium, and common very fine tubular pores; prominent medium clay skins; slightly acid.</td>
</tr>
</tbody>
</table>
Bashaw Clay

Location: SW 1/4, SE 1/4, Sec. 7, T. 11 S., R. 4 W., 5 miles NE of Corvallis.


Climate: MAT 10–12°C; MAP 100–150 cm.

Parent material: Recent alluvium from material of mixed mineralogy.

Topography: Level to depressional on alluvial bottomlands; elevation: 200–300 ft.

Vegetation: Ash, Oregon white oak, wild rose, poison oak, rushes, sedges, grasses.

Drainage: Poorly drained.

Land use: Spring grain, hay, pasture, wildlife.

Classification: Typic Pelloxerert; very fine, montmorillonitic, mesic.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ap</td>
<td>0–13</td>
<td>Black (10YR 2/1) clay, very dark gray (10YR 3/1) dry; strong, fine, subangular blocky structure; very hard, firm, very sticky and very plastic; many very fine roots; many fine interstitial pores; medium acid; clear, smooth boundary.</td>
</tr>
<tr>
<td>A12</td>
<td>13–28</td>
<td>Black (10YR 2/1) clay, very dark gray (10YR 3/1) dry; moderate, fine and medium, angular blocky structure; very hard, very firm, very sticky and very plastic; common very fine roots; common very fine pores; slightly acid; clear, smooth boundary.</td>
</tr>
<tr>
<td>AC1</td>
<td>28–74</td>
<td>Black (10YR 2/1) clay, very dark gray (10YR 3/1) dry; massive with many wedge-shaped aggregates and intersecting slickensides; very hard, very firm, very sticky and very plastic; few roots; many very fine pores; slightly acid; clear, smooth boundary.</td>
</tr>
<tr>
<td>AC2</td>
<td>74–102</td>
<td>Black (10YR 2/1) clay, dark gray (10YR 4/1) dry; massive with many wedge-shaped aggregates and intersecting slickensides; very hard, very firm, very sticky and very plastic; few very fine roots; common very fine pores; many slickensides; neutral; clear, wavy boundary.</td>
</tr>
<tr>
<td>Horizon</td>
<td>Depth (cm)</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>C1</td>
<td>102-116</td>
<td>Very dark gray (10YR 3/1) clay, dark gray (10YR 4/1) dry; massive with many, fine, wedge-shaped aggregates and many intersecting slickensides; very hard, firm, very sticky and very plastic; no roots; few very fine pores; neutral; clear, smooth boundary.</td>
</tr>
<tr>
<td>C2</td>
<td>116-152</td>
<td>Dark-gray (5Y 4/1) silty clay, gray (10YR 5/1) dry; common, medium, distinct, dark-brown (7.5YR 4/4) mottles; massive with many, fine, wedge-shaped aggregates and many intersecting slickensides; very hard, firm, very sticky and very plastic; no roots; few very fine pores; neutral.</td>
</tr>
</tbody>
</table>
Madras Loam

Location: Agency Plains, Jack Root farm; 180 ft N of hedge of field (SE corner).

Sampling and description: Dr. G. Kling, July 2, 1974.

Climate: MAP 20-25 cm.

Parent material: Residuum from underlying pumiceous and tuffaceous sandstone and conglomerate, small admixtures of fine pumice, volcanic ash, and loess.

Topography: Level to somewhat rolling upland plains.

Vegetation: Big sagebrush, bunchgrasses, rabbitbrush, annual grasses, juniper.

Drainage: Moderately well-drained, hardpan in subsoil.

Land use: Formerly dry farmed; presently irrigated, alfalfa, potatoes, oats, barley, wheat.

Classification: Xerollic Durargid; fine-loamy, mixed, mesic.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ap</td>
<td>0-8</td>
<td>Very dark grayish brown (10 YR 3/2) loam; weak medium subangular blocky structure; very friable; neutral; clear boundary.</td>
</tr>
<tr>
<td>Bl</td>
<td>8-26</td>
<td>Dark grayish brown (10YR 4/2) heavy loam; moderate medium subangular blocky structure; firm; slightly alkaline; a-rupt boundary.</td>
</tr>
</tbody>
</table>
APPENDIX II

X-RAY DIFFRACTION PATTERN OF SOIL ORGANIC-MINERAL DENSITY SUBFRACTIONS
Figure 1a: X-Ray diffractograms of untreated smp subfractions from Quillayute.
Figure 1b: X-ray diffractograms of untreated smp subfractions from Quillayute.
Figure 1c: X-Ray diffractograms of sump subfraction from Quillayute after removal of amorphous oxides.
Figure 1d: X-Ray diffractograms of some subfractions from Quillayute after removal of amorphous oxides.
Figure 2a: X-Ray diffractograms of untreated smp subfractions from Jory.
Figure 2b: X-Ray diffractograms of untreated smp subfractions from Jory.
Figure 2c: X-Ray diffractograms of samp subfraccions from Jory after removal of amorphous oxides.
Figure 2d: X-ray diffractograms of some subfractions from Jory after removal of amorphous oxides.
Mg-saturated 54% rel. humidity

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>1.6-1.7</th>
<th>1.7-1.8</th>
<th>1.8-1.9</th>
<th>&gt;1.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>7</td>
<td>10</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3a: X-Ray diffractograms of untreated sOMP subfractions from Blacklock.
Figure 3b: X-Ray diffractograms of untreated smp subfractions from Blacklock.
Figure 3c: X-Ray diffractograms of untreated somp subfractions from Blacklock.
Figure 3d: X-Ray diffractograms of untreated somp subfractions from Blacklock.
Figure 3e: X-Ray diffractograms of some subfractions from Blacklock after removal of amorphous oxides.
Mg-saturated Ethylene Glycol

Figure 3f: X-Ray diffractograms of untreated smp subfractions from Blacklock.
Figure 3g: X-Ray diffractograms of somp subfractions from Blacklock after removal of amorphous oxides.
Figure 4a: X-Ray diffractograms of somp subfractions from Mitaka after removal of amorphous oxides.
Figure 4b: X-Ray diffractograms of scmp subfractions from Mitaka after removal of amorphous oxides.
Figure 5a: X-Ray diffractograms of untreated smp subfractions from Woodburn.
Figure 5b: X-Ray diffractograms of untreated somp subfractions from Woodburn.
Figure 5c: X-Ray diffractograms of some subfractions from Woodburn after removal of amorphous oxides.
Figure 5d: X-Ray diffractograms of some subfractions from Woodburn after removal of amorphous oxides.
Figure 6a: X-Ray diffractograms of untreated smp subfractions from Bashaw.
Figure 6b: X-Ray diffractograms of untreated somp subfractions from Bashaw.
Mg-saturated
54% rel. humidity

Density (g/cc)
<1.95
>1.95

Mg-saturated
Glycerol

Density (g/cc)
<1.95
>1.95

Mg-saturated
Ethylene Glycol

Density (g/cc)
<1.95

Figure 6c: X-Ray diffractograms of smp subfractions from Bashaw after removal of amorphous oxides.
Figure 6d: X-Ray diffractograms of somp subfractions from Bashaw after removal of amorphous oxides.
Figure 7a: X-Ray diffractograms of untreated sump subfractions from Madras.
Figure 7b: X-Ray diffractograms of untreated sarp subfractions from Madras.
Mg-saturated
54% rel. humidity

Figure 7c: X-Ray diffractograms of some subfractions from Madras after removal of amorphous oxides.
Figure 7d: X-Ray diffractograms of smp subfractions from Madras after removal of amorphous oxides.