AN ABSTRACT OF THE THESIS OF

Scott R. Stewart for the degree of Doctor of Philosophy in Soil Science presented on March, 1997. Title: Origin and Age of Fe-Mn-P Concretions and Nodules in an Oregon Wetland

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Wetland soils with complex stratigraphy and redoximorphic features occur on the margin of the Willamette Valley, Oregon. In the Jackson-Frazier wetland, vertisols show three distinct stratigraphic units that rest uncomformably upon each other and correspond to the Bashaw series Bss, 2Bt and 3BC horizons. Holocene alluvium deposited as distal alluvial fan sediment overlies partially eroded valley floor lake deposits (Willamette formation) and is mineralogically distinct from the lower two strata. Fe-Mn concretions differ among horizons in distribution, morphology, mineralogy and chemistry. Pressure oriented clays coat the exterior of the Bss and 2Bt concretions; low porosity, stable isotopic composition and subtle differences in mineralogy appear to indicate an early onset of formation and a long-term protected weathering environment within the concretions and 3BC nodules. Photomicroscopy provides evidence that despite distinct, sharp boundaries the concretions/nodules began forming in their current location after the transport and mixing of materials with disparate provenance. The concretions/nodules are enriched in Fe and P, relative to the matrix soil, by as much as an order of magnitude. Mn enrichment can exceed two orders of magnitude. During the reduced phase of the annual redox cycle, concentration values for dissolved and KCl/HCl-Fe^{+2} are in the range of 40-60

and 500-6000mgFe^{+2}kg^{-1}soil, respectively, and are sufficient to support Bss concretion formation within the known age of the associated geomorphic surface. Comparing the age of the concretion-C^{14} and the stratum in which the concretions are formed, places the larger, older Bss concretions between 1500-3300y old. The amount of Fe+2 available in the reduced-soil phase compared to the degree of Fe$_{DCB}$ enrichment within the concretions suggests 2300-3500y for this enrichment to occur, with an average near 2800y. Some of the 3BC nodules may be near 38ky of age while the 2Bt concretions must be between 3.3ky and 15ky. The Bss-2Bt concretions and 3BC nodules appear to be currently forming in situ as a function of climate, redox and local valley stratigraphy.

Origin and Age of Fe-Mn-P Concretions and Nodules in an Oregon Wetland

by

Scott R. Stewart

A THESIS

submitted to

Oregon State University

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the requirements for the
degree of

Doctor of Philosophy

Completed March 31, 1997
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CONTRIBUTION OF AUTHORS

Dr. Reed Glassmann assisted in the mineralogical, photomicroscopy, and SEM characterization of concretions and nodules and the writing of this manuscript. Chemical analysis were performed in the soil chemistry laboratory under the supervision of Dr. John Baham who assisted in the analysis and interpretation of the chemical data. Dr. Herb Huddleston assisted in sample collection, the interpretation of data and the writing of this manuscript. David D'Amore installed the monitoring equipment in the Jackson-Frazier wetland and provided data and ideas.

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Chapter I.

Description of Study Area and Sampling Methodology

Soil strata were sampled within the Jackson-Frazier (J-F) wetland to separate and characterize redoximorphic concentrations - ie concretions and nodules. Concretions and nodules were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), polarizing microscope photography, and wet chemistry techniques to: i) determine their origin, ii) estimate their age and rate of formation, iii) decipher their history and the history of their location, iv) relate these features to field monitoring observations and, v) increase understanding of wetland functions on a more fundamental level.

The J-F wetland lies on the western margin of the Willamette Valley immediately east of highway 99W in northeast Corvallis, Benton County, Oregon (Fig. 1-1). The wetland is 64 hectares of shrub-scrub, forested and prairie palustrine plant communities on Holocene alluvial fan/valley fill material (Marshall, 1985; D'Amore, 1995) and ranges from 65m elevation in the southeast to 68m in the northwest (D'Amore, 1995). The wetland receives an average of 115 cm of rain per year, while the adjacent foothills receive slightly more. Ambient temperatures average 3°C in January and 18°C in July. The J-F wetland receives overland and subsurface flow, and the soil profile becomes saturated from both the top and the bottom of the profile. Much of the surface of the wetland can be ponded for up to 10 months per annum. The wetland is drained by Stewart slough to the southeast and a ditch from Frazier Creek which drains to the northeast.

The stratigraphy of the JF wetland consists of Holocene alluvium deposited over a clayey stratum that lies unconformably upon silty sediments of Pleistocene age (Fig. 1-2).
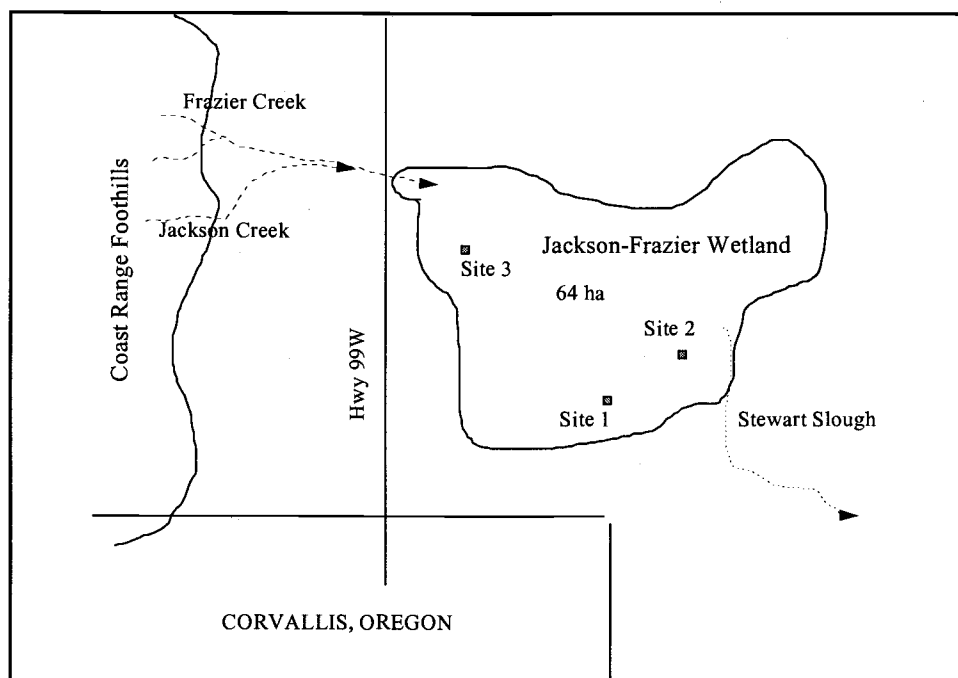
Figure 1-1. Location of study area and sampling sites.
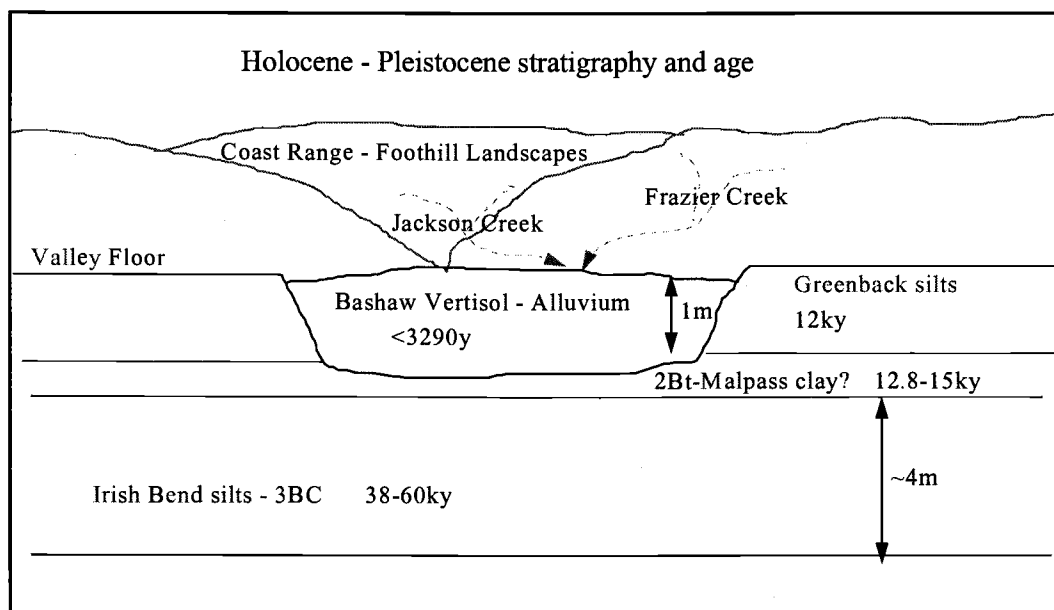
Figure 1-2. Jackson-Frazier wetland stratigraphy and ages.

The Holocene alluvium has been transported via Jackson and Frazier creeks which drain Fe-rich Ultisols overlying Fe-Mn rich alkalic and tholeiitic basalt parent materials of the Eocene Siletz River volcanics in the foothills of the Coast Range (Snavelly et al., 1968; Glasmann and Simonson, 1985). The J-F alluvium contains most of the secondary minerals identified as alteration products of these basalts (Glasmann and Simonson, 1985).

Complex Willamette Valley stratigraphy and geomorphology has resulted from catastrophic Pleistocene floods (Bretz, 1969), and the resulting alluvium (Willamette formation) has been divided into distinct stratigraphic units by Balster and Parsons (1969). At the Corvallis location the lowest and oldest unit is the Irish Bend (IB) member (Bashaw 3BC and 3C horizons) of the Willamette formation (38,410 ± 3,450y, Glenn, 1965; 40-60 ka, Reckendorf, 1992). This unit consists of "faintly bedded, micaceous, silty sediments with well defined upper and lower boundaries" and may be 4m thick at the J-F location (Balster and Parsons, 1969). It is unclear if the 2Bt silty clay horizon is the Malpass member of the Willamette formation or reworked IB materials. The Malpass is thought to be a distinct depositional unit between 12-34ky of age. More recently, Reckendorf (1992) states that the Malpass Member is "derived from multiple sources, with the predominant source being commingled Bonneville Flood (15ka to 14ka) and Bretz Flood (15ka to 12.8ka) sediment" and "appears to have been deposited in depressions or drainage ways". These "lake sediments are likely to reflect a large organic rich phosphorus sink because of sediment contributions from the surrounding landscape to the lake".

The uppermost member of the Willamette formation is the Greenback, which is "composed predominantly of silt-size quartz and feldspars with a significant content of coarse and sand-size iron-manganese oxide nodules near the base of the unit" (Balster and Parsons, 1969). Based on clay mineralogy the Greenback member appears to be absent within the J-F wetland.

The J-F wetland occurs on the Ingram geomorphic surface (555±100y - 3,290±120y) (Balster and Parsons 1968; Parsons and Herriman,1969). This surface is the highest of the two Willamette River floodplains and its major

tributaries. Topography is typically "undulating corrugations, with a maximum relief of 2.5m, produced by overbank channeling" (Parsons et al., 1970). The next older surface is the Winkle, which consists of abandoned flood plains with little relief, "subparallel corrugations of bar and swale topography of old channels". The youngest age for this surface is 5,250 ± 270y and it is concluded that the "change in stream systems that produced the abandoning of the Winkle surface was between 3,290 and 5,250 years ago" (Parsons et al.,1970).

The soil series identified within the wetland are the endosaturated Bashaw (very fine, montmorillonitic, mesic, Typic Endoaquert) and Cove series (Fine montmorillonitic, mesic, Vertic Haplaquolls). Only the Bashaw sites were sampled due to year-long wetness at the Cove site. At site 1 the Bashaw Bss horizons begin at 15-20cm and show a clear, smooth boundary with the 2Bt at 110cm, which has an abrupt, smooth contact with the 3BC at about 135cm (Fig. 1-3). The Bashaw profile is shallower at site 2 with the Bss-2Bt contact at about 80cm and the 2Bt-3BC contact at 100cm.

The vegetation at site one is dominated by water parsley (*Oenanthe sarmentosa*), with small amounts of reed canary grass (*Phalaris arundinacea*). The monitoring equipment at site two is placed in sloughsedge (*Carexobnupta*) which is bordered by cattail (*Typha latifolia*).

Bashaw Vertisol Profile

A1
Bss1
Bss2   ~1m
Bss3
2Bt
3BC - Irish Bend silts

~4m at this location
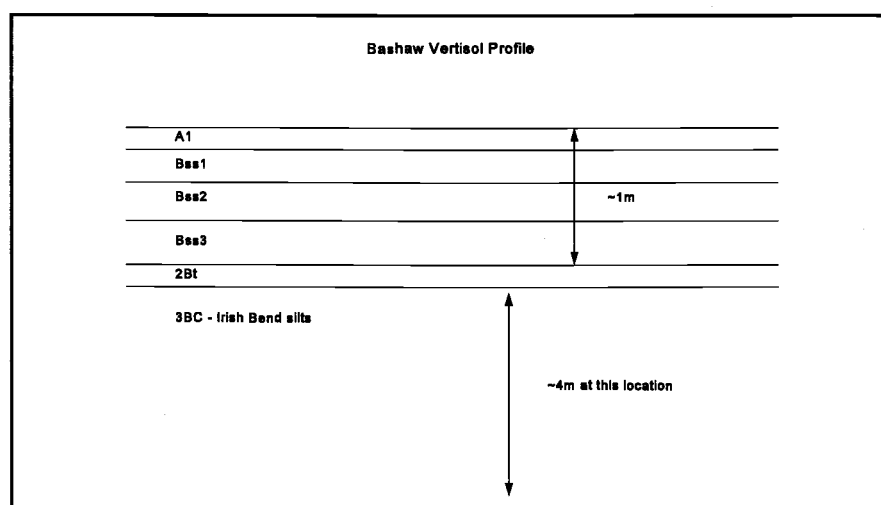
Figure 1-3. Bashaw series soil profile

Sampling Methods

Two sites were selected for detailed sampling and monitoring to provide large amounts of soil material for a variety of chemical, mineralogical, and physical analyses (Fig. 1-1). Soil pits were excavated to a depth of 2m at sites 1 and 2 in the Bashaw vertisol. The exposed faces of the Bss, 2Bt and 3BC horizons were sampled extensively (30-40kg soil/horizon) to provide large amounts of nodule and concretion-rich material. The Bashaw Bss was sampled in the upper, middle and lower parts of the horizon; the 2Bt and the upper part of the Irish Bend unit were sampled with no divisions. The horizons were not sampled at their vertical boundaries to avoid the possibility of sampling mixed materials. Sub-samples were dried, weighed and then dispersed by shaking overnight in Na-hexametaphosphate or $0.1\underline{N}$ Na_2CO_3. The sand and gravel fraction was separated by wet sieving and then dried and weighed. The amount of concretions/nodules (by weight and volume) was then determined after magnetic separation. Concretion/nodule densities were obtained by weighing, coating with liquid saran, and measuring the volume of H_2O displaced.

LITERATURE CITED

Balster, C. A. and R. B. Parsons. 1968. Geomorphology and Soils, Willamette Valley, Oregon. Or. Agric. Exp. Stn. Spec. Rep.265.

Balster, C. A. and R. B. Parsons. 1969. Late Pleistocene Stratigraphy, Southern Willamette Valley, Oregon. Northwest Sci. 43:116-129.

Bretz, J. H. 1969. The Lake Missoula Floods and the Channeled Scabland. J. of Geology. 77:505--543.

D'Amore, D. V. 1995. The Stratigraphy, Hydrology, and Redoximorphic Character of the Jackson-Frazier Wetland. M.S. Thesis. Oregon State University, Corvallis, Or.

Glasmann, J. R. and G. H. Simonsen. 1985. Alteration of Basalt in Soils of Western Oregon. Soil Sci. Soc. Am. J. 49:262-272.

Glenn, J. L. 1965. Late Quaternary Sedimentation and Geologic History of the North Willamette Valley, Or. Ph.D. thesis, Oregon State University, Corvallis, Or.

Marshall, J. 1985. A Value Assessment of the Jackson-Frazier Wetland. Unpublished MS thesis, Oregon State University, Corvallis, Or.

Parsons, R.B., C.A. Balster, and A.O. Ness. 1970. Soil Development and Geomorphic Surfaces, Willamette Valley Oregon. Soil Sci. Soc. Am. Proc. 34:485-491.

Parsons, R.B. and R.C. Herriman. 1970. Haploxerolls and Argixerolls Developed In Recent Alluvium, Southern Willamette Valley, Oregon. Soil Sci. 100:299-309.

Reckendorf, F. 1992. Geomorphology, Stratigraphy, and Soil Interpretations, Willamette Valley, Oregon. In: Proceedings of the Eighth International Soil Management Workshop: Utilization of Soil Survey Information for Sustainable Land Use. (ed. J. M. Kimble). July 11-24, 1992. May, 1993.

Snavely, P. D., N. S. MacLeod and H. C. Wagner. 1968. Tholeiitic and Alkalic Basalts of the Eocene Siletz River Volcanics, Oregon Coast Range. Am. J. Sci., 266:454-581.

Chapter II.

Mineralogy, Morphology, and Origin of Fe-Mn Concentrations In Stratigraphic Units of an Oregon Wetland.

S.R. Stewart, J.R. Glasmann, J. Baham, and J.H. Huddleston.

Abstract

Wetland soils with complex stratigraphy and redoximorphic features occur on the margin of the Willamette Valley, Oregon. In the Jackson-Frazier wetland, vertisols show three distinct stratigraphic units that rest uncomformably upon each other and correspond to the Bashaw series Bss, 2Bt and 3BC horizons. Holocene alluvium deposited as distal alluvial fan sediment overlies partially eroded valley floor lake deposits (Willamette formation) and is mineralogically distinct from the lower two strata. Fe-Mn concretions differ among horizons in distribution, morphology, mineralogy, and chemistry. X-ray diffraction analysis (XRD) of bulk soil and concretion material showed the presence of goethite, Fe-Mn phosphate (purpurite), Mn hydroxides, smectite, kaolinite, vermiculite, halloysite, randomly interstratified mixed-layer dioctahedral vermiculite-mica, and small amounts of additional Fe/Mn oxides/hydroxides. The 3BC horizon has little mixed interlayer vermiculite/mica and halloysite, but contains kaolinite, mica and small amounts of chlorite. There were no differences in matrix δO^{18} isotopic signatures between units in the <0.2µm size fraction. Mineralogy within the concretions/nodules was similar to their respective matrices. Nodule mineralogy lacked mixed layer components, contained less smectite, and more kaolinite, mica, and vermiculite relative to the matrix soil. Concretions within the Bss horizon have a concentric fabric, contain more halloysite than those in the lower strata, and have the same isotopic signature as the matrix fine clay. Concretions within the 2Bt contain less halloysite relative to kaolinite, and the fine clays (<0.2µm) have a δO^{18} signature 2.8 o/oo lower than their matrix values. The larger 2Bt concretions show concentric fabric and small (2-5µm) Fe-Mn spheres within a pore. Nodules within the 3BC horizon appear to be aggregates of small (<100µm) micronodules and lack concentric or radial fabric. These nodules contain small amounts of chlorite and halloysite, less smectite and significantly more mica, vermiculite and kaolinite. Angular quartz with step-cleavage surface and fresh Ca-feldspar are observed in the 3BC nodules. The 3BC nodules have a δO^{18} signature of 2.2 o/oo less than the matrix values. Lower isotopic values within the concretions/nodules relative to the matrix suggest an early onset of formation and

the trapping, by Fe-Mn cementation, of clays weathered in a less enriched meteoric environment and transported into the valley with catastrophic Pleistocene flooding. Disparate isotopic values for nodule vs. matrix clays suggests that nodule clays are not in equilibrium with modern meteoric waters. Pressure oriented clays coat the exterior of the Bss and 2Bt concretions; low porosity, isotopic difference and subtle differences in mineralogy appear to indicate an early onset of formation and a long-term protected weathering environment within the concretions and 3BC nodules. These features provide evidence that, despite distinct, sharp boundaries, these concretions/nodules began forming after the transport and mixing of materials with disparate provenance. Some of the 3BC nodules may be near 38ky of age while some of the Bss concretions may be as young as 600y. The Bss-2Bt concretions and 3BC nodules appear to be continuing to form in situ as a function of climate, redox, and local valley stratigraphy.

Introduction

Wetlands have been recognized for a variety of terrestrial ecosystem functions including flood control, groundwater recharge (Carter, 1986; Carter et al., 1979), wildlife habitat (Mitsch and Gosselink, 1993), bioremediation, and wastewater treatment (Knight et al., 1987). Occasionally there is controversy over the definition and function of hydric soils (wetlands) and the methods, analysis, and parameters for their delineation (Zinn and Copeland, 1982; Mitsch and Gosselink, 1993; Vepraskas 1994). Redoximorphic features such as depletions and concentrations are essential for the field soil scientist to identify and delineate hydric soils (U.S. Soil Survey Staff, 1992; Vepraskas, 1994). Understanding these features is important in deciphering the biogeochemical, hydrologic, and/or climatic history of an area (Bouma, 1983; Moorman and van de Wetering, 1985; Vepraskas, 1992), and increases understanding of wetland functions on a more fundamental level.

The Jackson-Frazier wetland is Holocene alluvial fan/valley fill that experiences repetitive annual flooding and drying cycles. These cycles, coupled with adequate organic C and temperature, facilitate microbial reductive dissolution and segregation of Fe, Mn and other redox-sensitive metals into redoximorphic concentrations and/or depletions (Somera, 1967; Cogger and Kennedy, 1992; Vepraskas, 1994; Miller et al., 1993; Lovely, 1993). There are three distinct stratigraphic units within the Jackson-Frazier wetland corresponding to the Bss, 2Bt, and 3BC horizons, all of which have prominent macroscopic concentrations in the form of Fe-Mn concretions and nodules. The large concretion size and distinct mineralogy of the Bss horizon suggests that the origin of concretions in this unit might be related to sedimentary processes - i.e., deposition of eroded, nodule rich clay from neighboring foothill landscapes. If the concretions are sedimentary in origin, they may be of different character from those generated by 'in situ' redoximorphic processes related to Holocene wetland genesis.

Willamette Valley Fe-Mn nodules were identified by Drosdoff and Nikiforoff (1940), and Balster and Parsons (1969). Drosdoff and Nikiforoff (1940), Somera (1967), and Seter and Baham (1994) studied the distribution and Fe-Mn chemistry of concretions/nodules with depth within different Willamette Valley soils. Various authors have discussed the presence and distribution of redoximorphic concentrations, the reductive dissolution of Fe, Mn, and redox sensitive elements, soft Fe masses and stains, oxide surface chemistry, and the mineralogy of Fe, Mn, and various redox sensitive metal-oxides as related to temperature and environment (Wang et al., 1993; Cogger et al., 1992; van Breeman, 1988; Schwertmann, 1988; Bartlett and James, 1993; Blaylock and James, 1992; Tardy and Nahon, 1985; Stumm and Sulzberger, 1992; Miller et al.,1993; Lovely, 1993; Vepraskas and Bouma, 1976; Blume, 1988; Hansen et al., 1994; Gunten and Zobrist, 1993). There is less information concerning the origin, internal morphology, age, history, and rate of formation of nodules and concretions.

Our objectives in this study were to characterize the mineralogy, elemental distribution, O^{18} and $H^2(D)$ isotope fractionation, and morphology of the soil concretions/nodules with respect to the matrix. These data will provide useful information to the field soil scientist in the interpretation of area(s) of origin, age, history, and associated redox/hydraulic environment of the concretions/nodules as a function of landscape, climate, and stratigraphy. These laboratory and field observations will increase our understanding of wetland functions on a more fundamental level.

Methods and Materials

Dried concretions and nodules were separated into two size classes by sieving; the Bashaw Bss and 2Bt nodules were separated into 0.5-1mm and 3-9mm size classes, and the 3BC nodules were separated into 0.5-1mm and 2-3mm classes due to the size differences between the nodules and concretions. The samples were then gently ground into a fine powder in a diamondite mortar and pestle (h=9).

Fresh samples were weighed for the dithionate-citrate-bicarbonate (DCB) extractions and 5mL of deionized H_2O and 5mL of 0.5M citrate:0.2M Na-bicarbonate stock was added to 50mg of sample in 50mL plastic centrifuge tubes. The samples were then placed in a 75C water bath for 5 minutes. Approximately 0.33g of sodium hydrosulfite was added to each of the tubes which were then shaken for 30 minutes. The samples were then centrifuged for 20 minutes at 3000 rpm (1086G) and the supernatant was decanted into 50mL volumetric flasks. This procedure was repeated two additional times on the same samples.

The Fe_{DCB} was analyzed after the method of Jackson et al., (1986) by placing 150μL of sample in 5.1mL nanopure H_2O, 0.25mL of 2% hydroxylamine hydrochloride, 0.25mL of 1.0M sodium acetate/acetic acid buffer and 0.25mL of 0.4% 1,10 phenanthroline. The samples were mixed and set aside for at least 0.5hr before being analyzed in a Hewlett Packard 8453 UV visible spectrophotometer. Standards were made in the linear working range of 0-2.5ppm from a 50ppm stock solution of ferrous ammonium sulfate hexahydrate. The DCB-Fe samples were air-bubbled for 2hr to oxidize the dithionite.

The Mn_{DCB} was analyzed by atomic absorption analysis in the Department of Oceanography, Oregon State University.

SEM

Whole and fractured concretions/nodules from each stratigraphic unit were mounted on Al stubs with Duco cement and sputter coated with Au-Pd and examined with an AMR 1000 scanning electron microscope equipped with a Kevex energy dispersive X-ray analyzer.

Clay Mineralogy

Matrix and concretion/nodule bulk powder samples from each of the three stratigraphic units were X-rayed on plastic sample holders and then on nonreflecting quartz slides after gently grinding the concretions/nodules and then magnetically separating both, the concretion/nodule, and matrix material.

Soil and ground concretion/nodule materials were prepared for clay mineral analysis after the method of Glasmann and Simonson (1985). All slides were X-rayed using monochromatic CuKα radiation at 40kV and 35mA with a 0.02° 2-theta increment and a 1s count time on a Phillips model XRG 3100 automated XRD unit with Jade software. The magnetically separated material was analyzed at 40mA, 0.04° 2-theta step count and a 5s count time.

Isotope Analysis

The <0.2μm component of both the bulk soil and the soil components within ground concretion/nodule material was prepared for O^{18} and H^2 isotope analysis after the removal of Fe, Mn and organic matter. Concretion/nodule material was prepared for isotope analysis by placing 20-30g in 500mL plastic containers and DI water overnight on a shaker where they were allowed to agitate against themselves to facilitate the removal of clays and organics adhered to the outer rind. After three repetitions (or until the solution cleared) the nodules were dried and gently crushed to powder.

Clays from the soil matrices and associated ground concretion/nodules were prepared for isotope analysis after the removal of organic matter and metal oxides by three alternating treatments of sodium hypochlorite and hydrogen peroxide and three separate dithionite-citrate-bicarbonate extractions. The clays

were then saturated with Mg to displace the Na and then rinsed repeatedly in DI water and centrifuged at 8,000rpm (7,719G) for 10min until the excess Na was removed (the <0.2µm fraction was resuspended). The <0.2µm fraction was concentrated and rinsed 3x in ethanol, centrifuging at 10,000rpm for 10min.

The clay fraction was analyzed by XRD to determine the nature of the clay mineral fraction and sub-samples were then sealed in small glass vials and sent to the University of Western Ontario, London, Ontario, Canada, for stable isotope analysis by mass spectrometry. Reproducibility is ±0.3 per mil for δO and ±2.0 per mil for δD values (Personal communication, Longstaffe, 1996).

Polarizing Microscope Photography

Polished thin sections of intact soil peds, single concretions, and nodules were prepared after vacuum-impregnation of samples with resin. Samples were prepared by Spectrum Petrographics, Winston, OR.

Physical characteristics

Density was measured by weighing a number of concretions and nodules, coating them with liquid saran, and measuring the volume of water displaced after immersion.

Estimates of porosity were made by taking between 15 and 20 concretions/nodules from each horizon and weighing them, placing them in beakers of water for several weeks, then gently drying the surfaces with chemwipes and immediately re-weighing.

Results

Concretion/Nodule Description and Distribution

Physical characterization data are shown in tables 2-1 and 2-2. The Bss Holocene alluvium had the largest concretions (on average and absolute size) of any horizon and ranged from <0.5-12mm in diameter (Table 2-1) with well-

rounded to sub-rounded shapes (Fig. 2-1a,b) and smooth surfaces. Most concretions were black, but, a few approached dark reddish brown (2.5YR 3/4) with little or no continuum of color between these values. A small percentage had fractured rinds that exposed an inner, harder, black (N 2/0) core. The Bss horizon averaged 1.7 percent concretions by weight, intermediate between the 2Bt and 3BC (Table 2-1).

The clay mineral assemblage of the Bss matrix-alluvium included Fe-rich smectite, halloysite, kaolinite, vermiculite, randomly interstratified vermiculite/mica and small amounts of illite. Smectite and halloysite were

Table 2-1. Concretion and nodule distribution, sizes, and densities.

Horizon	size	Distribution $dgkg^{-1}$	Std.Err. n=32	Density gcm^{-1}	Std. Err. n=6
Bashaw Bss	<0.5-12mm	1.69	0.062	2.1	0.10
Bashaw 2Bt	<0.5-7mm	0.77	0.029	2.1	0.08
3BC-IB	<0.5-3mm	1.98	0.041	1.9	0.07

concentrated in the <2.0µm size fraction which is approximately 60% smectite and 40% halloysite. The mixed interlayer vermiculite-mica, mica, and kaolinite tended to be more prevalent in the <15µm fraction (Table 2-3). Concretion mineralogy was similar to that of the matrix, but has little or no mixed-layer minerals, less smectite, and more vermiculite, kaolinite and mica. Goethite, purpurite ($FeMnPO_4$), and manganite also was detected and the presence of additional oxides/hydroxides of Fe/Mn is suggested (Fig. 2-4a). The Bss concretion density averaged $2.1gcm^{-3}$ (Table 2-1). Concretion porosity was 20-22% by volume.

The 2Bt concretions ranged from <0.5-7mm in diameter, shapes were rounded to sub-rounded with smooth to botryoidal surfaces (Fig. 2-1c). Colors were very dark grayish brown (10YR 3/2) to reddish brown (5YR 4/3).

Concretion density averaged 2.1gcm^{-3} and porosity was 28-30% by volume. The 2Bt horizon had the fewest concretions (by number and percent weight),

Table 2-2. Soil bulk densities, concretion/nodule distribution and porosity.

Horizon	Whole Soil Bulk Density	Distribution (% volume)	Std.Err. n=32	Porosity (%volume)
Bashaw Bss	1.25	2.11	0.078	20-22
Bashaw 2Bt	1.34	1.03	0.039	28-30
3BC-Irish Bend	1.36	2.69	0.056	30-32

averaging 0.8 percent by weight, less than half the amount in both the Bss and the 3BC.

The 2Bt matrix had the same clay mineral assemblage as the Bss matrix with the exception of having less mixed-layer vermiculite/mica and halloysite. The mixed-layer phase, vermiculite, kaolinite and mica were found predominantly in the 2-15μm size fraction; halloysite and smectite were dominant in the <2μm size fraction (Fig.'s 2-3a,b). The <0.2μm fraction was approximately 90 percent smectite and 10 percent halloysite (Fig. 2-8).

Concretion mineralogy was similar to that of the matrix, but has no mixed-layer phase, less smectite, small amounts of illite, and more vermiculite and kaolinite (Table 2-3; Fig. 2-2b). Concretion vermiculite, kaolinite and illite were found predominantly in the 2-15μm fraction (Table 2-3, Fig. 2-2b). The presence of goethite, manganite and purpurite is suggested within these concretions (Fig. 2-4b).

The 3BC horizon had the smallest nodules on average (<0.5-3mm diameter) but the largest percent by weight (2%) of any horizon. Nodule density was less in this horizon, averaging 1.9 gcm^{-3}, and nodule porosity was 30-32% by volume. Shapes were rounded to irregular with botryoidal surfaces (Fig. 2-1c).

a

b

Figure 2-1(a-d). Scanning electron micrographs of J-F concretions and nodules. (a) Fractured Bashaw Bss concretion. (b) Bss concretion-soil ped boundary.

c

d
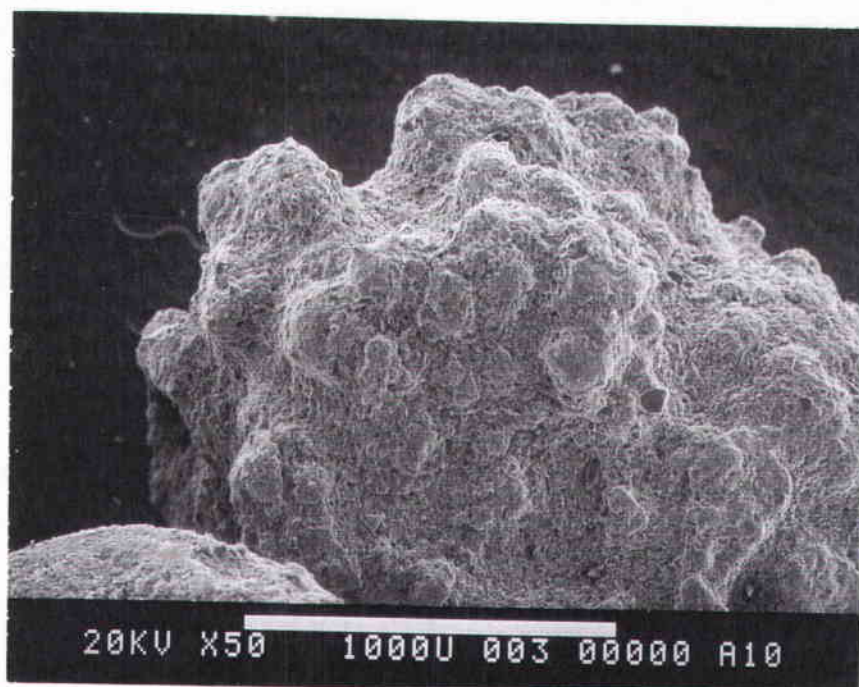
Figure 2-1 cont.'d. (c) Bashaw 2Bt concretion. (d) 3BC - Irish Bend nodule.

a

b
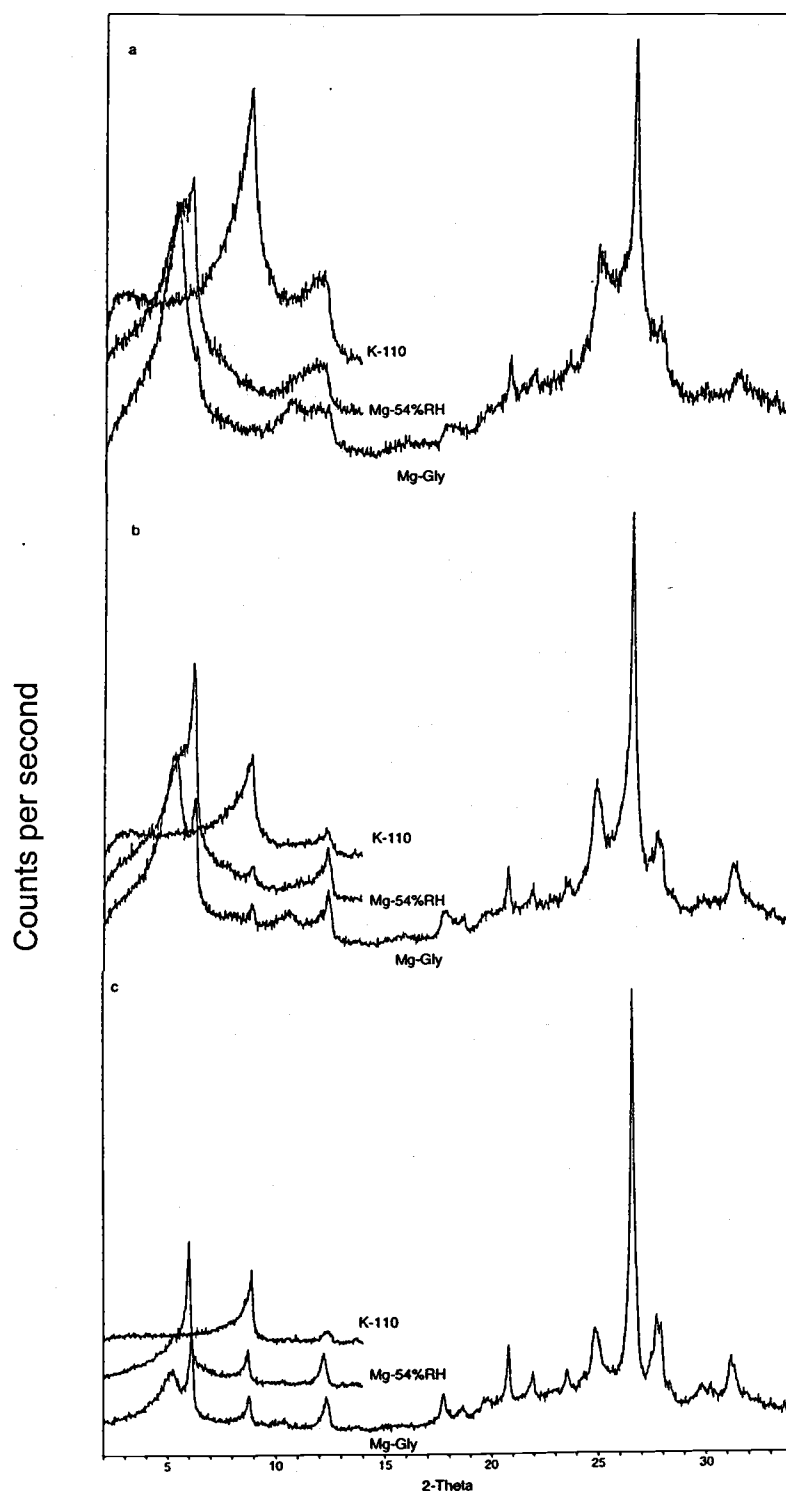
Figure 2-2 (a-f). Detailed concretion and matrix mineralogy with depth. (a) Bss concretion <2μm. (b) 2Bt concretion <2μm. (c) 3BC-Irish Bend nodule <2μm.

a

b

Counts per second
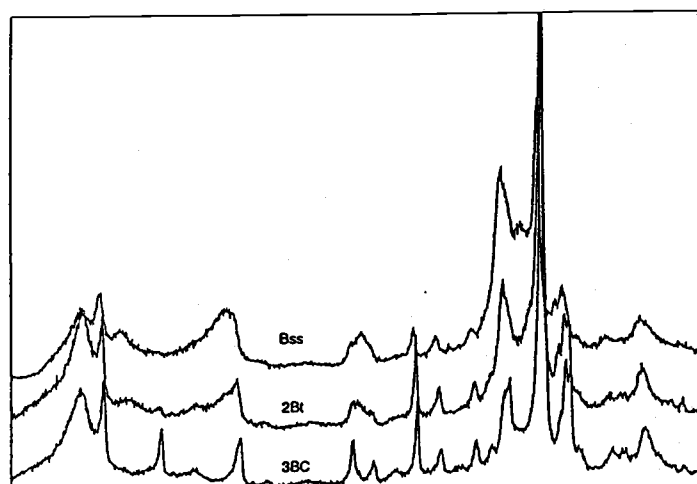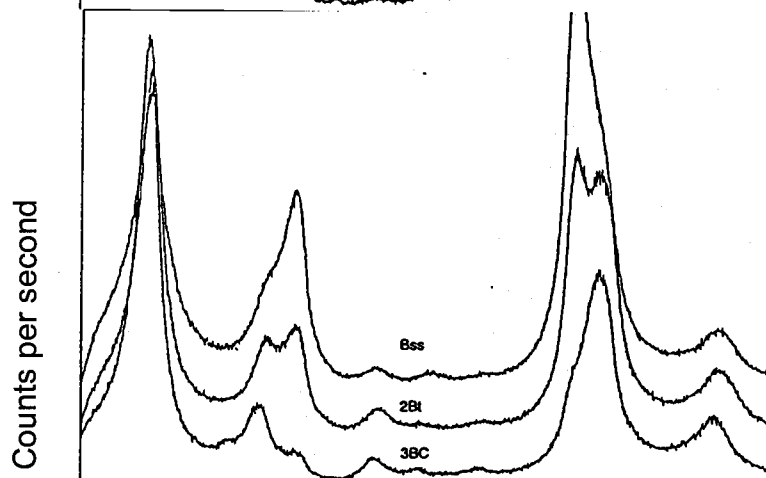
c
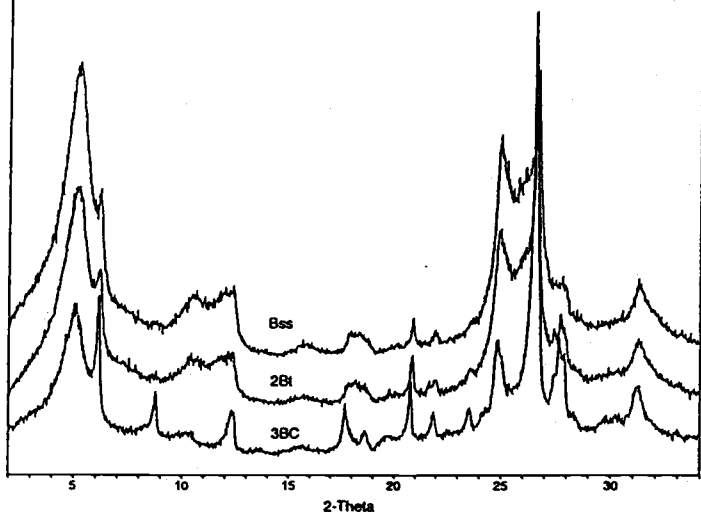
Figure 2-3 (a-c). Mineralogical differences with depth, Mg-glycol treatment. (a) Matrix <15μm. (b) Matrix <2μm. (c) Concretion/nodule <15μm.

Table 2-3. Summary of concretion, nodule, and matrix mineralogy for the three size classes.

	Bss-Matrix			Bss-concretion			2Bt-Matrix			2Bt-concretion			3BC-Matrix			3BC-nodule		
size	2-15	<2.0	<0.2	2-15	<2.0	<0.2	2-15	<2.0	<0.2	2-15	<2.0	<0.2	2-15	<2.0	<0.2	2-15	<2.0	<0.2
Sm	m	vs	vs	vs	vs	vs	s	vs	vs	s	s	vs	s	vs	vs	s	m	vs
Vm	s	vw	w	s	m	m	s	vw	w	s	s	w	vs	vw	w	vs	vs	s
H	m	vs	s	m	vw	s	w	vs	s	w	vw	s	vw	vw		vw	-	-
K	m	s	vw	m	vw	vw	w	s	vw	w	w	vw	s	vw	vw	s	s	vw
I	vw	-	-	vw		-	vw	w		vw	vw	-	w	w	vw	s	s	w
Q	vs	vw	NA	vs	s	NA	vs	vs	NA	vs	vs	NA	vs	vw	NA	vs	vs	NA
O	1,3	3	NA	1,3	3	NA	1-3	3	NA	2,3	2,3	NA	1-3	2-3	NA	2-3	2-3	NA

Mineralogy: Sm=smectite Vm=vermiculite H=halloysite K=kaolinite I=illite Q=quartz O=other
Other: 1=mixed interlayer (mica/vermiculite) 2=chloritic intergrade 3=feldspars
Relative peak intensities: very strong (vs) strong (s) moderate (m) weak (w) very weak (vw)
 not present or undetectible (-)   not measured (NA)

1> 29-0713: Goethite - FeO(OH)   2> 41-1379: Manganite - MnO(OH)
3> 37-0478: Purpurite - (Mn,Fe)PO4
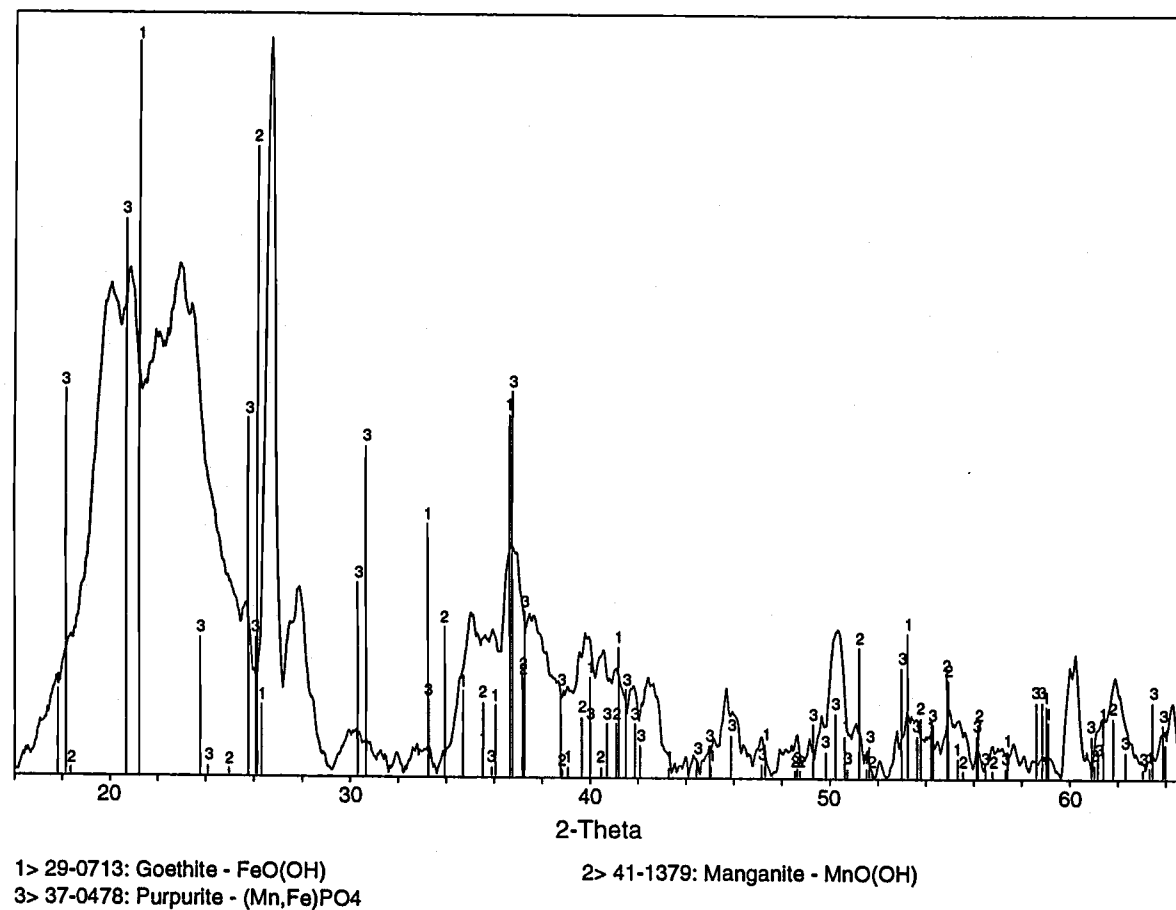
Figure 2-4 (a-d). Concretion/nodule Fe-Mn oxide/hydroxide mineralogy. (a) Bss concretion.

1> 29-0713: Goethite - FeO(OH)   2> 41-1379: Manganite - MnO(OH)
3> 37-0478: Purpurite - (Mn,Fe)PO4
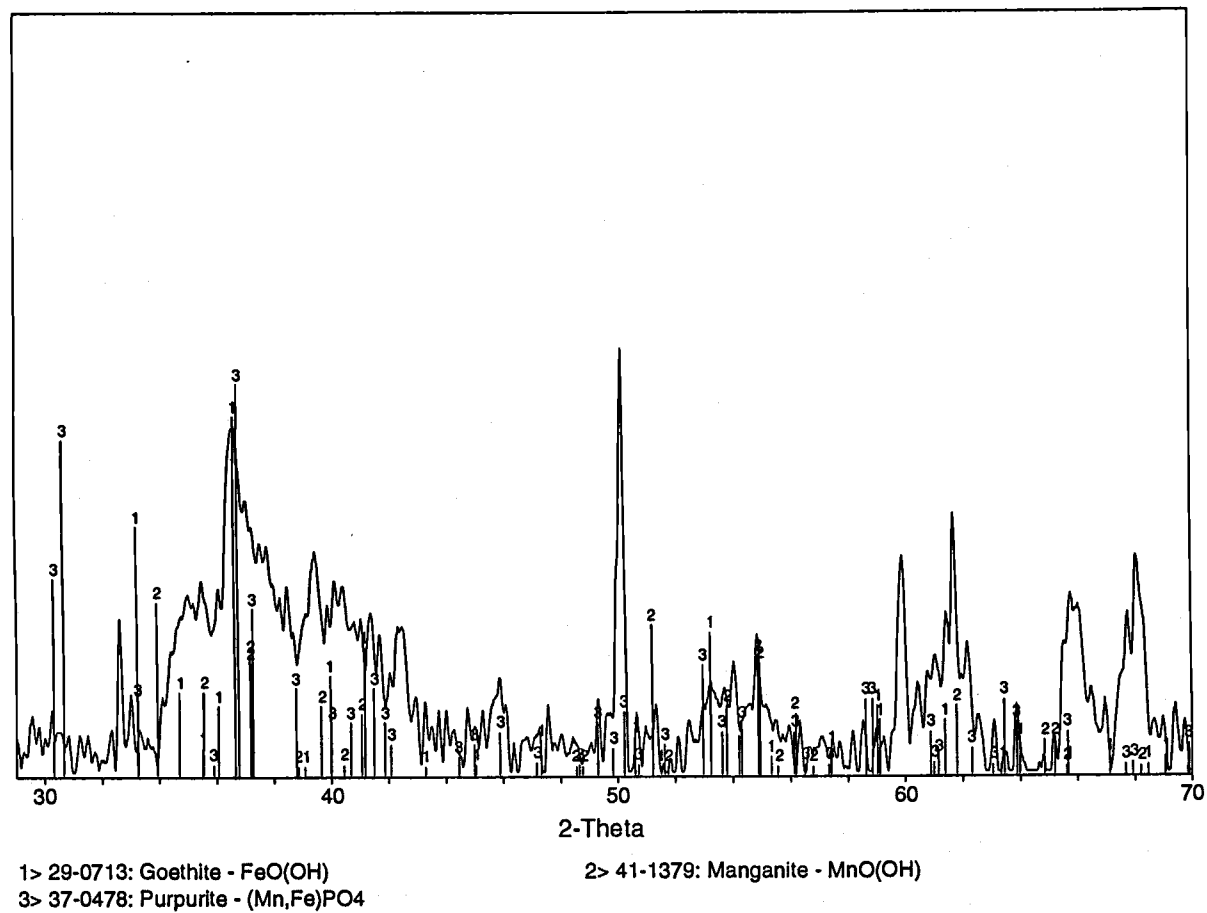
Figure 2-4 cont.'d. (b) 2Bt concretion.
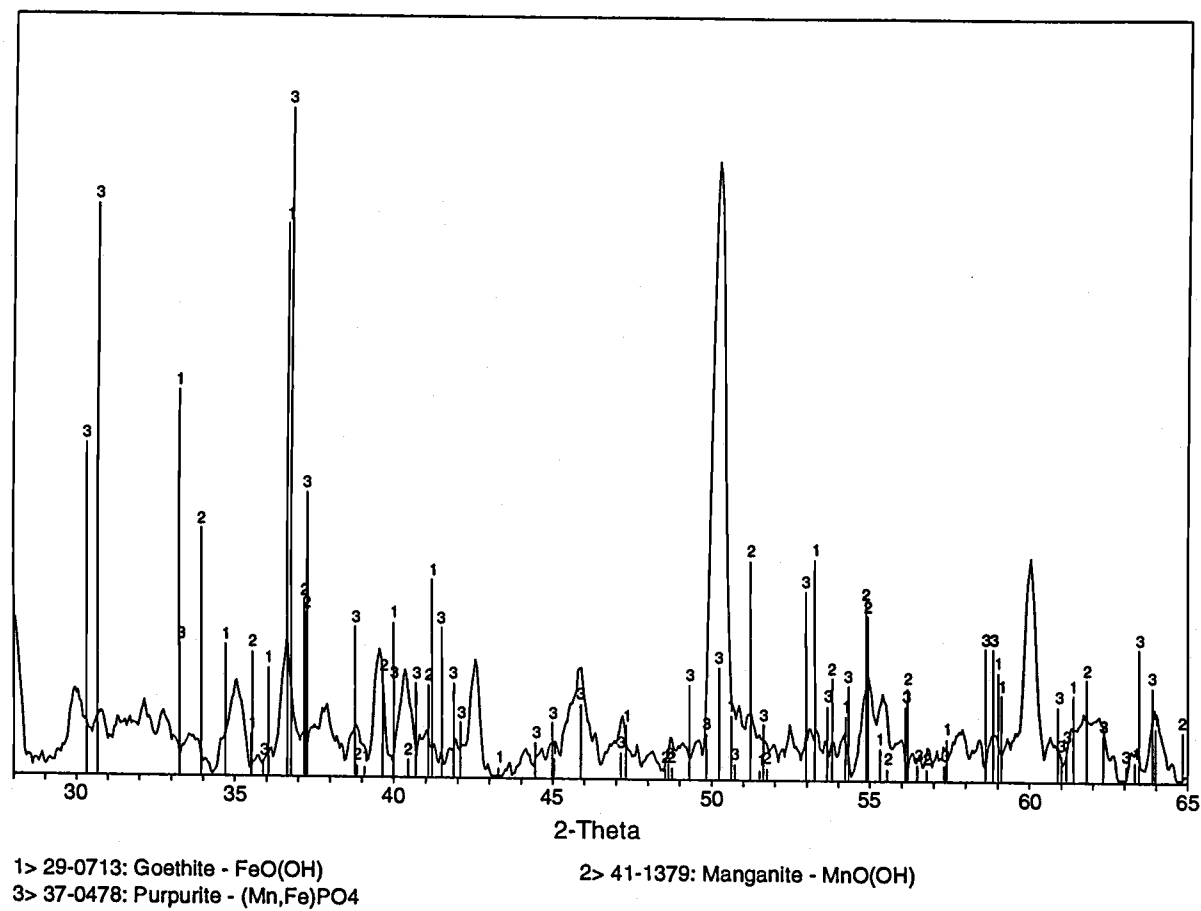
Figure 2-4 cont.'d. (c) 3BC-Irish Bend nodule.

1> 29-0713: Goethite - FeO(OH)
3> 37-0478: Purpurite - (Mn,Fe)PO4

2> 41-1379: Manganite - MnO(OH)

1> 39-1346: Maghemite-\ITC\RG, syn - Fe2O3   2> 33-0664: Hematite, syn - Fe2O3
3> 19-0629: Magnetite, syn - FeFe2O4   4> 29-0713: Goethite - FeO(OH)
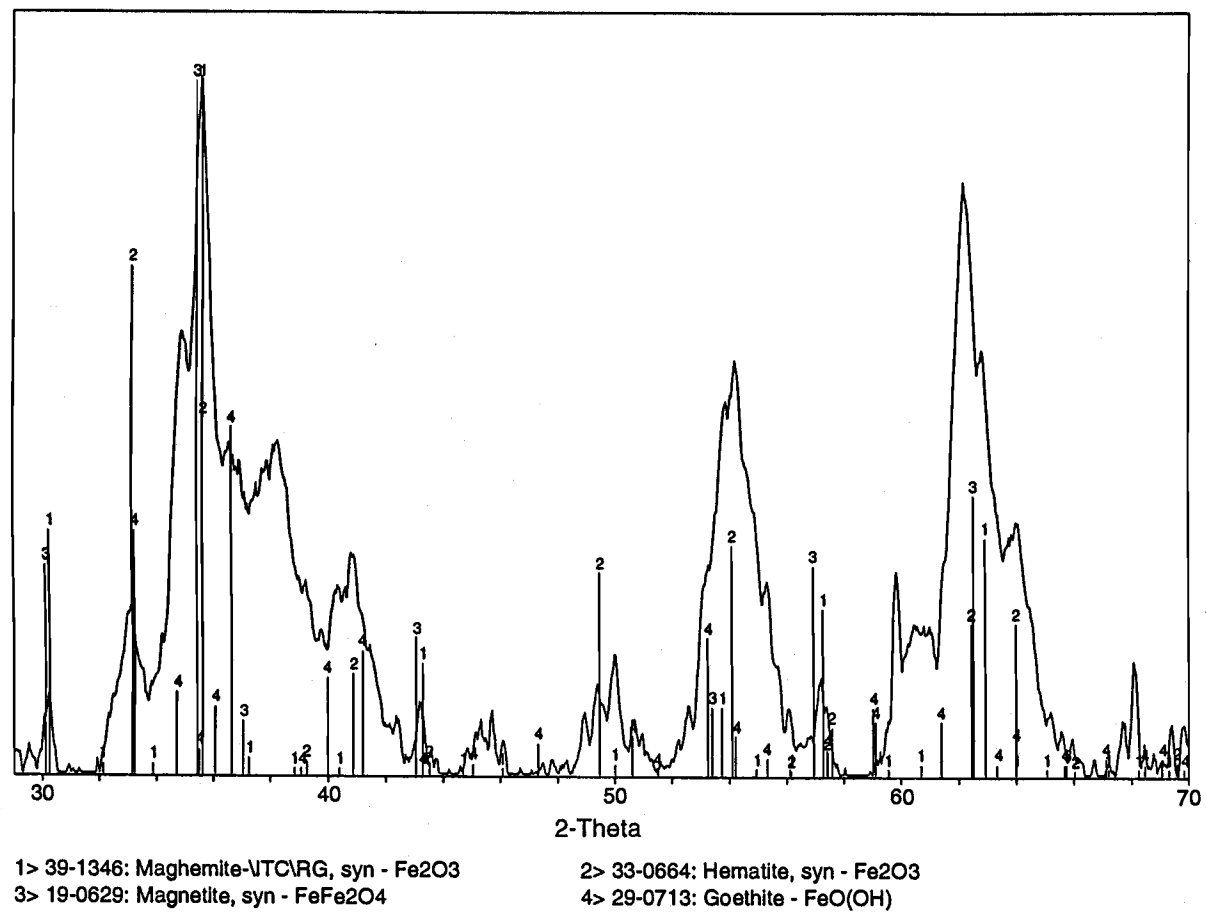
Figure 2-4 cont.'d. (d) Jory series nodules.

The surface color of the 3BC nodules ranged from pink (7.5YR 7/4) through reddish brown (Munsell) to very dark grayish brown (10YR 3/2). Color description was difficult due to the variegated appearance of these nodules. The interior colors range from pink to dark reddish brown (5YR 2.5/2), also in variegated patterns.

Mixed layer vermiculite/mica and halloysite were nearly absent from the 3BC matrix. Large amounts of mica and small amounts of chlorite were present, as was a sharp kaolinite peak (Fig. 2-3a). Smectite was found predominantly in the <2μm size fraction with some illite and kaolinite; mica, vermiculite, kaolinite and chlorite are predominately in the 2-15μm fraction (Table 2-3; Fig. 2-3b). Nodule mineralogy showed less smectite and more mica, kaolinite and vermiculite in the <2μm fraction relative to the matrix. Halloysite was absent in both the <2μm and <15μm size fractions (Table 2-3; Fig.'s 2-2c,2-3c). The presence of goethite, manganite and purpurite is suggested within these nodules (Fig. 2-4c).

The Ultisols at the head of Jackson and Frazier creeks contain numerous small <2mm nodules with distinctly different mineralogy, hardness (these nodules cannot be fractured by hand), and color than those found within the J-F wetland. These nodules are rich in kaolinite, goethite, maghemite and hematite, but lack mica (Fig. 2-4d).

SEM/Photomicroscopy Characterization

The internal morphology of the Bss concretions consists of silt-sized primary and secondary minerals adhered with clay, amorphous Fe-Mn oxides and, probably, organic material. The overall arrangement of the individual particles within the concretions is similar to that within the matrix, except for a concentric fabric with highly birefringent, pressure-oriented clays. These clays have parallel orientation and are observed within the concretion, as well as on the exterior (Fig.'s 2-7a,b). Most concretion boundaries are sharp; a few are diffuse. Quartz and Ca-plagioclase grains have been identified within these concretions, but the identification of many features with SEM is difficult due to smectite and amorphous Fe-Mn coatings within the concretion pores and upon the surfaces of

the primary minerals (Fig. 2-5d). Elemental mapping of Fe and Mn shows a slightly Mn-enriched interior and a homogeneous Fe distribution (Fig.'s 2-6a,b).

The internal morphology of the 2Bt concretions is similar to that of the Bss (Fig.'s 2-7c,d), and most concretion boundaries are sharp. Elemental mapping and line profiles show an Mn enriched core and an Fe-rich rind (Fig.'s 2-6c,d). Quartz, Ca-plagioclase laths, Ca-smectite, and small (3-4um) spherical nodules can be identified within the concretion pores and root tubules (Fig.'s 2-5a,c). These small nodules are nearly perfect spheres composed almost completely of Fe and Mn and are nearly identical in appearance to the ferrihydrite globular aggregates shown by Schwertmann and Taylor (1989). Photomicroscopy reveals 'halos' around some of the concretions and pressure oriented clay along pore depletions adjacent to ped concentrations (Fig.'s 2-7e,f).

The internal morphology of the 3BC nodules consists of an argillosepic fabric with a random individual distribution (Brewer,1976), a higher percentage of diffuse nodule boundaries with thin strands of Fe-Mn ('stringers') normal to the nodule surface, and a lack of concentric or radial fabric and pressure oriented clays (Fig.'s 2-7g,h,i). Quartz, feldspars, and mica can be seen within these nodules and the arrangement of framework components within the nodules is identical to the arrangement of components within the matrix (Fig.'s 2-5b,f; 2-7h). Some nodules appear to be aggregates of smaller micronodules, resulting in botryoidal morphologies (Fig.'s 2-1d; 2-7j). Some quartz grains show conchoidal step-cleavage patterns (Fig. 2-5f). Elemental mapping by line profile shows more Fe concentrated on the outer part of the nodules while Mn is concentrated in the nodule interior (Fig.'s 2-6e,f).

Chemistry

Dithionite-citrate-bicarbonate Fe-Mn data for both concretions/nodules and the matrices in which they occur are summarized in Table 2-5. Bss concretions contain 7-9x more DCB-Fe than the matrix in which they occur. Small concretions appear to be somewhat more enriched than the large ones. The 2Bt concretions contain 8x more Fe_{DCB} than the matrix, which contained the least

amount of Fe and Mn of all these strata. The 3BC nodules are the least enriched (4-5x) relative to the matrix. Although there were no apparent differences in Fe distribution between concretion size classes, the larger concretions contained more Mn (% weight) than the smaller sized ones.

The Bss concretions are enriched 25-50x in Mn_{DCB} with respect to the matrix. The 2Bt concretions are enriched 250-475x in Mn_{DCB} and the matrix is the most Mn depleted of the three stratigraphic units. The 3BC nodules are enriched 40-80x in Mn_{DCB} (Table 2-5).

Isotope fractionation

The δO^{18} and D composition were essentially the same for the Bss matrix and concretions, but the 2Bt and 3BC horizons had lower isotopic composition within the concretions than the corresponding matrix (Table 2-4). The fine clays (<0.2um) within the 2Bt concretions have a δO^{18} value of 2.8o/oo lower than the matrix and the 3BC nodules have values 2.2o/oo less than their surrounding matrix.

Discussion

Nodule and Concretion origin

The nodules from the ultisols (Jory) at the source of Jackson creek have distinctly different mineralogy (Fig. 2-4d) and appearance from the concretions and nodules in the sediments beneath the J-F wetland. This suggests that the concretions and nodules in the J-F sediments were not transported by overland flow with the sediments from the older geomorphic surfaces.

a

b
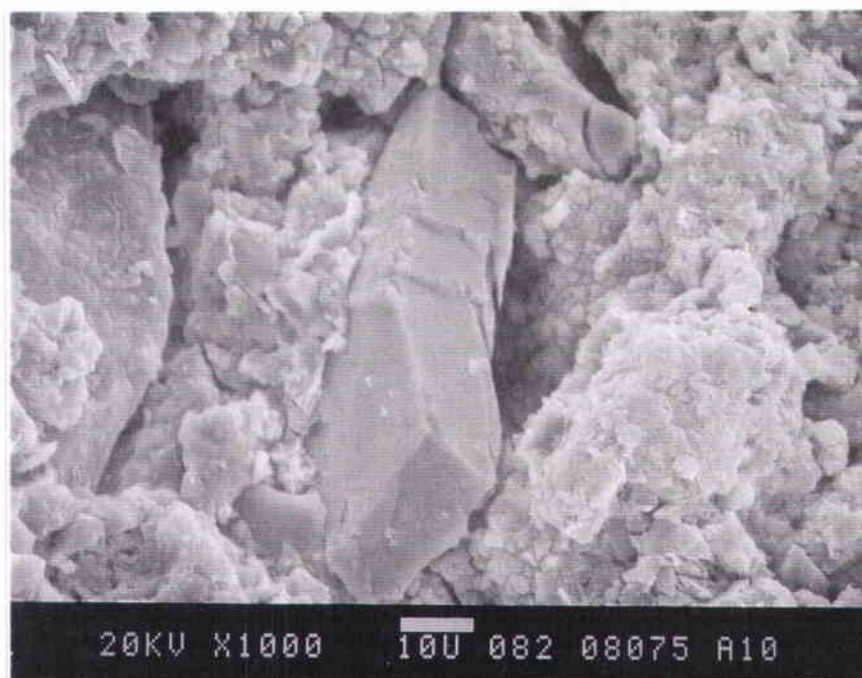
Figure 2-5 (a-f). Scanning electron micrographs of primary minerals and features found within concretions and nodules. (a) Ca-plagioclase lath within a 2Bt concretion. (b) Ca-plagioclase grain within a 3BC nodule.

c
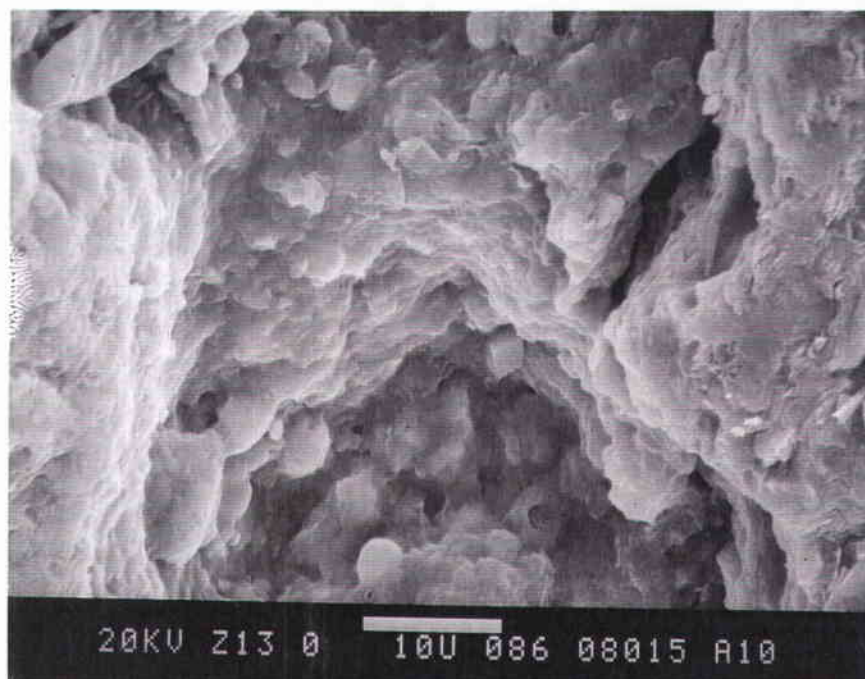
d
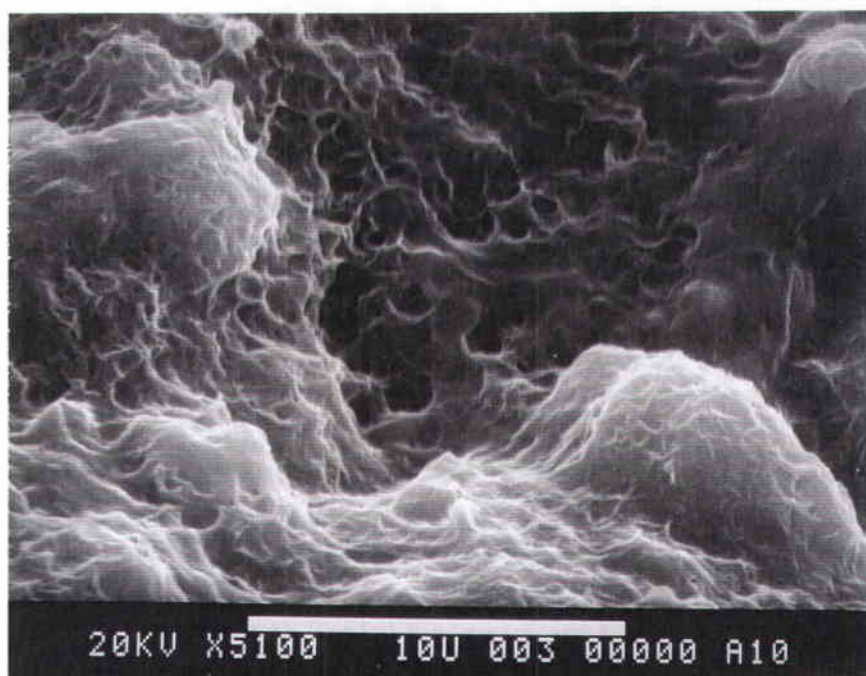
Figure 2-5 cont.'d. (c) Spherical Fe-Mn 'nodules' found within the pore of a 2Bt concretion. (d) Amorphous Fe-Mn and smectite coatings covering primary minerals within a Bss concretion.

e
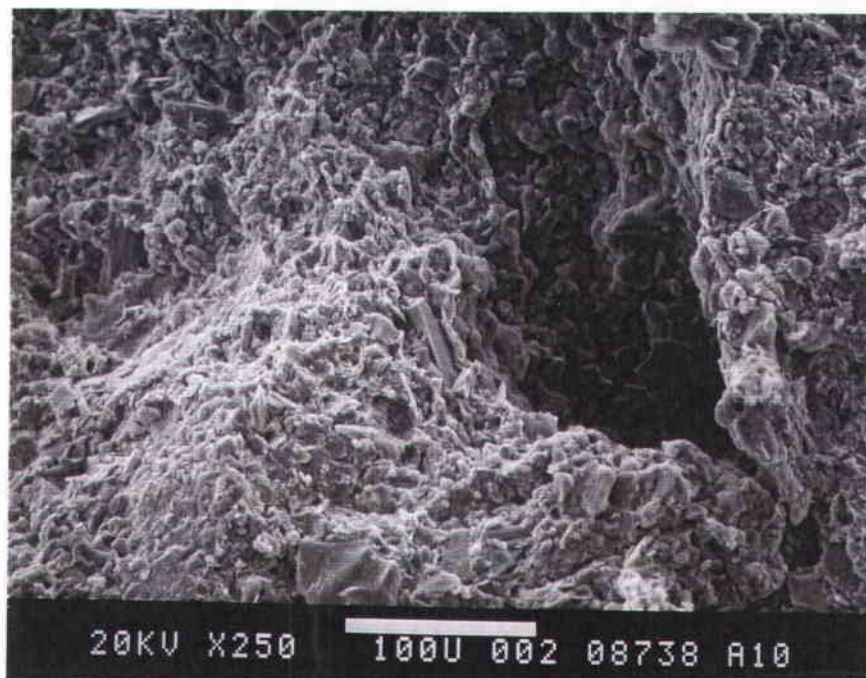
f
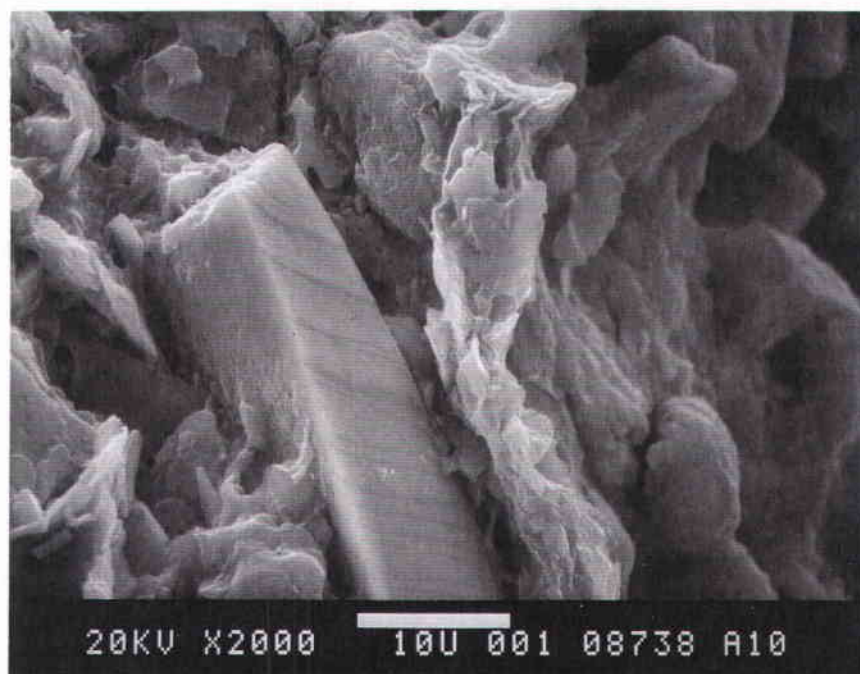
Figure 2-5 cont.'d. (e) Root tubule in a 3BC nodule. (f) Step-cleavage quartz located at the beginning of the root tubule within the same 3BC nodule.

a

20KV X44   1000U 013 08165 A10

b

20KV X29   1000U 011 08165 A10
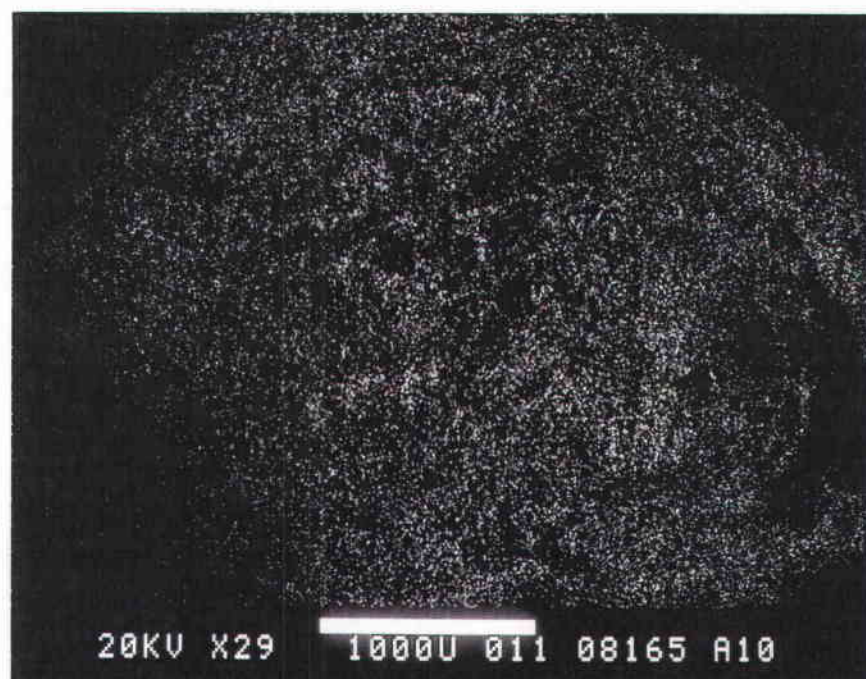
Figure 2-6 (a-f). Elemental mapping and line profiles for Fe and Mn in concretions and nodules. (a) Bss concretion-Fe. (b) Bss concretion-Mn.

c

d

Figure 2-6 cont.'d. (c) 2Bt concretion-Fe. (d) 2Bt concretion-Mn.

34
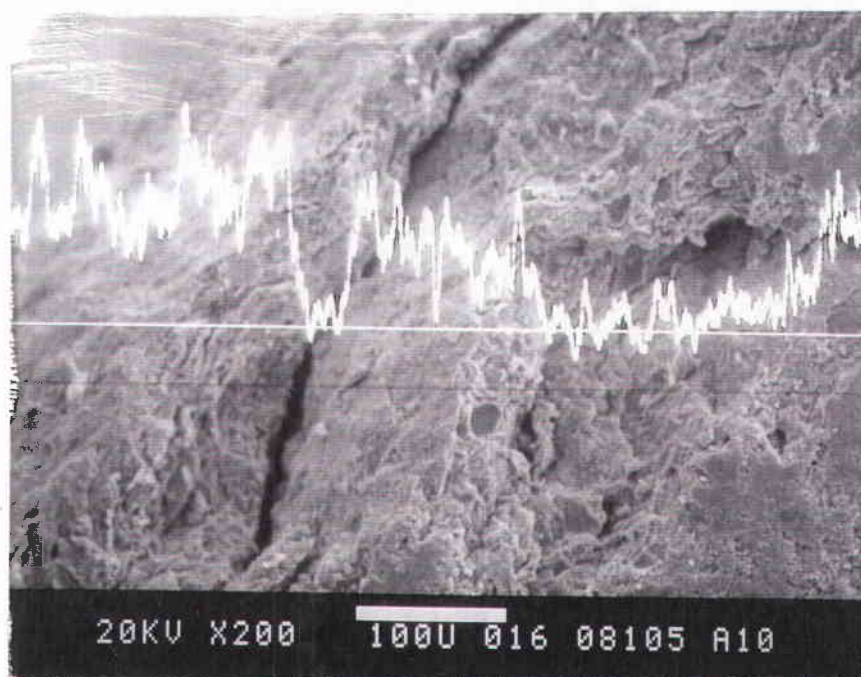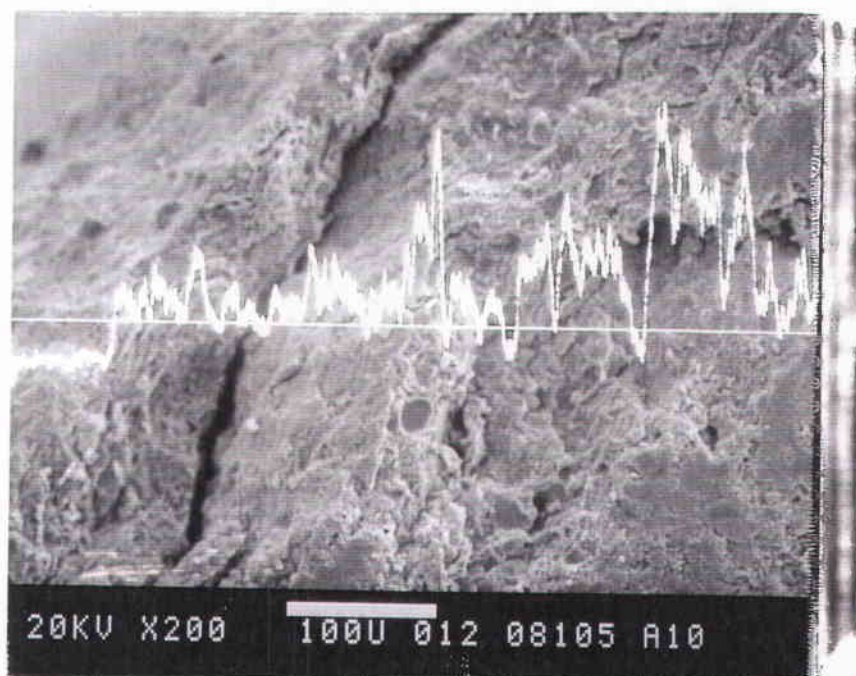
Figure 2-6 cont.'d. (e) 3BC nodule-Fe, line profile. (f) 3BC nodule-Mn, line profile.

a
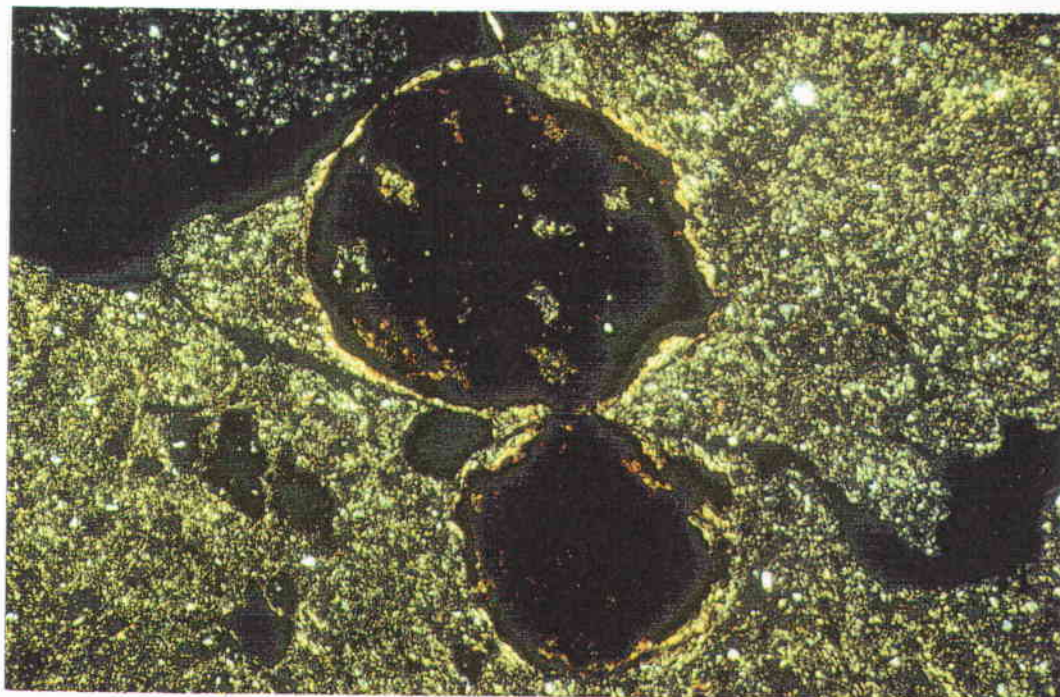
0.5mm

b
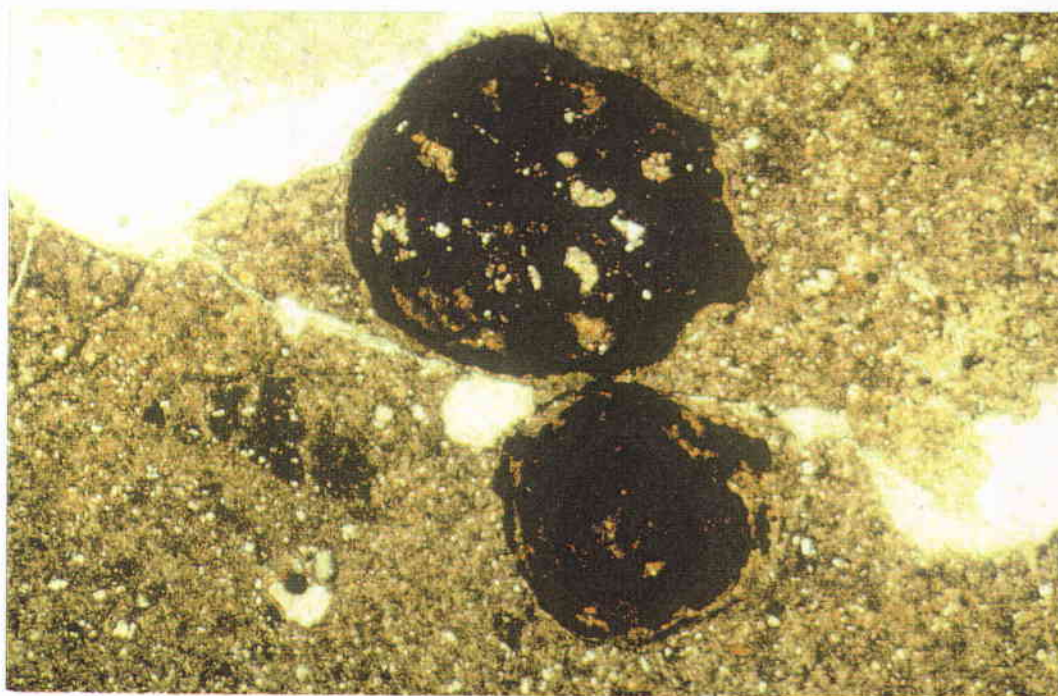
0.5mm

Figure 2-7 (a-l). Polarizing microscope photography on thin sections from intact peds. Bss concretions - (a) polarized light, (b) plain light.

c
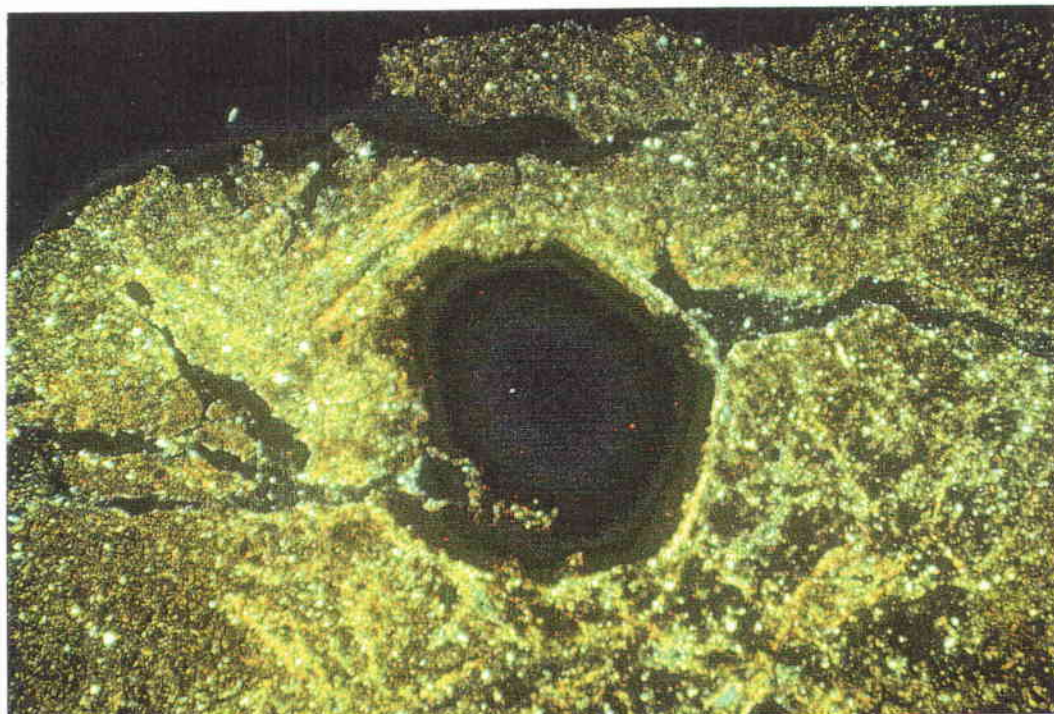
0.4mm

d
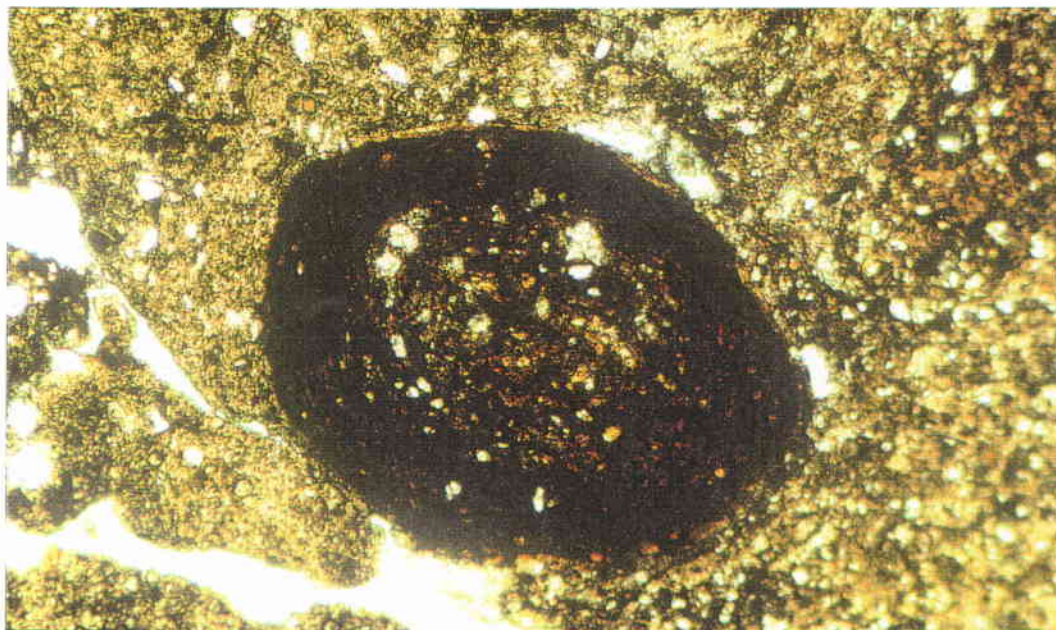
0.16mm

Figure 2-7 cont.'d. Bss concretions - (c) polarized light, (d) plain light.
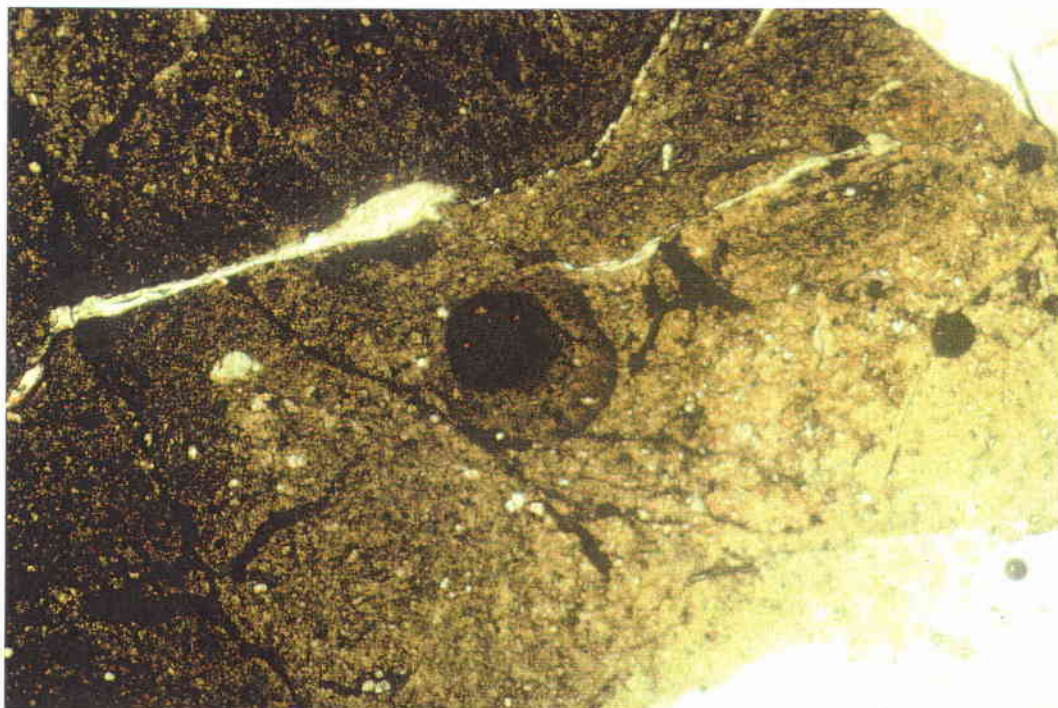
0.12mm
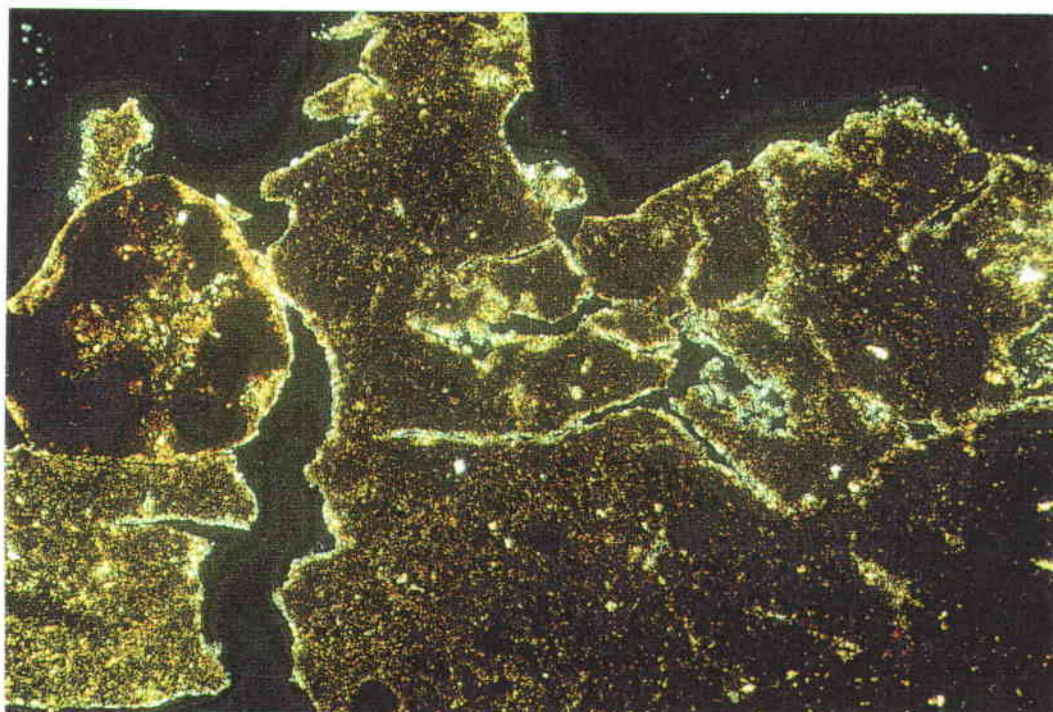
0.75mm

Figure 2-7 cont.'d. (e) 2Bt concretion with halo (plain light), (f) neoalbans lining pores, (polarized light).

g
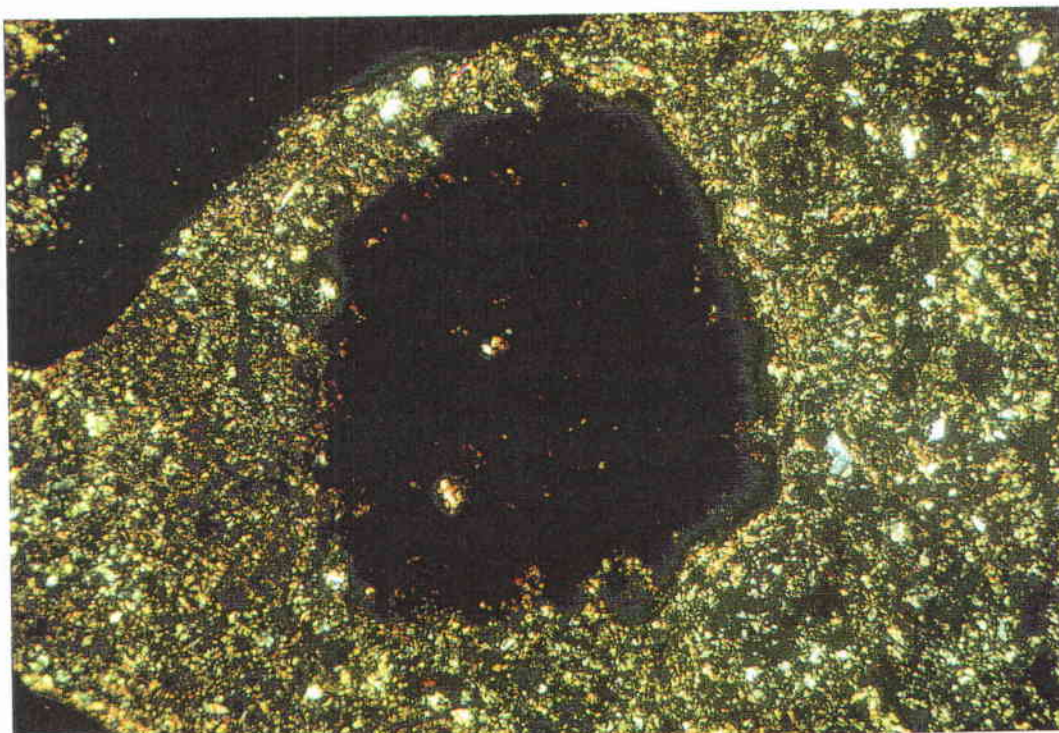
0.33mm

h
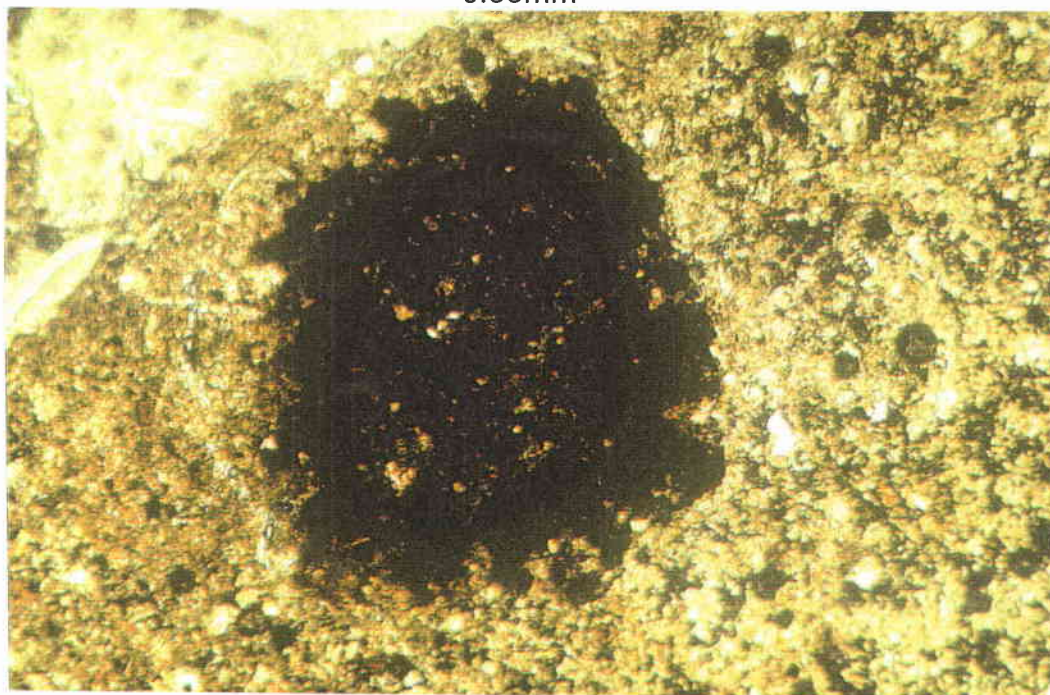
0.33mm

Figure 2-7 cont.'d. 3BC-Irish Bend nodule - (g) polarized light, (h) plain light.

i
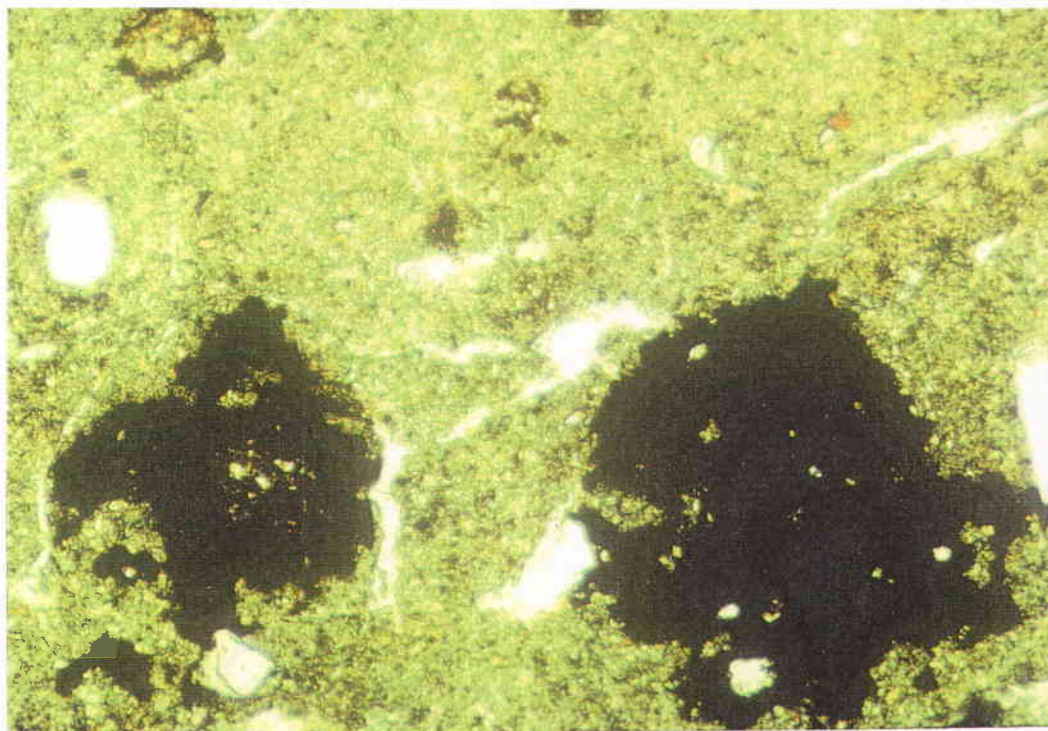
0.40mm

j
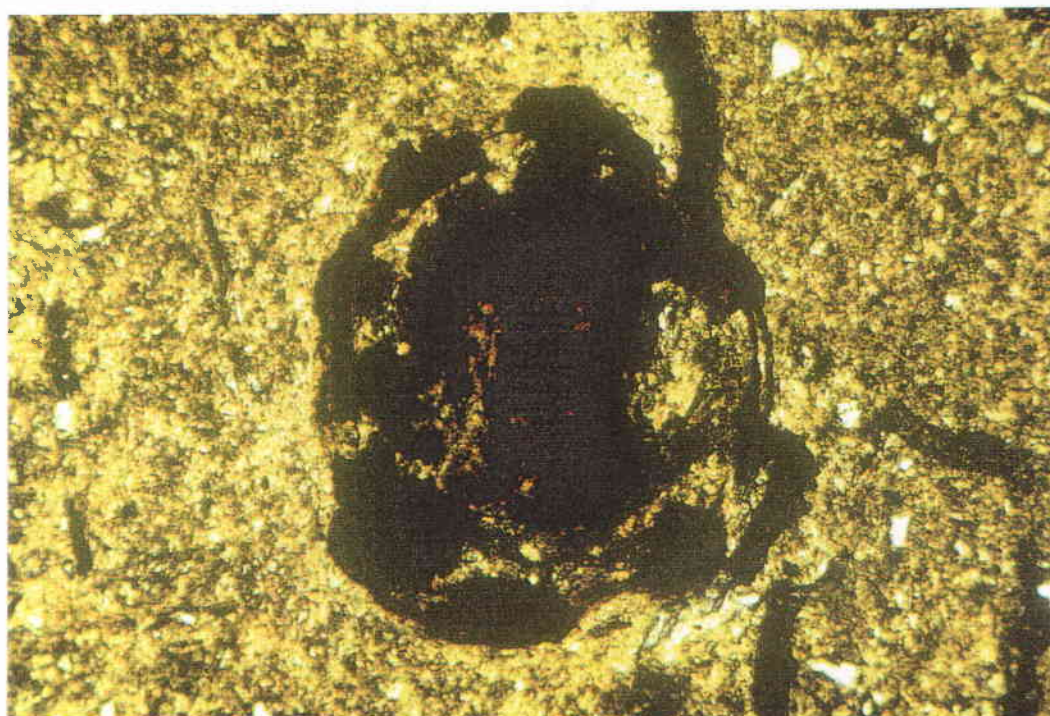
70µm

Figure 2-7 cont.'d. 3BC-Irish Bend nodules - (i) plain light, (j) polarized light.

k

1.0mm

l
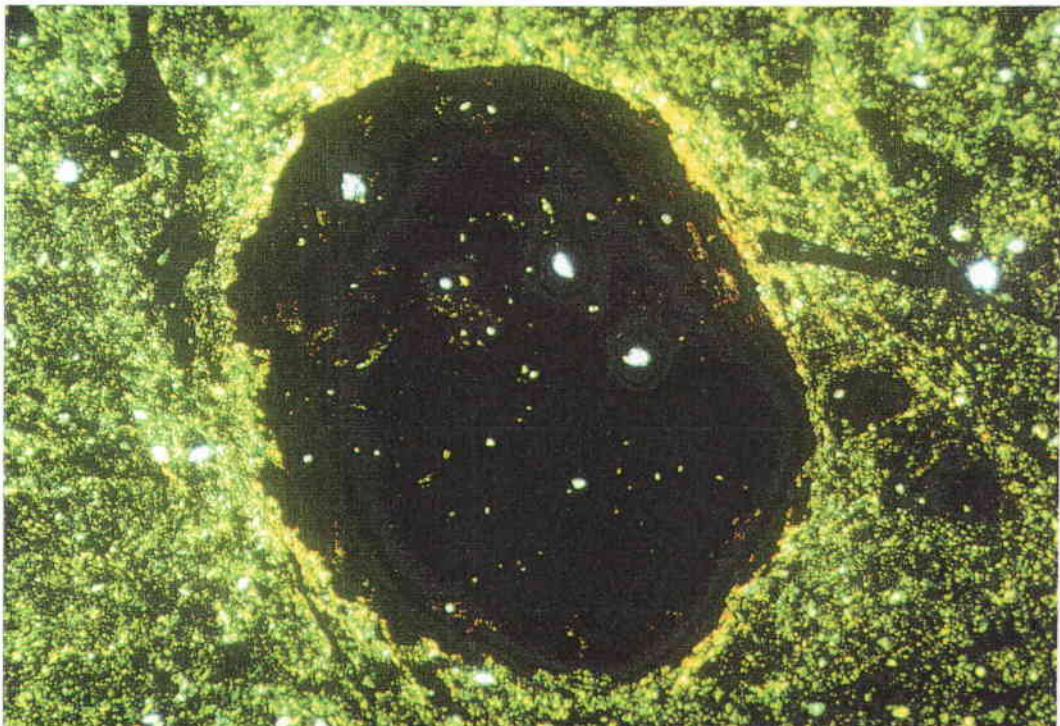
0.30mm

Figure 2-7 cont.'d. (k) Bss concretion (left), 3BC nodule (right), (l) Bss concretion (polarized light).

Table 2-4. Stable isotopic composition of the <0.2μm fraction of soil material from the J-F wetland.

Horizon	δO^{18} (o/oo)	δD (o/oo)
Bashaw Bss matrix	22.2	-83.0
Bashaw Bss concretion	22.0	-79.0
Bashaw 2Bt matrix	21.7	-88.0
Bashaw 2Bt concretion	18.9	-88.0
IB (3BC) matrix	21.8	-75.0
IB (3BC) nodule	19.6	-79.0
Dayton 2Bt matrix (malpass member)	21.6	-89.0

Halloysite has been found in young soils influenced by volcanic ash (Dudas and Harward, 1975) and deeply weathered soils derived from igneous material. Norgren (1962) has described small amounts of ash of probable Mazama origin in Willamette Valley soils, and there are large areas of extrusive igneous material within the foothills west of Corvallis. The halloysite in J-F could have resulted from the weathering of either of these materials and is a significant component of Jory mineralogy. Large amounts of kaolinite and halloysite within the J-F sediments, and lack of mica, K-feldspar, and hydroxy-interlayered components within the Bss matrix and concretions suggests the removal of the Greenback member prior to, or with, the deposition of the Holocene alluvium (Glasmann and Kling, 1980).

Table 2-5. **DCB-Fe-Mn** extracted from concretions, nodules, and soil matrix. n=6.

Horizon	Size	DCB-**Fe**	Std. Err.	DCB-**Mn**	Std. Err.
		----------------------- dgkg^{-1} ----------------------			
Bashaw Bss	large	16.61	1.62	7.78	1.03
Bashaw Bss	small	20.49	1.63	3.76	0.47
Bashaw Bss	matrix	2.33	0.03	0.16	0.011
Bashaw 2Bt	large	14.86	0.56	5.68	1.05
Bashaw 2Bt	small	14.76	2.42	3.01	0.20
Bashaw 2Bt	matrix	1.84	0.05	0.01	0.002
Irish Bend 3BC	large	8.55	1.26	1.09	0.04
Irish Bend 3BC	small	9.90	0.77	2.23	0.42
Irish Bend 3BC	matrix	2.08	0.07	0.03	0.003

a

1> 26-0911: Illite-2\ITM#1\RG - (K,H3O)Al2Si3AlO10(OH)   2> 99-0085: Mg-smectite, hydrated, n=3-7
3> 99-0120: DIVERMICULITE .5   DIVERMICULITE RE   4> 29-1487: Halloysite-7A - Al2Si2O5(OH)4
5> 14-0164: Kaolinite-1\ITA\RG - Al2Si2O5(OH)4

b

1> 26-0911: Illite-2\ITM#1\RG - (K,H3O)Al2Si3AlO10(OH)   2> 29-1487: Halloysite-7A - Al2Si2O5(OH)4
3> 99-0085: Mg-smectite, hydrated, n=3-7
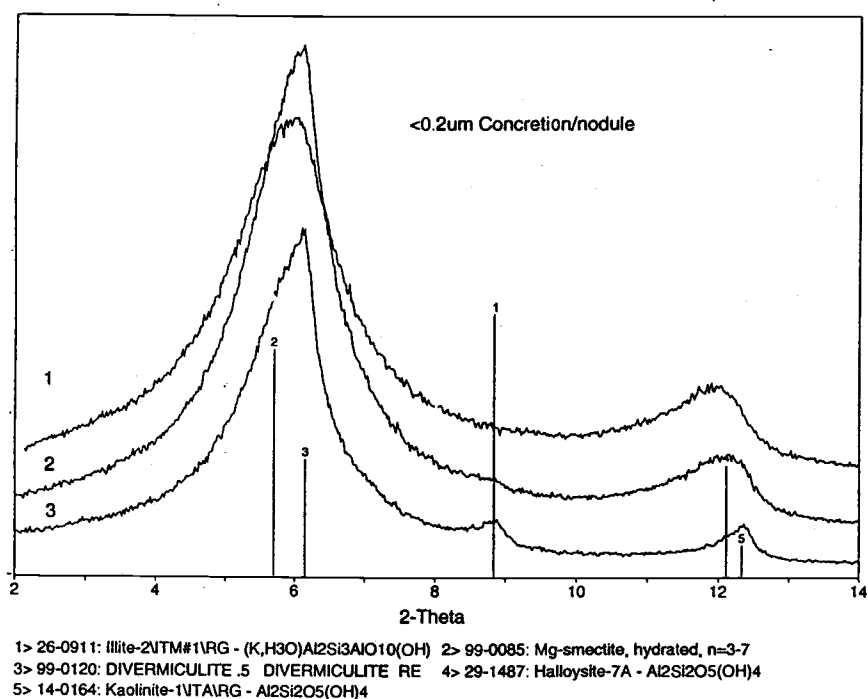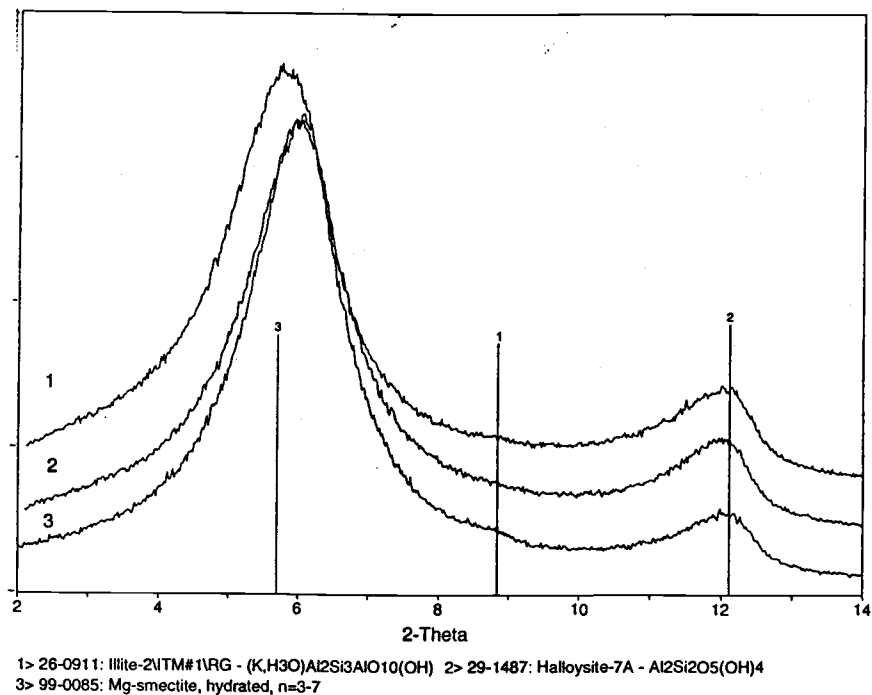
Figure 2-8 (a-b). Mineralogy of <0.2μm size fraction used for stable isotope analysis. (a) Concretion and nodule mineralogy. (b) Matrix mineralogy. 1=Bss 2=2Bt   3=3BC.

The amount of kaolinite, halloysite, and smectite in the J-F Bss reflect significant input of foothill materials since the deposition and possible removal of the Greenback member, sometime within the last 12ky. Large amounts of smectite are exported from the Coast Range/foothill landscapes as a function of stream dissection into deep, weathered profiles - the lower parts of which are smectite-rich (Glasmann, 1982).

The Bss matrix and concretions contain relatively fresh, unweathered Ca-plagioclase grains and laths whose probable origin is either the Coast Range tholeiitic and alkalic Siletz River basalts (Snavely et al., 1968) or the Columbia River basalts provenance. Abundant quartz within the alluvium and concretions is fresh, showing only slight etching and secondary precipitation features. These surface morphologies suggest that the source of this quartz is probably the Jory series or reworked Greenback remnants and its presence, with Ca-plagioclase grains, reflects the mixing of materials of different provenance, before the formation of the concretion. The Tyee is an arkosic sandstone and contains K-feldspar and white micas of Idaho batholith provenance (Heller et al. 1985). Potassium feldspar was not the dominant feldspar identified within the nodules and concretions within the J-F wetland and, along with Ca-feldspar and mica, should be largely removed in Jory soils due to weathering.

The similarity in isotopic composition of the < 0.2μm fraction of the Bss concretion and matrix fine clays demonstrates that these clays were either formed in the same (relatively enriched) meteoric environment and were not transported from widely different locations, or subsequently attained isotopic equilibrium with the modern groundwater. Similar concretion and matrix mineralogy, the incorporation of highly birefringent pressure oriented smectite and matrix components within the concretions, a significant decrease in Mn within the smaller concretions coupled with the same isotopic signatures between the matrix and concretion fine clays strongly suggests the current formation of the Bss concretions within the Holocene alluvium. It would not be possible to preserve the exterior pressure-oriented clays, or identical matrix fabric and individuals, during or after transport and mixing of soil materials.

Small pore sizes and pressure oriented clays around the outer shell of the concretions and the infilling of pores with Fe and Mn oxides (Schwertmann, 1988) will provide a restrictive environment to the diffusion of H_2O and gases and may create an environment protected from weathering with subtle effects on mineralogy and isotope signature. Clays formed in the same environment would show no differences in isotope signature through time, but a sealed surface and protected weathering environment could explain the subtle mica peaks, the lack of mixed layer phases, less halloysite, and an increase in vermiculite and kaolinite peaks (relative to smectite) within the Bss concretions.

The apparent lack of a difference in concretion distribution, the homogeneous matrix, and pronounced slickenside development throughout the Bss horizons, suggests the possibility that the alluvium is argillopedoturbated. This would make the estimation of where, within the 75+cm of Bss horizon, the concretions are predominantly formed, very difficult. Total OC concentration may provide a means for estimation. Rhoton et al., (1993) found the greatest amount of Fe-Mn concretions above the Btx contact in both eroded and uneroded soils. Nodule Iron and TOC were measured and, in the uneroded soil, nodule content and Fe_{DCB} increased and TOC values decreased with proximity to the Btx horizon. NRCS wet soils analytical data (1995) from this J-F location, show soil TOC contents of 4.56 percent in the Bashaw A horizon, 0.7% in the lower Bss horizon, 0.23 % in the 2Bt and 0.09% in the 3BC. The 2Bt and 3BC matrix-TOC data correspond to the values within the 2Bt concretions and 3BC nodules. Since matrix material is clearly incorporated into the Bss concretions among multiple bands of pressure oriented clays (Fig.2-7a-d), it is reasonable to assume that the concretion TOC may reflect the matrix value before cementation by Fe-Mn, and the sealing of the surface by pressure oriented smectite. If this assumption is correct, it would appear that these concretions are formed predominantly within the Bss3/Bss2 horizons (1-40 cm above the 2Bt contact). Extensive hydrology and redox data support this conclusion (Ch. 4).

It appears that the 2Bt is a separate stratigraphic unit and not a mixture of the Bss and 3BC horizons since it follows the contour of the underlying unit

(D'Amore, 1995), is intermediate in position, but is not intermediate in mica content, isotopic composition, chemistry, and concretion distribution. The 2Bt matrix and concretion mineralogy and matrix isotopic composition are nearly identical to those of the Bss, but the 2o/oo difference between matrix and concretion δO^{18} implies that the concretion clays precipitated from isotopically lighter meteoric water. These data suggest that these concretions formed rapidly enough, and are adequately cemented, to retain the signature of extra-valley provenance, while the matrix materials have continued to undergo pedogenic processes or illuviation which reflect the local meteoric signature and mask the extra-valley clays. Parsons et al. (1970) state that soils within the Willamette Valley have formed Bt horizons within 5250y, suggesting that significant illuviation of clay can occur within 5000y. There does seem to be some additional authigenesis of smectite before incorporation into concretions. The 2Bt concretion and 3BC nodule δO^{18} values seem to be an average between the 16-17o/oo that have been measured in better drained, Willamette formation extra-valley material (Glasmann, personal communication) and the values of 21-23o/oo that have been found in kaolinite and smectites weathered in Western Oregon (Lawrence and Taylor, 1971).

The 2Bt horizon has fewer redoximorphic concentrations than the Bss above and the 3BC below, and its matrix has the least amount of Fe and Mn. Pore depletions with oriented smectite in dense soil layers with perched water tables have been described by Vepraskas and Wilding (1983) as indicative of seasonal oxidation-reduction. These clays are presumably pressure-oriented as pores swell and close upon wetting, although this is not always a seasonal occurrence within the J-F Wetland. Neo-albans lining the pores, ped concentrations (Fig. 2-7f), diffuse boundaries and 'halos' around some concretions (Fig. 2-7e), Mn depleted rinds (Fig. 2-6d,f), and significantly less Mn in the smaller concretions (table 2-5) would indicate the continuing formation of concretions in a progressively Mn depleted matrix. Photomicroscopy of thin sections, matrix color, and DCB Fe-Mn concentrations suggests an inadequate amount of Fe-Mn to create the same distribution of concretions/nodules found within the Bss and

3BC horizons. Profile observations over two summers found the 2Bt horizon to remain wetter longer than either the Bss above and, the 3BC below. D'Amore (1995) found a longer duration of saturation and Fe-Mn reduction at the 100cm depth while water levels within the 3BC "dropped quickly" at this same J-F location. These observations and data indicate that the Fe-Mn within the 2Bt matrix stay reduced longer and have greater potential to be leached away with the rapidly falling lower water table. This suggests that 2Bt Fe and Mn have been removed after the deposition of this material.

The 3BC matrix and nodules show distinct mineralogical differences from the upper horizons, but they are isotopically indistinguishable from their counterparts in the 2Bt, suggesting similar provenance with the 2Bt. 2Bt concretions and 3BC nodule isotopic values indicate an extra-valley provenance due to lighter isotopic values, and grains of conchoidal step cleavage quartz in the 3BC nodules indicate origin in a glacial environment (Glasmann and Kling, 1980). Since the Willamette Valley and Coast Range were never glaciated and the "Willamette Valley lacks late Pleistocene continental till and associated outwash, and areas to the north show the definite presence of unmodified (by glaciers) Pleistocene non-glacial soil" (Reckendorf, 1992), these data support the interpretation that both the 3BC and 2Bt stratigraphic units formed by transport and deposition of sediments from Washington-Idaho-Montana with the 'Missoula floods'. Another factor may be isotopic contamination by metamorphic mica and/or vermiculite. The clay mineral data indicate that the amounts of these minerals were not sufficient to account for the stable isotopic differences.

The mineralogical similarities between the Bss and 2Bt strata, coupled with isotopic differences, suggest an extra-valley source for the 2Bt-concretion fine clay fraction. The Bss matrix and concretion is generally very smectitic with traces of halloysite and probably less than 2% illite. The 3BC mineralogy is quite different than the Bss and 2Bt. Although there is the presence of additional mica (10% illite) and vermiculite in the 3BC nodule-clay it appears as if the nodules formed early and inhibited weathering reactions that cause isotopic equilibrium with water. The preserved mica, vermiculite, kaolinite and trace chlorite is not in

isotopic equilibrium with modern day Willamette Valley pore water ($\delta O^{18} \sim -8o/oo$) and suggests this difference is also due to extra-valley provenance.

Currently we see very few roots in the 3BC horizon, but the peds from this horizon contain numerous tubular pores. Root tubules within some of the 3BC nodules surrounded by mineral grains of disparate provenance, coupled with a fragile, botryoidal external morphology indicates that these nodules were not transported and their initial formation began after the mixing of Missoula Flood materials with local Willamette Valley provenance and their deposition within an environment stable enough to colonize plants. It is possible that the botryoidal morphology could be a result of the cementation of smaller nodules called micronodules (Gallaher and Perkins, 1973), which could have been transported in the catastrophic valley flooding and later coalesced into the observed morphology, but mineralogy and photo-microscopy that relate the nodules to their current matrix do not support this supposition.

Micro-environmental Control on Concretion/Nodule/Matrix Chemistry

Iron and Mn chemistry are intimately linked, and the chemical differences between nodule size classes (Table 2-5) are important in deciphering the history of the redox environment and the age/time of formation of the nodules. The Fe-Mn enriched core, the Mn depleted rind, and the Mn 'depleted' smaller concretions (Fig.'s 2-6a-f), suggest that the concretions (Bss and 2Bt)have continued to form in a progressively Mn depleted matrix. We assume that the small nodules are younger relative to the large ones and are continuing to form as the matrix becomes depleted in Mn. Seter and Baham (1994) set up a transect within the Willamette Valley from better drained Argixerolls through poorly drained aqualfs and found large differences in nodule size and chemistry with depth, but also found the larger nodules to be more enriched in Mn relative to the smaller ones. The difference in shape and external morphology between the Bss-2Bt concretions vs. the 3BC nodules within the wetland appears to be related to soil texture and/or shrink-swell properties (Fig. 2-7k). The pressure oriented clay around the concretions, the general lack of birefringent oriented

material around the nodules, and the argillopedoturbation within the vertisol, suggests a mechanical explanation for the 'smoothing' and rounding of the surfaces. The continuing formation and the incorporation of pressure-oriented smectite, contributes to the creation of concentric-fabric concretions as opposed to irregularly shaped nodules.

Summary and Conclusions

Elemental distribution, fabric, structure, phyllosilicate and Fe oxide mineralogy between matrix and nodule material provide important data on the current, and long-term redox and hydrologic environment within the J-F wetland. Thin section and SEM evidence indicates that the Bss and 2Bt concretions, and the 3BC nodules began forming after the mixing of 'Missoula floods' material with materials of local provenance. SEM examination, Fe-Mn content distributions, isotopic composition, photo-microscopy, and XRD provide evidence that the Bss and 2Bt concretions within the J-F wetland are still forming today in a Mn 'depleted' matrix as a function of valley stratigraphy, climate and biogeochemical environment. These data provide evidence that Holocene wetland genesis appears to be continuing on specific landscapes and surfaces within the Willamette Valley.

Elemental distribution and photo-microscopy indicate the continuing formation of the concretions and nodules within the J-F environment. The disparate isotopic composition between the 2Bt/3BC matrices and their concretions/nodules indicate that the fine clays within these concentrations have formed in isotopically lighter water, are of probable 'Missoula floods' provenance, and were not initially weathered in the current meteoric environment. Isotopic differences suggest that the 2Bt concretions and 3BC nodules began forming quickly enough to retain more of their early meteoric (extra-valley) signature as soil genesis and clay illuviation/infiltration has continued to occur. Based upon stratigraphy, geomorphic surface and isotopic composition, it is likely that some

of the nodules in the 3BC may near 38ky, while the 2Bt concretions will be within 13-34ky and, the Bss nodules between 600y and 3300y.

Nearly identical mineralogy, stratigraphic position, and isotopic signatures between the Malpass member (Dayton 2Bt) and J-F 2Bt suggests that the two units are the same and the J-F alluvium may have incised an older surface after the deposition of the Malpass and Greenback units. Radiocarbon dating of the TOC within concretions/nodules and their respective matrices would be a logical next step to further understanding of their age and rate of formation. These data would, in turn, elucidate geomorphic relationships and long-term processes operating within the J-F and other Willamette Valley hydric soils on similar surfaces and/or landscape positions.

Literature Cited

Aguilera, N. H., and M. L. Jackson. 1953. Iron Oxide Removal from Soils and Clays. Soil Sci. Soc. Am. Proc. 17:359-364.

Arshad, M. A. and R. J. St. Arnaud. 1980. Occurrence and Characteristics of Ferromanganiferous Nodules in Some Saskatchewan Soils. Can. J. Soil Sci. 60: 685-695.

Austin, W. 1994. Duration of saturation and redox potentials in selected Willamette Valley soils. M.S. Thesis, Oregon State University, Corvallis, Or. 256 pp.

Balster, C. A. and R. B. Parsons. 1969. Late Pleistocene Stratigraphy, Southern Willamette Valley, Oregon. Northwest Sci. 43:116-129.

Bretz, J. H. 1969. The Lake Missoula Floods and the Channeled Scabland. J. of Geology. 77:505--543.

Bartlett, R. J. and B. R. James. 1993. Redox Chemistry of Soils. Advances in Agronomy. 50:151-208.

Boersma, L., G.H. Simonson and D.G. Watts. 1972. Soil Morphology and Water Table Relations: II. Correlation Between Annual Water Table Fluctuations and Profile Features. Soil Sci. Soc. Am. Proc. 36:649-654.

Blaylock, M. J. and B. R. James. 1992. Oxidation - Reduction Behavior of Selenite in Soils. Soil Sci. Soc. Am. J. (submitted)

Blume, H. P. 1988. The Fate of Iron During Soil Formation in Humid-Temperate Environments. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Bretz, J. H. 1969. The Lake Missoula Floods and the Channeled Scabland. J. of Geology. 77:505--543.

Brewer, R. 1976. Fabric and Mineral Analyses of Soils. Robert E. Krieger Publishing. Huntington, New York.

Carter, V., M. S. Bedinger, R. P. Novitski and W. O. Wilen. 1979. Water Resources and Wetlands, in Wetland Functions and Values : The State of Our Understanding, P. E. Greeson, J. R. Clark, and J E. Clark, eds., American Water Resources Assoc., Minneapolis, Minn., pp. 344-376.

Carter, V. 1986. An Overview of the Hydrologic Concerns Related to Wetlands in the United States, Can. J. Bot. 64:364-374.

Cogger, C. G., and P. E. Kennedy. 1992. Seasonally Saturated Soils in the Puget Lowland I. Saturation, Reduction and Color Patterns. Soil Sci. Vol. 153, No. 6.

Cogger, C. G., P. E. Kennedy, and D. Carlson. 1992. Seasonally Saturated Soils in the Puget Lowland II. Measuring and Interpreting Redox Potentials. Soil Sci. Vol. 154.

D'Amore, D. V. 1995. The Stratigraphy, Hydrology, and Redoximorphic Character of the Jackson-Frazier Wetland. M.S. Thesis. Oregon State University, Corvallis, Or.

Diers, R., and J. L. Anderson. 1984. Part I, Development of Soil Mottling, in Soil Survey Horizons, winter 1984. pp. 9-12.

Drosdoff, M., and C. C. Nikiforoff. 1940. Iron-manganese Nodules in Dayton Soils. Soil Sci. 49:333-345.

Dudas, M. J. and M. E. Harward. 1975. Weathering and Authigenic Halloysite in soils developed in Mazama Ash. Soil Sci. Soc. Am. Proc. 39:561-566.

Gallaher, R. N., and H. F. Perkins. 1973. Soil Nodules: I. X-ray Spectrograph and Electron Microprobe Analyses. Soil Sci. Soc. Amer. Proc. 37: 465-469.

Glasmann, J. R. 1982. Soil Solution Chemistry, Profile Development, and Mineral Authigenesis in Several Western Oregon Soils. Ph.D. Thesis, Oregon State Univ. Univ. Microfilms. Ann Arbor, Mich. (Diss. Abstr. 82:16636).

Glasmann, J. R. and G. F. Kling. 1980. Origin of Soil Materials in Foothill Soils of Willamette Valley, Oregon. Soil Sci. Soc. Am. J., 44:123-130.

Glasmann, J. R. and G. H. Simonson. 1985. Alteration of Basalt in Soils of Western Oregon. Soil Sci. Soc. Am. J. 49:262-272.

Glenn, J. L. 1965. Late Quaternary Sedimentation and Geologic History of the North Willamette Valley, Or. Ph.D. thesis, Oregon State University, Corvallis, Or.

Hansen, H. C. B., O.K. Borggard, and J. Serensen. 1994. Evaluation of the Free Energy of Formation of Fe(II) - Fe(III) hydroxide-sulphate (green rust) and its reduction of nitrite. Geochimica et Cosmochimica Acta, Vol. 58, No. 12, pp. 2599-2608.

Heller, P. L., Peterman, Z. E., O'Niel, J. R. and M. Shafiqullah. 1985. Isotopic Provenance of Sandstones from the Eocene Tyee Formation, Oregon Coast Range. Geological Soc. Am. Bull. 96:770-780.

Jackson, M. L. 1979. Soil Chemical Analysis-Advanced Course. 2nd ed., 11th Printing. Published by Author, Madison, WI 53705.

Jackson, M. L., Lim, C. H. and L. W. Zelazny 1979. Oxides, Hydroxides and Aluminosilicates. In A. Klute (ed.) Methods of Soil Analysis Part 1, 2nd ed.

Knight, R. L., T. W. McKim, and H. R. Kohl. 1987. Performance of a Natural Wetland Treatment System for Wastewater management. J. Water Poll. Control Federation. 59:746-754.

Lawrence, J. R. and H. P. Taylor. 1971. Deuterium and Oxygen-18 Correlation: Clay Minerals and Hydroxides in Quaternary Soils Compared to Meteoric Waters

Lovely, D. R. 1993. Dissimilatory Metal Reduction. Annu. Rev. Microbiol. 47:263-290.

Marshall, J. 1985. A Value Assessment of the Jackson-Frazier Wetland. Unpublished MS thesis, Oregon State University, Corvallis, Or.

Mehra, O. P. and M. L. Jackson. 1960. Iron Oxide Removal from Soils and Clays by a Dithionite-Citrate System Buffered with Sodium Bicarbonate. Clays Clay Miner. 7:317-327.

Miller, D.M., T. Tang and D. W. Paul. 1993. Electrolytic Reduction of Soil Suspensions. Soil Sci. Soc. Am. J. 57:356-360.

Minerals in Soil Environments. 1989. SSSA Book Series: 1 (eds.) J. B. Dixon and S.B. Wood. p.393.

Mitsch, W. J. and J. G. Gosselink. 1993. Wetlands. Van Nostrand Reinhold Publishing, New York, New York. 698 p.

Moormann, F. R., and H. T. J. van de Wetering. 1985. Problems in Characterizing wetland soils. pp. 53-68. In Anonymous (ed.). Wetland Soils: Characterization, Classification, and Utilization. Proc. of a workshop held March 26 to April 5, 1984. Int. Rice Res. Inst., Los Banos, Phillippines.

Natural Resource Conservation Service. 1995. Wet Soils Monitoring, Benton County, Oregon. (CP93-OR076).

Norgren, J. A. 1962. Thin-section Micromorphology of Eight Oregon Soils. M.S. Thesis. Oregon State Univ., Corvallis, OR.

Parsons, R.B., C.A. Balster, and A.O. Ness. 1970. Soil Development and Geomorphic Surfaces, Willamette Valley Oregon. Soil Sci. Soc. Am. Proc. 34:485-491.

Phillippe, W. R., Blevins, R. L., Barnhisel, R. I. and H. H. Bailey. 1972. Distribution of Nodules From Selected Soils of the Inner Blue Grass Region of Kentucky. Soil Sci. Soc. of Amer. Proc. 36: 171-173.

Reckendorf, F. 1992. Geomorphology, Stratigraphy, and Soil Interpretations, Willamette Valley, Oregon. In: Proceedings of the Eighth International Soil Management Workshop: Utilization of Soil Survey Information for Sustainable Land Use. (ed. J. M. Kimble). July 11-24, 1992. May, 1993.

Rhoton, F. E., Bigham, J. M. and D. G. Schulze. 1993. Properties of Iron-Manganese Nodules from a Sequence of Eroded Fragipan Soils. Soil Sci. Soc. Am. J. 57:1386-1392.

Schwertmann, U. 1988. Occurrence and Formation of Iron Oxides in Various Pedoenvironments. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Schwertmann, U. land R. M. Taylor. 1989. Iron Oxides. pp.379-437 In: F.B. Dixon and S.B. Weed (eds.) Minerals in Soil Environments. Soil Environments. Soil Sci. Soc Am., Madison, WI.

Seter, L. M. and J. Baham. 1994. Geochemical Characteristics of Iron-Manganese Nodules in Seasonally-Flooded Soils in the Willamette Valley, Oregon. P.249. In Agronomy Abstracts. ASA, Madison, WI.

Snavely, P. D., N. S. MacLeod and H. C. Wagner. 1968. Tholeiitic and Alkalic Basalts of the Eocene Siletz River Volcanics, Oregon Coast Range. Am. J. Sci., 266:454-581.

Soil Survey Staff. 1992. Keys to Soil Taxonomy, fifth edition. SMSS Tech. Monogr. No.7. Virg. Polytech Inst. and State Univ., Blacksburg.

Somera, R. D. 1967. Iron and Manganese Distribution and Seasonal Oxidation Changes in Soils of the Willamette Drainage Sequence. Unpublished M.S. Thesis. Oregon State University, Corvallis, Oregon.

Stumm, W. and B. Sulzberger. 1992. The Cycling of Iron in Natural Environments: Considerations Based on Laboratory Studies of Heterogenous Redox Processes. Geochimica et Cosmochimica Acta. 56:3233-3257.

Tardy, Y. and D. Nahon. 1985. Geochemistry of Laterites, Stability of Al-Goethite, Al-Hematite, and Fe^{+3}-Kaolinite In Bauxites and Ferricretes: An Approach to the Mechanism of Nodule Formation. Am. J. of Sci. 285:865-903.

van Breeman, N. 1988. Long-term Chemical, Mineralogical, and Morphological Effects Of Iron-redox Processes In Periodically Flooded Soils. 1988. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Vepraskas, M. J. and J. Bouma. 1976. Model Experiments On Mottle Formation Simulating Field Conditions. Geoderma. 15:217-230.

Vepraskas, M. J. 1992. Redoximorphic Features for Identifying Aquic Conditions. Technical Bulletin 301. North Carolina Agricultural Research Service, North Carolina State University, Raleigh, North Carolina.

Vepraskas, M. J. and L. P. Wilding. 1983. Albic Neoskeletans in Argillic Horizons as Indices of Seasonal Saturation and Iron Reduction. Soi Sci. Soc. Am J. 47:1202-1208.

von Gunten, U. and J. Zobrist. 1993. Biogeochemical Changes in Groundwater-infiltration Systems: Column Studies. Geochimica et Cosmochimica Acta. 57:3895-3906.

Wang, H. D., G. N. White, F. T. Turner and J. B. Dixon. 1993. Ferrihydrite, Lepidocrocite, and Goethite in Coatings from East Texas Vertic Soils. Soil Sci. Soc. Am. J. 57:1381-1386.

Zinn, J. A., and C. Copeland. 1982. Wetland Management, Congressional Research Service, The Library of Congress, Washington, D. C., 149 p.

Chapter III.

Age and Rate of Formation of Fe-Mn-P Concretions in an Oregon Hydric Soil.

S.R. Stewart and J. E. Baham.

Abstract

Wetland soils with complex stratigraphy and redoximorphic features occur on the margin of the Willamette Valley, Oregon. The Jackson-Frazier wetland vertisols have three distinct stratigraphic units which rest unconformably upon each other and are mapped on the Ingram geomorphic surface (600-3300y). These strata contain obvious, macroscopic concentrations in the form of concretions in the Bss and 2Bt horizons and nodules in the 3BC silts. The concretions/nodules are enriched in Fe and P, relative to the matrix soil, by as much as an order of magnitude. Mn enrichment can exceed two orders of magnitude. During the reduced phase of the annual redox cycle, concentration values for dissolved and KCl/HCl Fe^{+2} in Willamette Valley wet soils can be as high as (40-60mgFe^{+2}kg^{-1}soil) 0.8-1.1m$\underline{M}Fe^{+2}$ and (500-6900mgFe^{+2}kg^{-1}soil) 9-124m$\underline{M}Fe^{+2}$, respectively. These values are sufficient to support concretion/nodule formation within the known age of the associated geomorphic surface. Total organic C within the Bss concretions 4-9mm size fraction was dated at 1,500 ± 80y of age. Comparing the age of the concretion-C and the stratum in which the concretions are formed places the larger, older concretions between 1500-3300y old. The amount of Fe^{+2} available in the reduced-soil phase compared to the degree of Fe_{DCB} enrichment within the larger concretions suggests a period of 2300-3500y for this enrichment to occur, with an average near 2800y.

Introduction

Wetlands have been recognized for a variety of terrestrial ecosystem functions including flood control, groundwater recharge (Carter, 1986; Carter et al., 1979), wildlife habitat (Mitsch and Gosselink, 1993), bioremediation and wastewater treatment (Knight et al., 1987). Phosphorus is generally considered the limiting water quality nutrient (Meyer, 1979; Ryding and Rast, 1989) and one wetland mechanism for the improvement of water quality may be the sequestering of P within the nodules and concretions. Understanding the rate at which these concretions form will enable us to better estimate the capacity and the time frame for immobilization of P within the wetland.

The Jackson-Frazier wetland is Holocene alluvial fan/valley fill that experiences repetetive annual flooding and drying cycles. Coupled with available organic C and temperature, these cycles facilitate microbial reductive dissolution and segregation of Fe, Mn and other redox sensitive metals into redoximorphic concentrations and/or depletions (Somera, 1967; Cogger and Kennedy, 1992; Vepraskas, 1994; Miller et al., 1993; Lovely, 1993). There are three distinct stratigraphic units within the Jackson-Frazier wetland corresponding to the Bss, 2Bt, and 3BC horizons, all of which have macroscopic Fe-Mn-P concretions and nodules.

Willamette Valley Fe-Mn nodules have been studied by Drosdoff and Nikiforoff (1940), Somera (1967), Seter and Baham (1994), and Balster and Parsons (1969). Drosdoff and Nikiforoff, Somera, and Seter and Baham studied the distribution and Fe-Mn chemistry of concretions/nodules with depth within different Willamette Valley soils. Seter and Baham (1994) found nodules from wet soils within the Willamette Valley to be greatly enriched in P. Other authors have found a relationship between Fe and P. Arshaud and St. Arnaud (1980) found up to 1 percent P by weight in nodules, and Schwertmann and Fanning (1976) found nodules to be enriched in P by as much as 5 fold over the soil matrix.

The presence, distribution and quantities of redoximorphic concentrations, the reductive dissolution of Fe, Mn, and redox sensitive elements, oxide surface chemistry, and the mineralogy of Fe, Mn, and various redox sensitive metal-oxides as related to temperature and environment have been studied by various authors (Wang et al., 1993; Cogger et al., 1992; van Breemen, 1988; Schwertmann, 1988; Bartlett and James, 1993; Blaylock and James, 1992; Tardy and Nahon, 1985; Stumm and Sulzberger, 1992; Miller et al., 1993; Lovely, 1993; Vepraskas and Bouma, 1976; Blume, 1988; Hansen et al., 1994; Gunten and Zobrist, 1993).

There is very little discussion of age or rate of formation of concretions/nodules in the literature. Schwertmann and Fanning (1976) found that concretions in Bavarian Loess must have continued to form during the last 2000y based upon the incorporation of P from 2000y old bones, but there is little information concerning the age and/or rate of formation of nodules and concretions within soil profiles.

Our objectives in this study were to: i) estimate the age of the Bss concretions by dating the C^{14} within the concretions, ii) to estimate their rate of formation and, iii) estimate the rate at which they sequester P and, iv) characterize the Fe-Mn-P chemistry, elemental distribution, O^{18} and H^2 isotope fractionation, and v) to relate these data to the known age of the geomorphic surface upon which the J-F Holocene alluvium is deposited. These data will help us better determine the age and rate of formation of the Fe-Mn-P rich concretions within the Bss alluvium and the rate at which P is sequestered within them.

Methods and Materials

Dried concretions and nodules were separated into two size classes; the Bashaw Bss and 2Bt nodules were separated into 0.5-1mm and 3-9mm size classes to observe any differences between the largest and smallest size fractions. The 3BC nodules were separated into 0.5-1mm and 2-3mm classes due to size differences between the concretions and nodules. The samples were then gently ground into a fine powder in a diamondite mortar and pestle (h=9).

Acid Ammonium Oxalate Fe (Fe$_{ox}$)

Fifty milligrams of ground material were weighed into 50mL centrifuge tubes and 10mL of $0.2\underline{M}$ acid ammonium oxalate (AAO) was added to the powders. The addition of the AAO was performed in the absence of light. The tubes were shaken for 2.5 hours and then centrifuged at (1086G) for 30 minutes. The supernatant was decanted, diluted to 50mL and analyzed colorimetrically for Fe.

Dithionite-Citrate-Bicarbonate Fe (Fe$_{DCB}$)

Fresh samples were weighed for (DCB) extractions and 5mL of deionized H2O and 5mL of $0.5\underline{M}$ citrate:$0.2\underline{M}$ Na-bicarbonate stock were added to 50mg of sample. The samples were then placed in a 75C water bath for 5 minutes. Approximately 0.33g of sodium hydrosulfite was added to each of the tubes which were then shaken for 30 minutes. The samples were then centrifuged for 20 minutes at (1086G) and the supernatant was decanted into 50 mL volumetric flasks. This procedure was repeated two additional times on the same samples.

KCl/HCl Fe^{+2}

Soil cores were taken at 15cm intervals from 0-90cm depth and placed in 250mL plastic bottles containing 100mL of $1.0\underline{M}$ KCl in $0.1\underline{N}$ HCl solution to prevent the oxidation of Fe^{+2}. Samples were shaken for 12hr and centrifuged.

Colorimetric Analyses

The Fe_{ox}, KCl/HCl-Fe, and Fe_{DCB} were analyzed after the method of Lim and Jackson (1982). 150µL of sample were placed in 5.1mL nanopure H_2O, 0.25mL of 1.0M sodium acetate/acetic acid buffer, 0.25mL of 2% hydroxylamine hydrochloride, and 0.25mL of 0.4% 1,10 phenanthroline. The samples were mixed and set aside for at least 0.5hr before being analyzed in a Hewlett Packard 8453 UV visible spectrophotometer. Standards were made in the linear working range of 0-2.5ppm from a 50ppm stock solution of ferrous ammonium sulfate hexahydrate.

Colorimetric determination of DCB and AAO-Phosphorus

Phosphorus was determined colorimetrically using the Olsen and Summers method as modified by Wolfe and Baker (1990). All reagents and procedures were identical with the exception of an additional 650µL of 0.17M ammonium molybdate solution to eliminate the interference due to complexation of the molybdate with the oxalate. The final sample volume was 6mL and was analyzed on the Hewlett Packard 8453 UV visible spectrophotometer.

The Fe_{DCB} samples were bubbled with air for 2hr to oxidize the dithionite. The DCB samples were bubbled with air for 2hr to oxidize the dithionite. This eliminates the "over reduction" of molybdate and inaccuracy in the analysis of P.

Total Organic Carbon

Total organic C was determined by dry combustion and subsequent analysis of CO_2.

SEM Characterization

Whole and fractured concretions/nodules from each stratigraphic unit were mounted on Al stubs with Duco cement and sputter coated with Au-Pd and examined with an AMR 1000 scanning electron microscope equipped with a Kevex energy dispersive X-ray analyzer.

C^{14}

Approximately 130g of concretions, size 4-9mm, were gently ground to a fine powder. This material was C^{14} dated by atomic mass spectrometry at the department of Anthropology at the University of Riverside, California.

Results

Chemistry

Fe_{DCB}, Fe_{OX}, Mn_{DCB}, Mn_{OX}, TOC, and P data are summarized in tables 3-1 through 3-5. There are subtle differences in Fe-Mn chemistry between the concretion rind and core, and significant differences between matrix and concretion/nodule chemistry as a function of stratigraphy and size. One of the most striking features of all concretions/nodules is their elemental enrichment relative to the surrounding matrix soil (Tables 3-2 and 3-3). The Bss concretions are enriched 7-9x in Fe_{DCB} and 11-13x in Fe_{OX} with respect to the matrix, depending on size class. The 2Bt concretions are enriched 8x in Fe_{DCB} and 20-24x in Fe_{OX} and the 2Bt matrix is the most depleted (in Fe_{DCB} and Fe_{OX}) of these strata. The 3BC nodules show the least enrichment relative to the matrix, being only 4-5x enriched in Fe_{DCB} and 13-17x in Fe_{OX}. Potassium chloride/HCl-Fe values ranged from 6900mgkg^{-1} in the surface 15 cm to 3000mgkg^{-1} in the Bss3 horizon at 75-90cm depth (Table 3-5).

Although there were no significant differences in Fe content between concretion size classes, the larger concretions contained more Mn (% weight) than the smaller size class. The Bss concretions showed the least enrichment of Mn, 25-50x in Mn_{DCB} and 5-13x in Mn_{OX} with respect to the matrix. The 2Bt concretions show the greatest enrichment, 250-475x in Mn_{DCB} and 70-150x in Mn_{OX}. 2Bt-concretion-Mn values are comparable to the Bss and 3BC; the high enrichment value is a function of the matrix depletion of Mn. The 3BC nodules are enriched 40-80x in Mn_{DCB} and 30-40x in Mn_{OX}.

Phosphorus concentrations are summarized in table 3-4 and are high within the concretions/nodules and matrixes, but showed less enrichment than Fe or Mn. The enrichment factor of P_{DCB} within the concretions and nodules increased with depth. The Bss concretions were enriched by only 1.7x, the 2Bt concretions by a factor of 2.4x, and the 3BC nodules by a factor of 3.0x. This trend was reversed for the P_{ox} with the greatest enrichment occurring in the Bss concretions - 2.2x. The 2Bt concretions and 3BC nodules were enriched 1.3x.

The total organic carbon (TOC) within the concretions, nodules and matrix decreased with depth ranging from 1.2 percent weight in the Bss concretions, to 0.1 percent in the 3BC nodules. Values averaged 0.8 percent within the Bss concretions; 0.5 percent within the 2Bt concretions and 0.2 percent within the 3BC nodules (Table 3-1).

Table 3-1. Mean values for total organic carbon in concretions, nodules, and matrices.

Stratigraphic Unit	Concretion/Nodule	Std. Err. n=6	*Matrix
	----------------------------------dgkg-1-------------------------		
Bashaw Bss	0.77	0.082	1.0-4.6
Bashaw 2Bt	0.47	0.052	0.23
Irish Bend	0.18	0.122	0.12

* NRCS wet soils monitoring data, Benton County, 1995.

Table 3-2. Total **Fe** extracted from soil matrix, and large and small concretions/nodules. n=6.

Horizon	Size	Fe_{DCB}	Std. Err.	Fe_{OX}	Std. Err.
		----------------------------dgkg^{-1}----------------------------			
Bashaw Bss	large	16.61	1.62	3.37	0.173
Bashaw Bss	small	20.49	1.63	3.88	0.205
Bashaw Bss	Matrix	2.33	0.03	0.31	0.003
Bashaw 2Bt	large	14.86	0.56	3.70	0.139
Bashaw 2Bt	small	14.76	2.42	2.97	0.096
Bashaw 2Bt	Matrix	1.84	0.05	0.15	0.009
Irish Bend 3BC	large	8.55	1.26	3.84	0.064
Irish Bend 3BC	small	9.90	0.77	2.94	0.019
Irish Bend 3BC	Matrix	2.08	0.07	0.22	0.006

Table 3-3. Total **Mn** extracted from soil matrix, and large and small concretions/nodules. n=4.

Horizon	Size	Mn_{DCB}	Std. Err.	Mn_{OX}	Std. Err.
		---------------------------dgkg^{-1}--------------------------			
Bashaw Bss	large	7.78	1.03	1.83	0.038
Bashaw Bss	small	3.76	0.47	0.51	0.026
Bashaw Bss	matrix	0.16	0.011	0.14	6.7E-4
Bashaw 2Bt	large	5.68	1.05	1.46	0.05
Bashaw 2Bt	small	3.01	0.20	0.68	0.02
Bashaw 2Bt	matrix	0.01	0.002	0.01	3.3E-4
Irish Bend 3BC	large	1.09	0.04	0.58	0.02
Irish Bend 3BC	small	2.23	0.42	0.83	0.03
Irish Bend 3BC	matrix	0.03	0.003	0.02	3.3E-4

Table 3-4. **P** extracted from concretions, nodules and soil matrix. n=6.

Horizon	Size	P_{DCB}	Std. Err.	P_{OX}	Std. Err.
		\-dgkg^{-1}\-			
Bashaw Bss	Concretions	0.34	0.055	0.08	0.011
Bashaw Bss	Matrix	0.21	0.019	0.04	0.003
Bashaw 2Bt	Concretions	0.37	0.051	0.08	0.008
Bashaw 2Bt	Matrix	0.16	0.022	0.06	0.005
3BC-Irish Bend	Nodules	0.56	0.068	0.09	0.019
3BC-Irish Bend	Matrix	0.19	0.041	0.07	0.002

Table 3-5. **KCl/HCl-Fe^{+2}** with depth in the Bashaw Bss horizons. n=3

Depth	KCl/HCl-Fe^{+2}	Std. Err.
----------cm----------	------------------mgkg^{-1} soil------------------	
15-30	6909	2427
30-45	4354	2296
45-60	6695	567
60-75	3784	45
75-90	3075	463

Discussion

The segregation of Fe and Mn into various redoximorphic concentrations and depletions has been shown to be common in soils that undergo cycles of oxidation and reduction. The difference in these elements between concretion/nodule size classes is important in deciphering the history of the redox environment and the age/time of formation of the nodules. The more homogeneous distribution of Fe and Mn within the Bss concretions relative to the 2Bt concretions, coupled with the amounts of Fe and Mn in the Bss matrix, is probably a function of stratigraphic position, seasonal deposition of fresh material, argillopedoturbation, and the age of the depositional surface (Fig. 1-2). The Fe-Mn enriched core, the Mn depleted rind (Fig.2-6), and the Mn 'depleted' smaller concretions (Table 3-2), suggests that these features have continued to form in a progressively Mn depleted matrix, and the smaller concretions are younger relative to the large ones. This elemental distribution agrees with results reported by Arshad and St. Arnaud (1980), Schwertmann and Fanning (1976), Phillippe et al. (1972) and Drosdoff and Nikiforoff (1940). It is difficult to compare the trends found in J-F with these studies due to the fact that analytical

techniques were not given (Drosdoff and Nikiforoff), were different (Arshad and St. Arnaud) and/or, were performed on different, much older soils with different climate, texture, vegetation, and hydrologic character.

The most detailed study on the distribution of nodules with depth was done by Seter and Baham (1994). They found large differences in nodule size and chemistry with depth, which did not occur below the A horizon in J-F, probably due to argillopedoturbation within the Bss horizons of the vertisol. Seter and Baham (1994) also studied the Dayton soil series and reported slightly higher values than Drosdoff and Nikiforoff. The upper 3BC under the J-F vertisol had greater amounts of nodules than indicated by either study (2.0% by weight), but was more like that found by Seter and Baham (1.5%) as opposed to Drosdoff and Nikiforoff (0.8%) at the same stratigraphic location. The fact that the differences in Mn concentrations between concretion and nodule size classes agreed with the results found by Seter and Baham (1994), and Drosdoff and Nikiforoff (1940), suggests that these features within hydromorphic soils in the Willamette Valley are continuing to form as the matrix becomes progressively Mn depleted. A number of studies note this trend and suggest the more rapid depletion of Mn within the soil matrix.

Enrichment of P_{DCB} increased with depth in the J-F wetland. This distribution is different than that found by Rhoton et al. (1993) in the Mississippi River Valley and Seter and Baham (1994) within the Willamette Valley. The high shrink-swell smectites, long-term saturated conditions, and lithologic discontinuities within the J-F wetland make comparisons of the total amounts and distributions of concretions/nodules with other studies of soils lacking these features, problematic. Phosphorus concentrations and degrees of enrichment within the J-F concentrations are comparable to values found within other nodules. Arshad and St. Arnaud (1980) found nodule-P up to 1% by weight, and Schwertmann and Fanning (1976) found up to 5 fold enrichment of P compared to the soil matrix. Given the estimated age of the Bss concretions, we calculate an average rate of P sequestration at $0.4 kgPha^{-1}y^{-1}$. It is assumed that P sequestered in concretions and nodules is unavailable for plant uptake and is

not readily transported. These data indicate an additional important geochemical mechanism in water quality dynamics and the treatment of water by wetlands, aside from plant uptake of P.

Age by Geomorphic Surface and Stratigraphic Unit

The Jackson-Frazier wetland has been shown to be composed of older foothill alluvium deposited as alluvial fan/valley fill material with macroscopic Fe-Mn concretions. Although the concretions and nodules in the wetland began forming after the transport and deposition of material of disparate provenance, the age of the geomorphic surface and underlying stratigraphy allow us to make only the roughest estimates of age. The age of the J-F stratigraphic units places the 3BC nodules at <38ky; the 2Bt concretions at <15ky, and the Bss concretions at <3300y. Evidence of continuing nodule/concretion formation makes the estimation of their rate of formation less problematic.

Isotopic Data

The upper age limit of the 3BC nodules and 2Bt concretions can be estimated using the δO^{18} isotopic signatures. We know that these features initially formed rapidly enough to retain the isotopic signature of extra-valley provenance, which has since been masked in the matrix due to continued authigenesis and/or infiltration of the clayey alluvium from above. Coupled with the age of the stratigraphic units, these data indicate that the oldest 3BC nodules and 2Bt concretions may be near 38ky and 15ky, respectively. The similar O^{18} signature for the fine clays within the Bss concretions and matrix indicate that these clays were formed within the same meteoric environment and location, show no extra-valley provenance, and therefore must have been formed or deposited after the last of the Pleistocene flooding (<10ky). The age of the geomorphic surface upon which the Bss alluvium is deposited refines this value to <3290y.

Age by Radiocarbon Dating

Total organic C decreased with depth as would be expected. The Bss concretions contain the greatest total concentration of C, therefore we used these features for C dating. Low amounts of TOC in the 2Bt and 3BC concretions and nodules, combined with the age of the stratigraphic units (2Bt:<34ky, 3BC:>38ky) made C dating within the 3BC nodules and 2Bt concretions expensive and impractical. We would, however, based upon knowledge that the Holocene alluvium was deposited as alluvial fan material upon the Ingram surface, expect the C within the Bss concretions to yield an age of >600y and <3300y. The age of the C^{14} within the Bss concretions was 1500±80y. Since it has been demonstrated that concretion genesis in the Bss is continuing (chapter 2), 1500y must represent an average of all organic C within the concretions. Therefore, 3000y may be a reasonable age for the larger (4-9mm) concretions. This value was derived using a simple model with two endpoints, one in the present and one in the past. Using a recent endpoint of 2y[1] and the 1500y average, a value of 2998y is calculated for the second endpoint. The age of the Bss concretion-C^{14} and the calculated endpoint fall within the known age range of the Ingram geomorphic surface. If we assume: i) continuous formation through time, ii) the older C is distributed at, or near, the concretion core, iii) the younger C is distributed near the concretion rind and, iv) a homogeneous distribution of C within the concretion, we can conclude that the Bss-C^{14} date is weighted toward the younger value due to the volume differences between the inner and outer parts of a sphere. These assumptions, if correct, would place the age of the older (larger) Bss concretions at >1500y and <3000y.

Age by Seasonal Fe-reduction and Total Fe_{DCB} Enrichment

Iron is more evenly distributed throughout the concretion and is less depleted in the soil matrix than Mn (Fig.1-9a,b; Table 3-1). This distribution suggests that

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[1]The soil from which the concretions were obtained was removed and dried two years before C^{14} analyses, determining one of the age endpoints used in the calculation of the average.

the accumulation of Fe has occurred at a constant rate during the genesis of the Bss concretion. Water samples from Ar-purged surface wells were collected in 1995 from soils at a similar study site. Differences in redox potentials, soluble Fe, and soluble P have been observed between open and closed shallow wells in Willamette Valley wet soils. Open piezometer wells at the J-F sites precluded sampling these sites for soluble Fe^{+2} thus, KCl/HCl-Fe was used to correlate the J-F environment to other wet soils with known seasonal-soluble Fe^{+2} and KCl/HCl-Fe concentrations. Model assumptions are: i) the amount of Fe accumulation is constant, ii) there is seasonal oxidation of the soluble Fe pool, iii) the annual soluble production is from the matrix, iv) the soluble pool is available for concretion genesis and, v) the amorphous Fe pools remain in the matrix. Massive Fe-staining on the J-F surface and the presence of Fe incrusted roots observed during drying periods, suggest high values of seasonally reduced Fe^{+2}. To calculate the time required for the current degree of Fe_{DCB} enrichment to occur we used: i) the average Fe_{DCB} concentration for the larger size concretions (this was the size fraction C^{14} dated) $16.6dgkg^{-1}$ ($166,000mgFekg^{-1}$ soil), ii) the higher value of $60mgkg^{-1}$ soluble Fe was used to reflect the high Fe environment of the J-F wetland and, iii) the current matrix Fe_{DCB} concentration ($2.3dgkg^{-1}$ or $23,000mgFekg^{-1}$ soil) as a 'background' level and subtracted this value as a 'non-enriched' starting point. From these assumptions we calculate the degree of Fe_{DCB} enrichment to occur within 2-3ky with an average at 2300y ($166,000mgFekg^{-1}soil - 23,000mgFekg^{-1}soil/ 60mgkg^{-1}$ solubleFe y^{-1} = 2383y).

Summary and Conclusions

The age of the Ingram geomorphic surface indicates that the oldest Bss concretions must be <3300y. Modeling the rate of formation of the Bss concretions from values of seasonal Fe^{+2} concentrations and total accumulation of Fe within the concretions suggests a time of 2-3ky for the concretions to form. Radiocarbon dating of the TOC within the Bss concretions shows the 4-9mm

diameter size fraction, on average, to be a minimum age of 1,500±80y. Given that this is an average value of all organic C within the concretions - an age of >1,500y and <3,000y is reasonable.

Isotopic data for the concretion and nodule fine clay fraction suggests that the initial formation of the 2Bt concretions and 3BC nodules was rapid enough to preserve the signature of extra-valley provenance. This signature has since been masked by additional authigenesis and infiltration of clays within the matrix. Identical isotopic signatures within the Bss concretions and matrix suggests that these features were formed in the same meteoric environment and location after late Pleistocene flooding.

Estimation of the 2Bt-concretion and 3BC-nodule age is dependent upon the known age range of the stratigraphic units. The most recent interpretation suggests that these concretions and nodules began forming <15ka and <38ka, respectively.

The amount of concretions (1.7%) and the age of this stratigraphic unit (600-3300y) suggests the greatest rate of concretion formation occurs in the Bss horizon. The age of the 2Bt horizon (12.8-15ky) with 0.8% concretions by weight and the 3BC horizon (38-50ky) with 2% nodules by weight, suggest that the slowest rate of nodule/concretion formation occurs in these horizons.

These data and estimates of age, coupled with P content of nodules and concretions, suggest an average of $0.4kg\text{-}Pha^{-1}y^{-1}$ is sequestered in the Bss concretions within the J-F wetland. Due to the degree of Fe and Mn cementation and pressure oriented smectite within the concretions, and at their surface, it is assumed that this P is unavailable for plant uptake or movement and this mechanism plays a role in water quality dynamics of wetland systems.

Literature Cited

Arshad, M. A. and R. J. St. Arnaud. 1980. Occurrence and Characteristics of Ferromanganiferous Nodules in Some Saskatchewan Soils. Can. J. Soil Sci. 60:685-695.

Bartlett, R. J. and B. R. James. 1993. Redox Chemistry of Soils. Advances in Agronomy. 50:151-208.

Blaylock, M. J. and B. R. James. 1992. Oxidation - Reduction Behavior of Selenite in Soils. Soil Sci. Soc. Am. J. (submitted)

Blume, H. P. 1968. Zum mechanisms der Marmorierung and Konkretionsbildung in Stauwasserboden Z. Pflanzenernaehr. Bodenkd. 119:124-134.

Blume, H. P. 1988. The Fate of Iron During Soil Formation in Humid-Temperate Environments. In:Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Carter, V., M. S. Bedinger, R. P. Novitski and W. O. Wilen. 1979. Water Resources and Wetlands, in Wetland Functions and Values : The State of Our Understanding, P. E. Greeson, J. R. Clark, and J E. Clark, eds., American Water Resources Assoc., Minneapolis, Minn., pp. 344-376.

Carter, V. 1986. An Overview of the Hydrologic Concerns Related to Wetlands in the United States, Can. J. Bot. 64:364-374.

Cogger, C. G., and P. E. Kennedy. 1992. Seasonally Saturated Soils in the Puget Lowland I. Saturation, Reduction and Color Patterns. Soil Sci. Vol. 153, No. 6.

Cogger, C. G., P. E. Kennedy, and D. Carlson. 1992. Seasonally Saturated Soils in the Puget Lowland II. Measuring and Interpreting Redox Potentials. Soil Sci. Vol. 154.

Drosdoff, M., and C. C. Nikiforoff. 1940. Iron-manganese Nodules in Dayton Soils. Soil Sci. 49:333-345.

Hansen, H. C. B., O.K. Borggard, and J. Sørensen. 1994. Evaluation of the Free Energy of Formation of Fe(II) - Fe(III) hydroxide-sulphate (green rust) and its reduction of nitrite. Geochimica et Cosmochimica Acta, Vol. 58, No. 12, pp. 2599-2608.

Klotz, R.L. 1985. Factors Controlling Phosphorus Limitation in Stream Sediments. Limnol. Oceanogr. 30(3) 543-553.

Knight, R. L., T. W. McKim, and H. R. Kohl. 1987. Performance of a Natural Wetland Treatment System for Wastewater management. J. Water Poll. Control Federation. 59:746-754.

Lovely, D. R. 1993. Dissimilatory Metal Reduction. Annu. Rev. Microbiol. 47:263-290.

Meyer, J.L. 1979. The Role of Sediments and Bryophytes in Phosphorus Dynamics in a Headwater Stream Ecosystem. Limnol. Oceanogr. 24(2) 365-375.

Miller, D.M., T. Tang and D. W. Paul. 1993. Electrolytic Reduction of Soil Suspensions. Soil Sci. Soc. Am. J. 57:356-360.

Mitsch, W. J. and J. G. Gosselink. 1993. Wetlands. Van Nostrand Reinhold Publishing, New York, New York. 698 p.

Phillippe, W. R., Blevins, R. L., Barnhisel, R. I. and H. H. Bailey. 1972. Distribution of Nodules From Selected Soils of the Inner Blue Grass Region of Kentucky. Soil Sci. Soc. of Amer. Proc. 36: 171-173.

Rhoton, F. E., Bigham, J. M. and D. G. Schulze. 1993. Properties of Iron-Manganese Nodules from a Sequence of Eroded Fragipan Soils. Soil Sci. Soc. Am. J. 57:1386-1392.

Schwertmann, U. and D. S. Fanning. 1976. Iron and Manganese Concretions in Hydrosequences of Soils in Loess in Bavaria. Soil Sci. Soc. Am. J. 40:731-738.

Seter, L. M. and J. Baham. 1994. Geochemical Characteristics of Iron-Manganese Nodules in Seasonally-Flooded Soils in the Willamette Valley, Oregon. P.249. In Agronomy Abstracts. ASA, Madison, WI.

Somera, R. D. 1967. Iron and Manganese Distribution and Seasonal Oxidation Changes in Soils of the Willamette Drainage Sequence. Unpublished M.S. Thesis. Oregon State University, Corvallis, Oregon.

Stumm, W. and B. Sulzberger. 1992. The Cycling of Iron in Natural Environments:Considerations Based on Laboratory Studies of Heterogenous Redox Processes. Geochimica et Cosmochimica Acta. 56:3233-3257.

Tardy, Y. and D. Nahon. 1985. Geochemistry of Laterites, Stability of Al-Goethite, Al- Hematite, and Fe^{+3}-Kaolinite In Bauxites and Ferricretes: An Approach to the Mechanism of Nodule Formation. Am. J. of Sci. 285:865-903.

van Breeman, N. 1988. Long-term Chemical, Mineralogical, and Morphological Effects Of Iron-redox Processes In Periodically Flooded Soils. 1988. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Vepraskas, M. J. and J. Bouma. 1976. Model Experiments On Mottle Formation Simulating Field Conditions. Geoderma. 15:217-230.

Vepraskas, M. J. 1994. Redoximorphic Features for Identifying Aquic Conditions. Technical Bulletin 301. North Carolina Agricultural Research Service, North Carolina State University, Raleigh, North Carolina.

von Gunten, U. and J. Zobrist. 1993. Biogeochemical Changes in Groundwater-infiltration Systems: Column Studies. Geochimica et Cosmochimica Acta. 57:3895-3906.

Wang, H. D., G. N. White, F. T. Turner and J. B. Dixon. 1993. Ferrihydrite, Lepidocrocite, and Goethite in Coatings from East Texas Vertic Soils. Soil Sci. Soc. Am. J. 57:1381-1386.

Wolfe, A. M., and D. E. Baker. 1990. Colorimetric Method for Phosphorus Measurement in Ammonium Oxalate Soil Extracts. Commun. In Soil Sci. Plant Anal., 21(19&20), 2257-2263.

Chapter IV.

Stratigraphic Control of Hydrology, Redox, and Concretion/Nodule Distribution in an Oregon Wetland

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Abstract

Willamette Valley soils have complex stratigraphic relationships due to cataclysmic Pleistocene flooding and subsequent Holocene alluvial events. The Jackson-Frazier wetland, located on the western margin of the Willamette Valley, shows three distinct stratigraphic units that rest unconformably upon each other and correspond to the Bashaw series Bss, 2Bt (Malpass member), and 3BC (Irish Bend silts) horizons. Each horizon has macroscopic Fe-Mn-P concentrations in the form of concretions within the Bss and 2Bt horizons and nodules within the 3BC horizon. Differences in concretion/nodule distribution and chemistry between horizons are related to seasonal differences in hydrology and redox, which are a function of climate and stratigraphy. The 2Bt horizon has the fewest concretions, averaging 0.8% concretions by weight, less than half the amount in the Bss and almost one third less than the 3BC-Irish Bend. The 2Bt matrix also contains the least DCB and AAO-extracted Fe and Mn. This horizon exhibited the greatest duration of saturation and reduction (<200mV SHE) through four years of observation. The 3BC-Irish Bend contains little more Fe and Mn than the 2Bt and the least organic C, but the upper part of this stratum has the greatest percent by weight (2.0%) and number of nodules. This is the oldest of the three strata at 38,410y, and appears to show the slowest rate of nodule formation (Ch. 3). The 3BC silts had the most rapid hydrologic response of the three strata, and even though they were at the greatest depth, they were frequently more oxygenated than the two strata above them during periods of saturation and reduction. The Bss horizon is the youngest of the strata at 3ky and has the greatest concentrations of DCB and AAO-Fe and Mn. Although intermediate in amount of concretions (1.7% by weight), this horizon has the fastest rate of concretion formation.

Introduction

Wetlands have a variety of terrestrial ecosystem functions including flood control, groundwater recharge (Carter, 1986; Carter et al., 1979), wildlife habitat (Mitsch and Gosselink, 1993), bioremediation and wastewater treatment (Knight et al., 1987). Occasionally there is controversy over the definition and function of hydric soils (wetlands) and the methods, analysis and parameters for their delineation (Zinn and Copeland, 1982; Mitsch and Gosselink, 1993; Vepraskas 1992). Wetlands have been defined in different ways with respect to the perceptions of the observers such as soil scientists, farmers, developers, engineers or agronomists. Cowardin et al., (1979) defined them as lands "where the water table is usually at or near the surface or the land is covered by shallow water", while Mitsch and Gosselink (1989) defined them as transitional areas between upland and aquatic habitats.

Agencies currently concerned with wetland definition and delineation focus on three parameters: soils, hydrology, and vegetation. The use of hydrophytic vegetation to define wetland areas is problematic due to the adaptations of diverse plant communities to wetter and drier environments (Tiner, 1991). Descriptions of soil redoximorphic characteristics and long term monitoring of hydrology must be used to accurately describe and classify hydric soils. Redoximorphic features such as depletions and concentrations are essential for the field soil scientist to identify and delineate hydric soils (U.S. Soil Survey Staff, 1992; Vepraskas, 1994). Understanding these features is important in deciphering the biogeochemical, hydrologic and/or climatic history of an area (Bouma, 1983; Moorman and van de Wetering, 1985; Vepraskas, 1994) and increases understanding of wetland functions on a more fundamental level.

The Jackson-Frazier wetland is Holocene alluvial fan/valley fill that has experienced repetetive annual flooding and drying cycles. These cycles, coupled with adequate organic C and mild temperatures, facilitate microbial reductive dissolution and segregation of Fe, Mn and additional redox sensitive metals into redoximorphic concentrations and/or depletions (Somera, 1967;

Cogger and Kennedy, 1992; Vepraskas, 1992; Miller et al., 1993; Lovely, 1993).

There are three distinct stratigraphic units within the Jackson-Frazier wetland corresponding to the Bss, 2Bt, and 3BC horizons, all of which have macroscopic concentrations in the form of Fe-Mn concretions and nodules. Evidence suggests that despite the mineralogy, morphologies and distinct, sharp boundaries that may suggest transport, or relict features (Vepraskas, 1994), the concretions within the J-F stratigraphic units are currently forming in place as a function of biogeochemical, hydrological, and redox environments (Ch.1). Fe-Mn nodules were identified as early as 1940 by Drosdoff and Nikiforoff (1940), and later by Balster and Parsons (1969). Drosdoff and Nikiforoff (1940), Somera (1967) and Seter and Baham (1994) studied the distribution and Fe-Mn chemistry of concretions/nodules with depth within different Willamette Valley soils. All found 'concretions' within the Dayton 2Bt (Malpass clay) and 3BC (Irish Bend) horizons. Seter and Baham (1994) found the greatest amount of nodules in the wettest (poorly drained) soils in their transect.

Various authors have discussed the presence and distribution of redoximorphic concentrations, the reductive dissolution of Fe, Mn, and redox sensitive elements, soft Fe masses and stains, oxide surface chemistry, and the mineralogy of Fe, Mn, and various redox sensitive metal-oxides as related to temperature and environment (Wang et al., 1993; Cogger et al., 1992; van Breeman, 1988; Schwertmann, 1988; Bartlett and James, 1993; Blaylock and James, 1992; Tardy and Nahon, 1985; Stumm and Sulzberger, 1992; Miller et al.,1993; Lovely, 1993; Vepraskas and Bouma, 1976; Blume, 1988; Hansen et al., 1994; Gunten and Zobrist, 1993). Some have stated, however, that to characterize and define wet soils only by soil morphological features associated with the reduction and oxidation of Fe and Mn is inadequate, since not all wet soils show reducing features. Concentrations and/or depletions may not develop if there is insufficient Fe or C, or if Fe and Mn exist in largely crystalline forms. Also complicating the issue may be relict or transported features that do not reflect current hydrologic or redox environments. "Additional research on the correlation between soil morphology and actual hydraulic conditions is needed if

we are to establish relevant criteria for the characterization of wet soils" (Dudal, 1992).

The objective of this part of our study was to correlate the distribution of Fe, Mn, and redoximorphic concentrations in the form of concretions and nodules, throughout the J-F stratigraphy, with hydrologic and redox data. This information will help field soil scientists interpret redox features and hydrologic environments as a function of landscape, climate, and stratigraphy and will facilitate the identification and delineation of hydric soils in similar valley landscapes.

Although the use of Pt electrodes has been found to be problematic with respect to specific redox couples (Drever, 1988), it has also been observed that the use of Pt electrodes and calculated Eh values can provide useful information on the soil redox environment (Drever, 1988; Sposito, 1989). We have used them in this study to provide additional data verifying the reduction of Fe and Mn. Iron and Mn are among the most important redox couples in the range of Eh values found in these soils (Cogger and Kennedy, 1992).

Methods and Materials

Long term observations of subsurface water dynamics and piezometric surfaces were made using permanently installed piezometers. These were constructed from 0.75in 200 PVC pipe by cutting seven horizontal slots 1cm apart in the bottom of each pipe and covering them with textile fabric to prevent clogging.

An acrylic tube containing a styrofoam float was placed inside the PVC pipe to register the level of water in the tube. The piezometers were placed in the soil by boring a 7cm hole to the required depth in the soil. The holes were then excavated an additional 2.54cm and the bottom filled with fine sand. The piezometer tube was then placed in the hole and the space between piezometer and soil backfilled with fine sand to the top of the perforation of the PVC pipe. The hole was then backfilled with bentonite to seal the tube from surface leakage. Piezometer wells were placed in triplicate in the monitoring plots at depths of 25, 50, and 100cm.

One 200cm piezometer was placed in each plot. Readings were taken weekly (D'Amore, 1995).

A more detailed description of piezometer construction and placement is given by Austin (1994). The 100cm depth at site 1 was just above the Bss-2Bt contact, while the same depth at site 2 was precisely at the 2Bt-3BC contact (Fig. 1-2).

Platinum electrodes were used to verify conditions sufficiently anaerobic and reducing enough to reduce Fe (<200mV SHE). These were constructed after the methods of Faulkner et al. (1989) and Szogi and Hudnall (1990), with the exception that instead of a mercury junction, a copper wire lead was then soldered to the Pt tip, which was then sealed by filling the glass tube with epoxy (D'Amore, 1995; Austin, 1993). The electrode placements were identical in number and depths to those for the piezometers. Eh values were calculated from the Nernst equation relative to the standard hydrogen electrode (SHE).

An Orion 820 self-calibrating dissolved oxygen sensor was used for dissolved O^2 measurements. The probe was lowered to the bottom of the well and moved up and down to obtain a flow of $1cms^{-1}$ by the membrane until a stable value was reached. The wells were not pumped before measurement due to aeration of the soil solution upon the slow refill time for the wells. 'Fresh' soil solution moved into the piezometer tube to attain equilibrium upon the removal of the inner acrylic tube and the resulting increased volume within the piezometer well. This allowed sampling of the soil solution without pumping the wells and risking aeration and the introduction of error in the DO values.

Results

Hydrology

The hydrologic and redox character of these two sites has been described in detail for the 1992-1994 monitoring period (D'Amore, 1995). The second phase of weekly monitoring at these J-F sites began in November, 1994. At this time water was present in piezometers at all depths at both sites. The soil surface

became saturated and ponded by late November, but the total soil profile was not saturated until December when the upper and lower water tables combined (Fig.'s 4-1a,b). The Willamette Valley experienced extremely wet years in 1994-1996, had record rainfall, and a 100y flood event in 1996. The J-F profile remained saturated at the 25 through 100cm depths at both sites from December 1992 through early summer 1996 except for an extended period in 1993, late summer 1994, and brief intermittent periods after that. The surface of the wetland was ponded continuously from late November, 1993 through June, 1994, from October, 1994 through July, 1995, and from late September, 1995 through July, 1996. No data was collected from June, 1994 through October, 1994.

Water levels fell most rapidly in the piezometers installed in the 3BC-Irish Bend silts (the 200cm piezometer at site 1 and the 200 and 100cm piezometers at site 2). Water levels in piezometers installed in the Bss clay declined very slowly. Visual examination of the soil profile in early September, 1994 and 1995 revealed that the 2Bt horizon never dried and remained wetter than the Bss horizon above and the 3BC horizon below.

Electrodes

When the second phase of monitoring began in November, 1994 the potentials (Eh values) for all electrodes at all depths were between 0 and 200mV at both J-F sites (Fig.'s 4-3,4). At site 1, electrodes at 100cm showed the longest duration of Fe reduction (<200mV), while at site 2 the 50 and 25cm electrodes showed the longest duration of Fe reduction. The 100cm depth electrodes at site 1 remained strongly reducing, even through the extended periods of desaturation in late summer and fall of 1993. All electrodes at site 2 became oxidizing for Fe (>200mV SHE) in the soil profile at site 2 during the summer of 1994 and 1995. In subsequent years all depths at site 1 briefly became oxidizing during late December and early January, when soil temperatures fell.
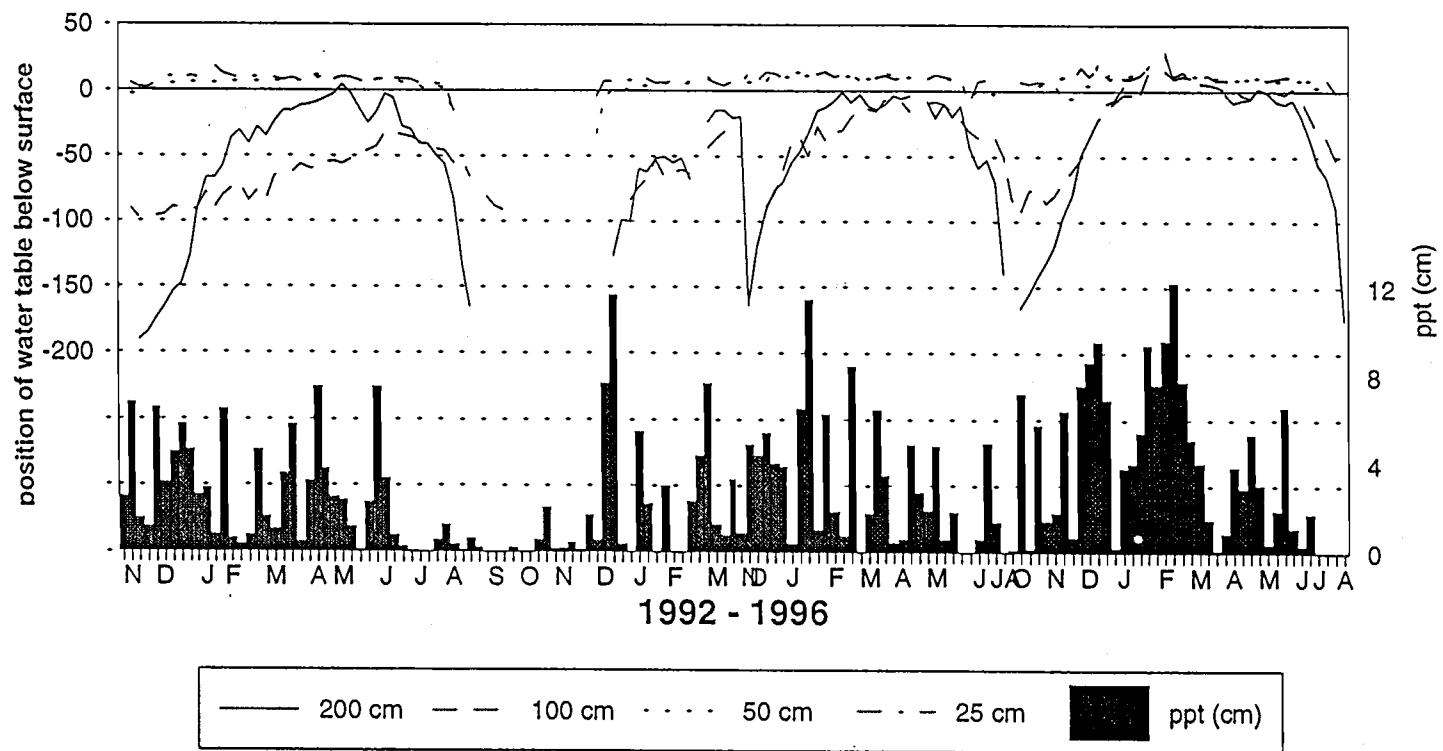
Figure 4-1(a-b). Precipitation (bottom) and water position (top) as observed in piezometers. (a) Site 1.
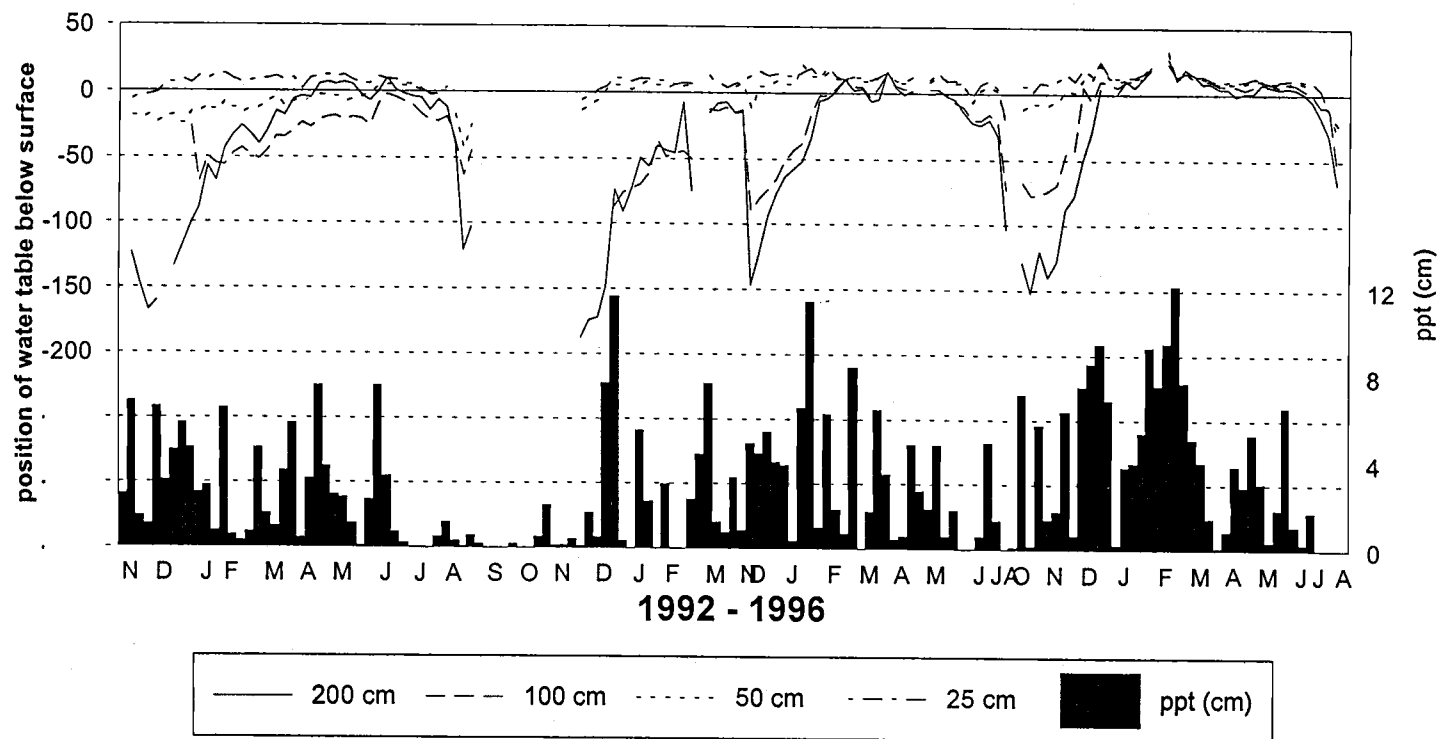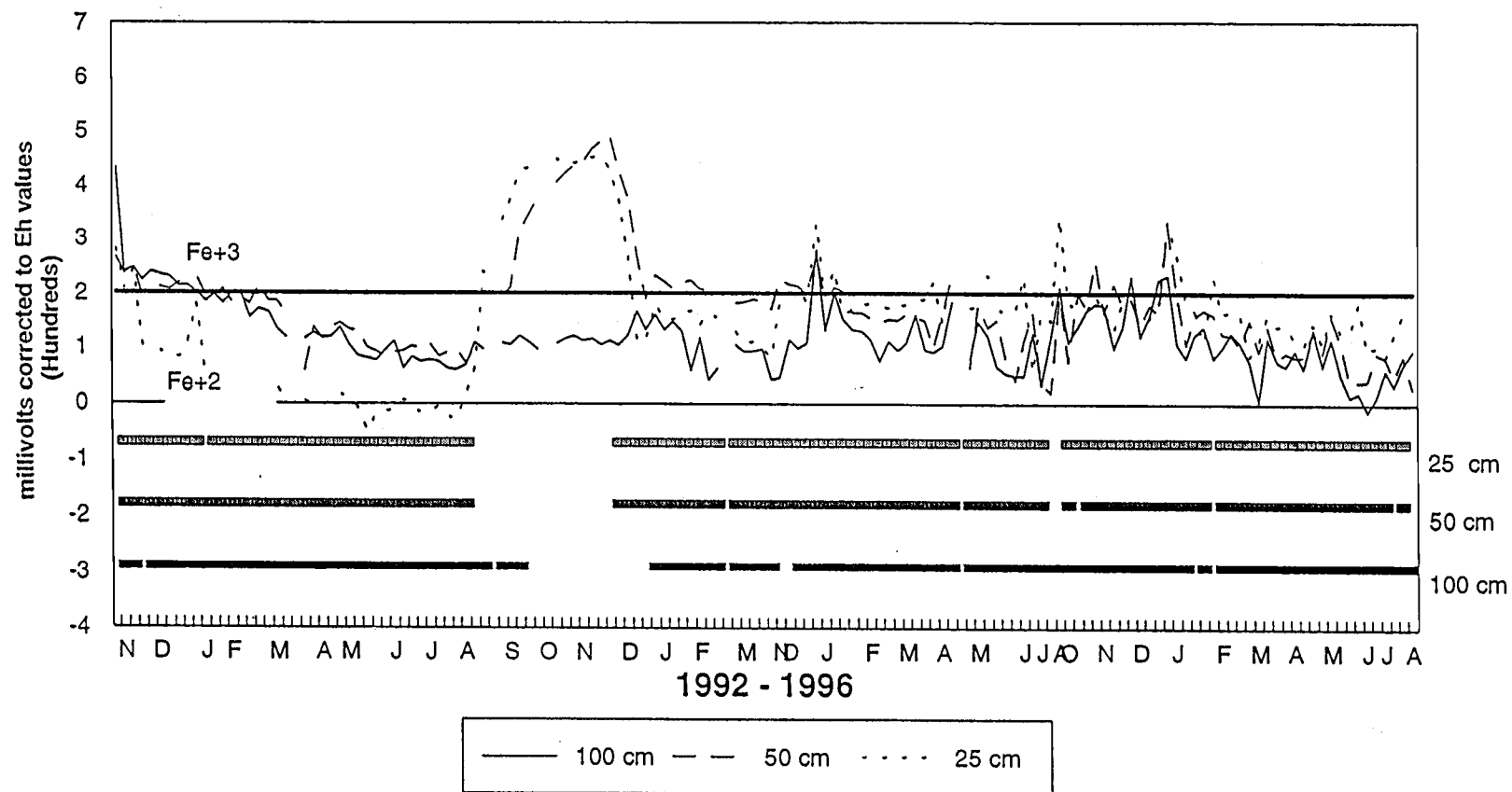
Figure 4-1 cont.'d. (b) site 2.

Figure 4-2 (a-b). Duration of saturation determined by piezometers (bottom) with Eh values (top). (a) site 1.
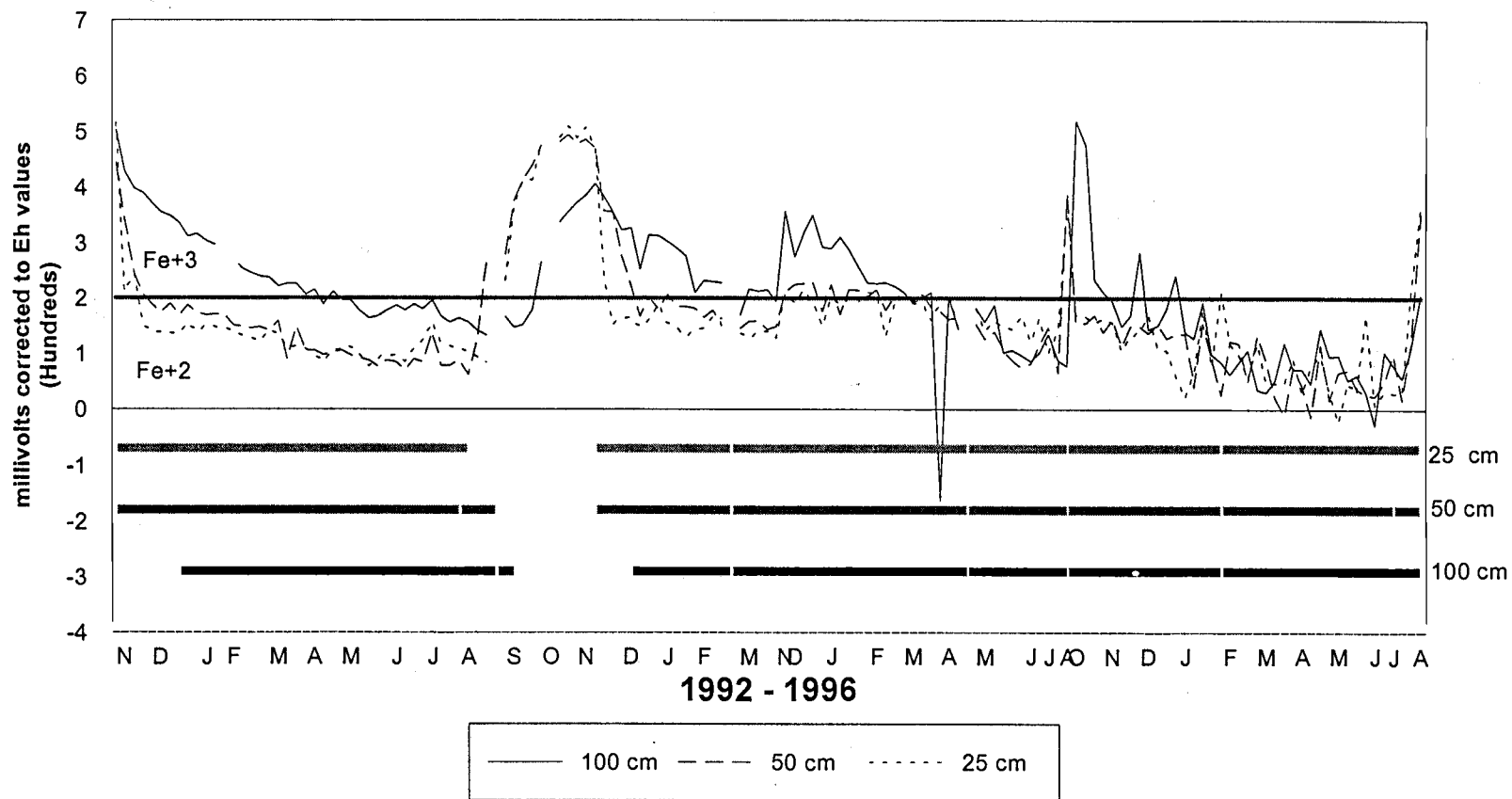
Figure 4-2 cont.'d. (b) site 2.

All depths at site 2 became oxidizing in the winter of 1994-95 and in late summer, 1995. Only the 25 and 100cm depths at site 2 approached oxidizing conditions during the winter of 1995-96.

Dissolved Oxygen

DO values generally were lower during the 1994-96 monitoring period in which the wells were unpumped. At both sites DO values were highest during breaks in saturation and in the winter months. Values were high in the early part of the winter saturated season presumably due to decreased temperatures and slower microbial consumption. The highest values during these periods generally were observed at the 200cm depth at both sites, with the exception of the 25cm depth at site 2 during October, 1995 (Fig.'s 4-5,6). The lowest DO values occurred during spring and summer at the 100 and 50cm depths at both sites and were near $0mgL^{-1}$ for extended periods of time. During periods of saturation and reduction, when there was enough water in the piezometers to assure no atmospheric O2 contamination, values ranged between 0 and $3.5mgL^{-1}$ at all depths at both sites. At the 100cm depth at site 1, DO values were occasionally at $0mgL^{-1}$ in the spring.

Concretion/Nodule Distribution

Characterization data for concretions in all three stratigraphic units are shown in Table 1-1. The Bss Holocene alluvium had the highest clay content and the largest concretions (on average and absolute size) of any horizon. On a weight basis the Bss horizon has 1.7% concretions, intermediate between the 2Bt and 3BC horizons. Concretion density in the Bss averaged $2.1gcm^{-3}$.

The 2Bt was the horizon having the fewest redoximorphic concentrations and the lowest percentage in weight, averaging less than half the amount in the Bss and almost one third less than the 3BC. Concretion density averaged $2.1gcm^{-3}$ and matrix clay content was 43%.
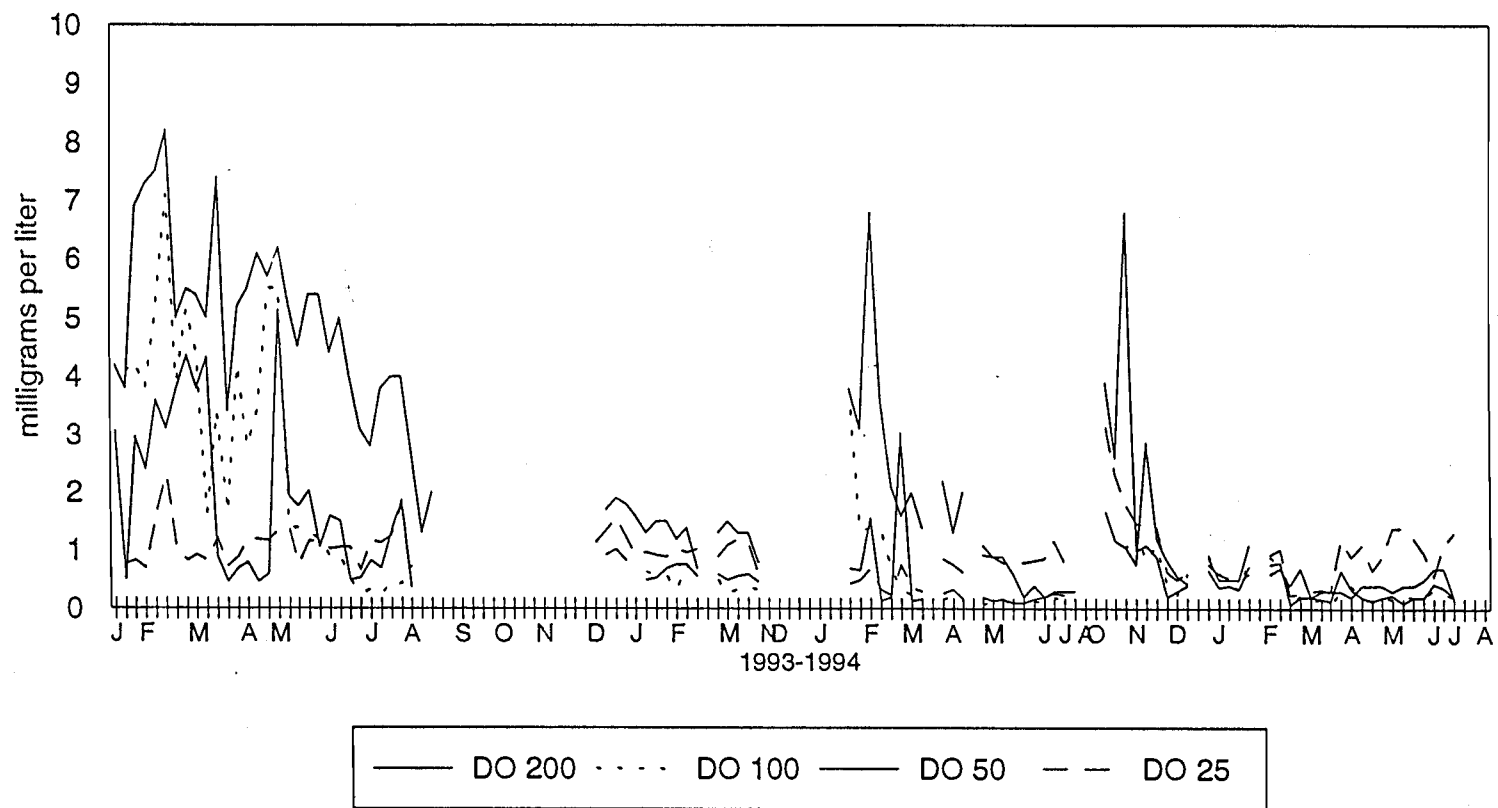
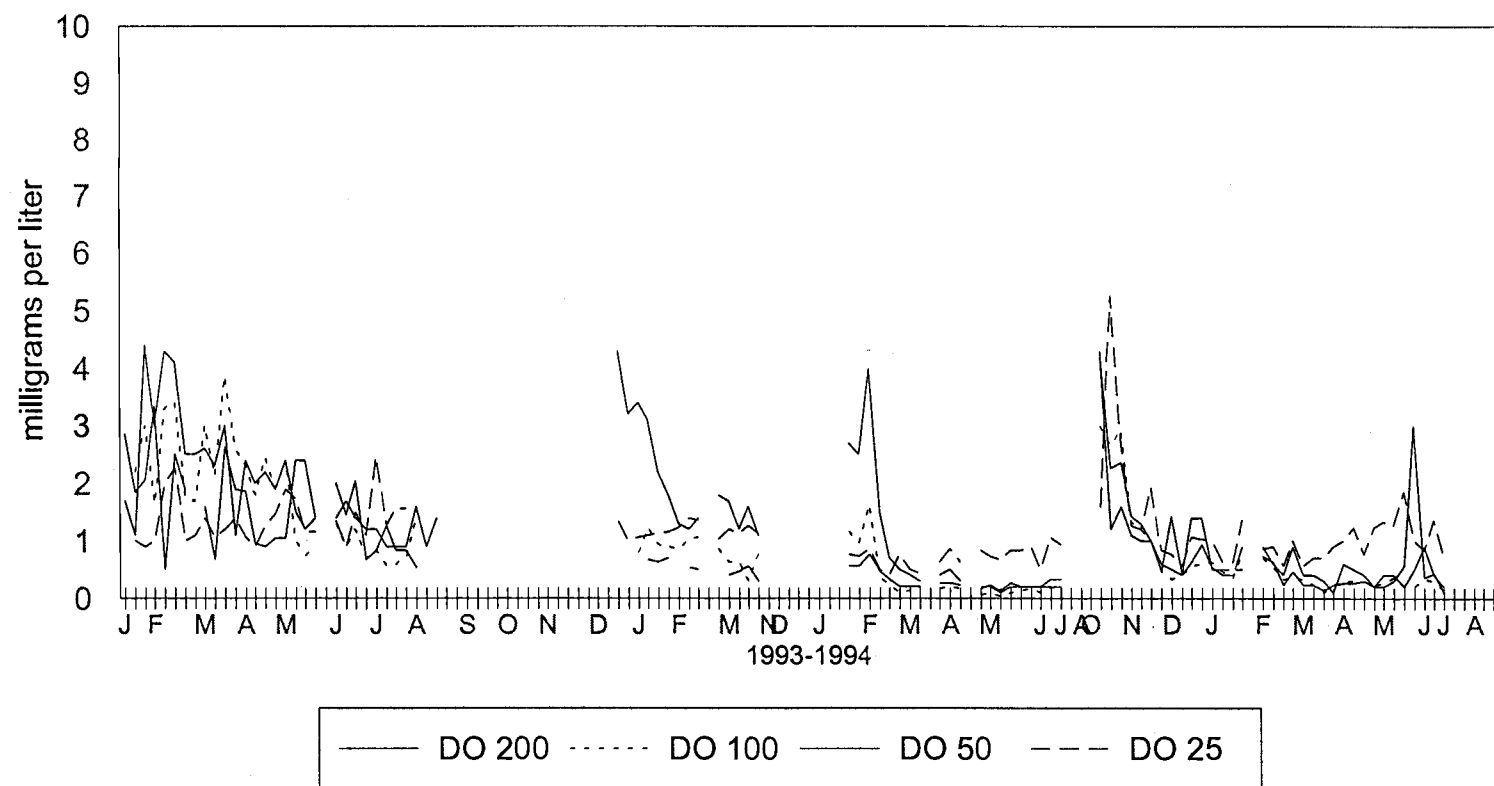Figure 4-3(a-b). Dissolved oxygen values. (a) site 1.

Figure 4-3 cont.'d. (b) site 2.

The 3BC-Irish Bend silts had the smallest nodules on average (<0.5-3mm diameter) but the largest percent by weight (2%) of any horizon. Nodule density is less in this horizon, averaging 1.9 gcm^{-3}. This horizon had the least clay of the three strata at 26-31% (NRCS,1995).

Chemistry

Iron-Mn data for both concretions/nodules and the matrices in which they occur are summarized in Tables 3-2 and 3-3. Bss concretions contain 7-9x more Fe_{DCB} and 11-13x more Fe_{OX} than the matrix in which they occur. The 2Bt concretions contain 8x more Fe_{DCB} and 20-24x more Fe_{OX} than the matrix, which had the least Fe_{DCB} and Fe_{OX} of these three strata. The 3BC nodules show the least enrichment in Fe_{DCB} relative to the matrix (4-5x) but they contain 13-17x more Fe_{OX} than the matrix. There was a decrease in concretion-nodule Fe_{DCB} /Fe_{OX} ratios with depth of stratigraphic unit ranging from 5x in the Bss to 2x in the 3BC.

The Bss concretions are enriched 25-50x in Mn_{DCB} and 4-13x in MN_{OX} with respect to the matrix. The 2Bt concretions are enriched 250-475x in Mn_{DCB} and 65-145x in MN_{OX}, the largest enrichment of any horizon. The 3BC nodules are enriched 39-80x in Mn_{DCB} and 29-42x in MN_{OX}. Concretion-nodule Mn_{DCB}/MN_{OX} ratios showed two trends: a decrease with depth ranging from 7x in the Bss to 3x in the 3BC. Small concretion-nodules showed greater ratios than the large fraction (1-3x).

The total organic carbon (TOC) within the concretions and nodules decreased with depth ranging from 1.2 percent by weight in the Bss concretions, to 0.1 percent in the 3BC nodules. Values averaged 0.8 percent within the Bss concretions, 0.5 percent within the 2Bt concretions, and 0.2 percent within the 3BC nodules (Table 3-1). The NRCS (1995) provided matrix TOC data which is also summarized in table 3-1. Total OC decreased with depth and ranged from 4.56-1.02% in the Bss, to 0.23 and 0.12% within the 2Bt and 3BC horizons, respectively.

Discussion

Hydrology

Soil profiles can be saturated from water moving upward from a deeper water table or from surface water moving downward through the profile. Both types of saturation occur in the J-F wetland. Surface horizons are rapidly saturated at the onset of the rainy season, followed by a slowly rising water table in the 3BC silts later in the winter.

The Bashaw A and Bss horizons have a significant amount of high shrink-swell clay that develops large vertical cracks upon drying. These cracks facilitate rapid entry of water and saturation of the upper 50cm soon after the onset of the fall rains. After these cracks swell shut there is an unsaturated zone somewhere between 50 and 100cm that may be several weeks in duration. It is unclear, however, if the J-F wetland is episaturated due to the duration of the unsaturated zone, or endosaturated due to the ultimate saturation of the whole profile by the upward movement of water from the lower water table. The potential of the water in the 25, 50 and 200cm piezometers, combined with the slower saturation of the profile between 50 and 100cm depths, clearly indicate the presence of an aquitard and underlying confined aquifer in the J-F profile. This feature "creates horizontal flow...along the topographic gradient of the Irish Bend silt" (D'Amore, 1995).

Later in the rainy season water moved into the 100cm piezometer before levels in the 200cm piezometers had risen to 100cm below the surface. This indicates that, initially, surface water moving through cracks and macropores reached the 100cm level before complete swelling of the Bss horizons. In the later part of the wet season there was a rapid response of water in the 100cm wells, due to potential from the confined aquifer, when the piezometeric surface in the 200cm wells approached the soil surface. During drying trends in early summer, water in the 100cm wells fell rapidly as water in the 200cm piezometers fell. This behavior was observed at both sites. These observations suggest that pressure head from the lower water table influences the hydrologic response at

the 100cm depth after the onset of both the wet, and the dry season. D'Amore (1995) also observed this behavior in the previous monitoring phase and suggested that the falling water table within the 3BC silts creates a suction on the 2Bt horizon when the surface horizons are still sealed. This may help explain the rapid hydrologic response within the 2Bt and lower Bss horizons at site 1. Later, with or without continued suction, water in the upper profile must permeate into the 2Bt and lower Bss horizon, contributing to the duration in saturation and reduction observed in these strata.

Water levels falling most rapidly in the 3BC silts followed later by desaturation of the Bss-2Bt silty clay would also be expected on the basis of horizon texture. Visual observations in the two soil pits in late September, 1994 and late August, 1995 revealed that the 2Bt remained wetter than the Bss above, and the 3BC below, during these breaks in saturation. The fact that the 100cm piezometer data at site 1 showed duration of saturation through the summer and into early fall, 1993 and through the summer and fall, 1995, supports these visual observations.

Stratigraphic control of the duration of saturation provides an explanation for the relative lack of redoximorphic concentrations and lesser amounts of Fe and Mn in the 2Bt. The rapidly falling water table in the 3BC silts could be a factor in the removal of reduced Fe and Mn from the 2Bt into the more oxygenated lower silts, contributing to greater amounts of Fe and Mn in the 3BC relative to the 2Bt. Rhoton et al., (1993) and, Arshad and St. Arnaud (1980) also found that the greatest amount of nodules/concretions did not coincide with the wettest part of the profile. Blume (1968) also states that "more permanent wetness leads to mottling or even complete loss of Fe and Mn".

Eh and DO

The duration of Fe reduction (<200mV) at the 100cm depth at site 1 correlates well with the observations that this depth also had the greatest duration of saturation, lowest DO values, and was the wettest part of the profile during unsaturated periods in 1994 and 1995. The duration of reduction and low

DO levels at the 100cm depth at site 1 also help to explain the lesser amounts of Fe, Mn, and redoximorphic concentrations in the 2Bt matrix, since it is generally accepted that alternating conditions of reduction and oxidation are needed for the formation of nodules/concretions (Rhoton et al, 1993; Blume, 1988). The fine smectite and halloysite clays within and above the 2Bt reduce the rate of water movement, both laterally and vertically. The 3BC silts are the most well drained part of the profile and are oxidized more frequently than the 2Bt.

Although no electrodes were placed at the 200cm depth, the higher DO concentrations in the 3BC-silts indicate a more oxidized environment relative to the 2Bt and would explain greater amounts of both DCB and AAO extracted Fe and Mn, due to precipitation by oxidation. It is unclear whether greater amounts of Fe than Mn within this stratum are a function of the greater amount of Fe than Mn in the 2Bt, the precipitation of Fe at lower redox potentials than that of Mn, inherited initial differences, redox potentials low enough to reduce Mn, leading to its loss by leaching, but not low enough to reduce Fe.

We would expect the greatest duration of saturation and reduction to occur at the 50cm depth at site 2 due to the placement of the 100cm electrodes at the 2Bt-3BC contact. The 100cm electrodes will be influenced by the more oxygenated 3BC-silts and should result in higher potentials and less duration of reduction, which is what the data reflect. The 50cm depth showed the greatest duration in saturation and was nearly identical to the 25cm depth in duration and degree of reduction. Eh values were lowest at the 25 and 50cm depths in spring-summer due to increased temperatures and moist soil.

Distribution of Fe, Mn, and Concretions/Nodules

D'Amore's field observations, site descriptions, and monitoring data from the J-F wetland led to inferences of what we might find upon a more quantitative examination of the three stratigraphic units for amounts of Fe, Mn, OC, and concretions at this location.

   The J-F environment receives frequent inputs of alluvium via Jackson and Frazier creeks, the source of which is Fe-rich ultisols and parent materials at the headwaters (Snavelly et al., 1968). Due to these inputs we would expect the Bashaw Bss stratigraphic unit to have the highest total amounts of Fe and Mn, which should support the greatest amounts of segregated Fe-Mn concentrations relative to the other two strata. The Bss horizon did contain the greatest amounts of DCB and AAO extracted Fe and Mn of any strata, but the percent weight and volume of concretions was intermediate between the 2Bt and 3BC horizons. The lesser amounts of concretions in the Bss horizon relative to the 3BC is, presumably, an artifact of age. The Bss stratigraphic unit is <3.3ky compared to the 3BC which is >34ky. With respect to the young age of this unit relative to the other strata, and the indications that concretions and nodules are still continuing to form in all strata (chapter 2), the Bss appears to have exhibited the greatest rate of concretion formation.

   Through 41 months of observation the 2Bt experienced the longest duration of saturation (37 months) and reduction (39 months), though not continuously. The 2Bt was visually observed to be the wettest stratigraphic unit during breaks in saturation in 1994 and 1995 supporting the piezometer and electrode data. Although we don't know the initial concentrations of Fe and Mn in this unit immediately following it's deposition, we would expect this horizon to be the most depleted in redox-sensitive metals that are reduced above 0mV (SHE), and to show the least amount of Fe-Mn concretions/nodules of the three strata due to the potential for transport of metals in the reduced phase, and the infrequent oxidation that would help to retain these metals. The Fe-Mn chemical data and the concretion data from the 2Bt horizons helps support this hypothesis. The larger enrichment factors of Fe and Mn in the 2Bt concretions relative to the matrix is due to much lower concentrations of these elements within the matrix relative to the other strata. The 2Bt matrix had the lowest ratio of Mn_{DCB}/Mn_{OX} (1x) suggesting that what little Mn there is within this horizon is mostly in the poorly crystalline to amorphous form.

Though Drosdoff and Nikiforoff (1940), Somera (1967), and Seter and Baham (1994) all found 'concretions' or 'nodules' in specific Willamette Valley soils, including the Dayton series, the most recent and detailed study was by Seter and Baham (1994). The Dayton series contains both the 2Bt-3Bt and Irish Bend stratigraphic units, which correspond to the Bashaw 2Bt and 3BC horizons beneath the J-F wetland. Seter and Baham observed a marked decrease in 'nodules' within the 2Bt-3Bt horizons, finding none within the lower 20cm of the 3Bt before a gradual increase with depth in the Irish Bend silts. The Dayton stratigraphic units contained much lower amounts of nodules than in the equivalent stratigraphic units beneath the J-F wetland (an average of 0.03% in the Dayton 2Bt-3Bt and 0.5% by weight in the upper Irish Bend silts). This difference can be explained by annual inputs of fresh Fe-Mn rich material in the J-F wetland, whereas the stable surface of the Dayton soil receives no new iron-bearing sediment. Mineralogical and isotopic evidence suggests that there is illuviation of material through the J-F profile (Ch. 2). The J-F profile is saturated longer than the Dayton series (Austin, 1994; D'Amore, 1995).

In the 3BC silts piezometer data and DO levels demonstrate that cycles of wetting/drying and some degree of oxidation/reduction likely occur, although we have no confirming Eh data. This suggests that the present-day environment of the 3BC is conducive to the formation of redoximorphic concentrations, dependent upon the availability of Fe, Mn, and OC. The 3BC has the least amount of OC of all three horizons (0.09%), less than half that in the 2Bt but, the greatest amount of nodules. Based on thermodynamic considerations this amount of OC (if available) in the 3BC is sufficient to reduce the amorphous or poorly crystalline Fe in the 3BC horizon, but reduced Fe values and the amount of C available for microbial processes is unknown. The greater amount of nodules in this horizon is most likely a function of age since this horizon is at least 30ky older than the Bss.

Summary and Conclusions

Complex stratigraphy at the western margin of the Willamette Valley has resulted from episodic Pleistocene flooding followed by Holocene alluviation with sediments derived from Fe and Mn-rich parent materials west of the Jackson-Frazier wetland. These stratigraphic relationships influence hydrologic processes in the J-F soil profile which in turn influence DO levels and Eh. The distribution of Fe, Mn, concretions/nodules through the profile reflect these hydrologic and redox environments. The redox and hydrologic environments in each stratigraphic unit can be determined by long-term monitoring using piezometers, Pt electrodes, and DO probes and correlated to the amount of redoximorphic features such as concretions and nodules.

The upper (Bss) horizon, which has formed entirely in Holocene alluvium, contains the greatest amounts of Fe, Mn, and OC but, was intermediate in amount of concretions. Being the youngest of the three strata (3ky), it appears to have the greatest rate of concretion formation (chapter 2).

The 2Bt stratigraphic unit had the fewest concretions (in number and percent weight) and the lowest amounts of Fe-Mn within the matrix, reflecting the duration of saturation and Fe-reducing (<200mV SHE) conditions in this horizon. These conditions could facilitate the loss of Fe and Mn.

The 3BC horizon had the least amount of OC and only slightly more Fe and Mn than the 2Bt but, had the greatest amount of nodules, by number and percent weight, of any strata. The age of this unit (>34ky), however, suggests these concretions form much more slowly than those within the Bss - or formed earlier and are now relict features, although our data did not support this.

Literature Cited

Arshad, M. A. and R. J. St. Arnaud. 1980. Occurrence and Characteristics of Ferromanganiferous Nodules in Some Saskatchewan Soils. Can. J. Soil Sci. 60: 685-695.

Austin, W. 1994. Duration of saturation and redox potentials in selected Willamette Valley soils. M.S. Thesis, Oregon State University, Corvallis, Or. 256 pp.

Balster, C. A. and R. B. Parsons. 1970. Soil Development and Geomorphic Surfaces, Willamette Valley, Oregon. Soil Sci. Soc. Am. Proc. 34:485-491.

Balster, C. A. and R. B. Parsons. 1969. Late Pleistocene Stratigraphy, Southern Willamette Valley, Oregon. Northwest Sci. 43:116-129.

Bartlett, R. J. and B. R. James. 1993. Redox Chemistry of Soils. Advances in Agronomy. 50:151-208.

Blaylock, M. J. and B. R. James. 1992. Oxidation - Reduction Behavior of Selenite in Soils. Soil Sci. Soc. Am. J. (submitted)

Blume, H. P. 1968. Zum mechanisms der Marmorierung and Konkretionsbildung in Stauwasserboden Z. Pflanzenernaehr. Bodenkd. 119:124-134.

Blume, H. P. 1988. The Fate of Iron During Soil Formation in Humid-Temperate Environments. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Bouma, J. 1983. Hydrology and soil genesis of soils with aquic moisture regimes. pp.253-281. In L.P. Wilding, N.E. Smeck, and G.F. Hall (eds.). Pedogenesis and Soil Taxonomy. I. Concepts and Interactions. Elsevier, Amsterdam.

Bretz, J. H. 1969. The Lake Missoula Floods and the Channeled Scabland. J. of Geology. 77:505-543.

Carter, V., M. S. Bedinger, R. P. Novitski and W. O. Wilen. 1979. Water Resources and Wetlands, in Wetland Functions and Values : The State of Our Understanding, P. E. Greeson, J. R. Clark, and J E. Clark, eds., American Water Resources Assoc., Minneapolis, Minn., pp. 344-376.

Carter, V. 1986. An Overview of the Hydrologic Concerns Related to Wetlands in the United States, Can. J. Bot. 64:364-374.

Cogger, C. G., and P. E. Kennedy. 1992. Seasonally Saturated Soils in the Puget Lowland I. Saturation, Reduction and Color Patterns. Soil Sci. Vol. 153, No. 6.

Cogger, C. G., P. E. Kennedy, and D. Carlson. 1992. Seasonally Saturated Soils in the Puget Lowland II. Measuring and Interpreting Redox Potentials. Soil Sci. Vol. 154.

Cowardin, L.M., V. Carter, F.C. Golet, and E.T. LaRoe. 1979. Classification of Wetland and Deepwater Habitats of the United States. U.S. Fish and Wildlife Service, Wash. D.C. FWS/OBS-79/31.

D'Amore, D. V. 1995. The Stratigraphy, Hydrology, and Redoximorphic Character of the Jackson-Frazier Wetland. M.S. Thesis. Oregon State University, Corvallis, Or.

Drosdoff, M., and C. C. Nikiforoff. 1940. Iron-manganese Nodules in Dayton Soils. Soil Sci. 49:333-345.

Dudal, R. 1990. Proceedings of the Eighth International Soil Correlation Meeting (VIII ISCOM): Characterization, Classification, and Utilization of Wet Soils. pp.1-4.

Faulkner, S.P., W.H. Patrick, and R.P. Gambrell. 1989. Field Techniques for Measuring Wetland Soil Parameters. Soil Sci. Soc. of Am. J. 53:883-890.

Glasmann, J. R. and G. F. Kling. 1980. Origin of Soil Materials in Foothill Soils of Willamette Valley, Oregon. Soil Sci. Soc. Am. J., 44:123-130.

Glenn, J. L. 1965. Late Quaternary Sedimentation and Geologic History of the North Willamette Valley, Or. Ph.D. thesis, Oregon State University, Corvallis, Or.

Hansen, H. C. B., O.K. Borggard, and J. Sᴏrensen. 1994. Evaluation of the Free Energy of Formation of Fe(II) - Fe(III) hydroxide-sulphate (green rust) and its reduction of nitrite. Geochimica et Cosmochimica Acta, Vol. 58, No. 12, pp. 2599-2608.

Knight, R. L., T. W. McKim, and H. R. Kohl. 1987. Performance of a Natural Wetland Treatment System for Wastewater management. J. Water Poll. Control Federation. 59:746-754.

Lovely, D. R. 1993. Dissimilatory Metal Reduction. Annu. Rev. Microbiol. 47:263-290.

Marshall, J. 1985. A Value Assessment of the Jackson-Frazier Wetland. Unpublished MS thesis, Oregon State University, Corvallis, Or.

Miller, D.M., T. Tang and D. W. Paul. 1993. Electrolytic Reduction of Soil Suspensions. Soil Sci. Soc. Am. J. 57:356-360.

Mitsch, W. J. and J. G. Gosselink. 1993. Wetlands. Van Nostrand Reinhold Publishing, New York, New York. 698 p.

Moormann, F. R., and H. T. J. van de Wetering. 1985. Problems in Characterizing wetland soils. pp. 53-68. In Anonymous (ed.). Wetland Soils: Characterization, Classification, and Utilization. Proc. of a workshop held March 26 to April 5, 1984. Int. Rice Res. Inst., Los Banos, Phillippines.

Phillippe, W. R., Blevins, R. L., Barnhisel, R. I. and H. H. Bailey. 1972. Distribution of Nodules From Selected Soils of the Inner Blue Grass Region of Kentucky. Soil Sci. Soc. of Amer. Proc. 36: 171-173.

Rhoton, F. E., Bigham, J. M. and D. G. Schulze. 1993. Properties of Iron-Manganese Nodules from a Sequence of Eroded Fragipan Soils. Soil Sci. Soc. Am. J. 57:1386-1392.

Schwertmann, U. and D. S. Fanning. 1976. Iron and Manganese Concretions in Hydrosequences of Soils in Loess in Bavaria. Soil Sci. Soc. Am. J. 40:731-738.

Seter, L. M. and J. Baham. 1994. Geochemical Characteristics of Iron-Manganese Nodules in Seasonally-Flooded Soils in the Willamette Valley, Oregon. p.249. In: Agronomy Abstracts. ASA, Madison, WI.

Snavely, P. D., N. S. MacLeod and H. C. Wagner. 1968. Tholeiitic and Alkalic Basalts of the Eocene Siletz River Volcanics, Oregon Coast Range. Am. J. Sci., 266:454-581.

Soil Survey Staff. 1992. Keys to Soil Taxonomy, fifth edition. SMSS Tech. Monogr. No.7. Virg. Polytech Inst. and State Univ., Blacksburg.

Somera, R. D. 1967. Iron and Manganese Distribution and Seasonal Oxidation Changes in Soils of the Willamette Drainage Sequence. Unpublished M.S. Thesis. Oregon State University, Corvallis, Oregon.

Sposito, G. 1989. The Chemistry of Soils. Oxford University Press, New York.

Stumm, W. and B. Sulzberger. 1992. The Cycling of Iron in Natural Environments:Considerations Based on Laboratory Studies of Heterogenous Redox Processes. Geochimica et Cosmochimica Acta. 56:3233-3257.

Szogi, A.A. and W.H. Hudnall. 1990. Measurement of Redox Potentials in Soils with Permanently installed Platinum Electrodes. Manuscript 91-09-5227. Louisiana Agricul. Exp. Stn.

Tardy, Y. and D. Nahon. 1985. Geochemistry of Laterites, Stability of Al-Goethite, Al- Hematite, and Fe^{+3}-Kaolinite In Bauxites and Ferricretes: An Approach to the Mechanism of Nodule Formation. Am. J. of Sci. 285:865-903.

Tiner, R. W. 1984. Wetlands of the United States: Current Status and Recent Trends, National Wetlands Inventory, Fish and Wildlife Service, U.S. Department of Interior, Washington, D.C., 58p.

van Breeman, N. 1988. Long-term Chemical, Mineralogical, and Morphological Effects Of Iron-redox Processes In Periodically Flooded Soils. 1988. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Vepraskas, M. J. and J. Bouma. 1976. Model Experiments On Mottle Formation Simulating Field Conditions. Geoderma. 15:217-230.

Vepraskas, M. J. 1992. Redoximorphic Features for Identifying Aquic Conditions. Technical Bulletin 301. North Carolina Agricultural Research Service, North Carolina State University, Raleigh, North Carolina.

von Gunten, U. and J. Zobrist. 1993. Biogeochemical Changes in Groundwater-infiltration Systems: Column Studies. Geochimica et Cosmochimica Acta. 57:3895-3906.

Wang, H. D., G. N. White, F. T. Turner and J. B. Dixon. 1993. Ferrihydrite, Lepidocrocite, and Goethite in Coatings from East Texas Vertic Soils. Soil Sci. Soc. Am. J. 57:1381-1386.

Zinn, J. A., and C. Copeland. 1982. Wetland Management, Congressional Research Service, The Library of Congress, Washington, D. C., p. 149.

Chapter V.

Summary and Conclusions

Complex stratigraphy within the Willamette Valley can exert profound effects upon hydrologic response within the soil profiles and facilitate the creation of redoximorphic features within hydric soils. The J-F wetland lies on the western valley margin and receives input from upland soils, formed in Fe-Mn rich parent materials, via Jackson and Frazier Creeks. These relationships are responsible for the distribution of Fe, Mn, and P throughout the soil profile and the subsequent development of redoximorphic features in the form of concretions in the Bss and 2Bt horizons and nodules within the 3BC. These features reflect specific hydrologic and redox environments within the wetland that can be evaluated and correlated using piezometers, Pt electrodes, and DO probes.

The elemental distribution, fabric, structure, phyllosilicate and Fe oxide mineralogy of the concretions and nodules relative to their respective matrices also provide important data on the current and long-term redox/hydrologic environment within the J-F wetland. The large amounts of kaolinite and halloysite within the J-F strata reflect the significant input of secondary minerals derived from deeply weathered igneous extrusive material from the foothills of the Oregon Coast Range.

Polarizing microscopy and SEM characterization indicates that the Bss/2Bt concretions and the 3BC nodules began forming after episodic Pleistocene flooding and the mixing of materials of disparate provenance. SEM examination, DCB and AAO extracted Fe-Mn, isotopic signature, photo-microscopy, and XRD provide evidence that the Bss and 2Bt concretions within the J-F wetland are still forming today in a Mn 'depleted' matrix as a function of stratigraphy, climate, and biogeochemical environment. Holocene wetland genesis appears to be continuing on this landscape and this surface in the J-F wetland.

The disparate clay mineral isotopic compositions between the 2Bt/3BC

matrices and their concretions/nodules indicate that the fine clays within these concentrations have formed in isotopically lighter water, are of probable 'Missoula floods' provenance, and were not initially weathered in the current meteoric environment. Isotopic differences suggest that the 2Bt concretions and 3BC nodules began forming quickly enough to retain more of their early meteoric (extra-Willamette Valley) signature. This signature has since been masked within the matrix, presumably by additional authigenesis or infiltration of clays from the upper stratum. Identical isotopic signatures between the Bss concretions and matrix suggests that the concretions were formed in the same meteoric environment and location after late Pleistocene flooding. Identical stratigraphic position, similar mineralogy, and the same isotopic composition between soil horizons formed in a known Malpass member (the Dayton 2Bt and 3Bt) and J-F 2Bt suggests that the two units are the same and the J-F alluvium may have been deposited on an older surface incised into the Malpass and Greenback units. Sratigraphy, geomorphic surfaces, and isotopic composition suggest that the older nodules in the 3BC silts may be near 38ky and the 2Bt concretions between 3.3-15ky.

More precise estimates of age can be made for the Bss concretions. While the age of the Ingram geomorphic surface suggests that the older Bss concretions may be near 3300y, modeling their rate of formation by seasonal Fe^{+2} availability relative to the degree of DCB-Fe enrichment suggests a period of 2-3ky, with an average near 2,333y, for this degree of enrichment to occur. Radiocarbon dating of the Bss concretion-C14 indicates the 4-9mm diameter size fraction to be a minimum age of 1,500±80y. Given that this is an average value of all organic C within the concretion - an age of >1,500y and <3,000y is reasonable. Phosphorus data in conjunction with these age estimates suggest an average of $0.4kg\text{-}Pha^{-1}y^{-1}$ is sequestered in the Bss concretions within the J-F wetland. Due to the cementation of the concretions and nodules with Fe and Mn and the presence of pressure oriented smectite within the concretions, and at their surface, it is assumed that this P is unavailable for movement or plant uptake and this mechanism plays a role in water quality dynamics of wetland

systems. The amount of concretions (1.7%) and the age of this stratigraphic unit suggests that the greatest rate of concretion formation has occurred in this horizon. The age of the 2Bt horizon (12.8-15ky), with 0.8% concretions by weight and, the 3BC horizon (38-50ky) with 2% nodules by weight, suggest that the slowest rate of nodule/concretion formation has occurred in these horizons. The low amounts of DCB and AAO-Fe and Mn, and the small number and weight of concreitons, reflect the almost continual saturated and reduced (<200mV SHE) condition of the 2Bt horizon.

This study elucidates geomorphic and stratigraphic relationships and long-term processes operating within the J-F and other Willamette Valley hydric soils on similar surfaces and/or landscape positions and help us to understand how wetlands function on a more fundamental level.

Bibliography

Aguilera, N. H., and M. L. Jackson. 1953. Iron Oxide Removal from Soils and Clays. Soil Sci. Soc. Am. Proc. 17:359-364.

Arshad, M. A. and R. J. St. Arnaud. 1980. Occurrence and Characteristics of Ferromanganiferous Nodules in Some Saskatchewan Soils. Can. J. Soil Sci. 60: 685-695.

Austin, W. 1994. Duration of saturation and redox potentials in selected Willamette Valley soils. M.S. Thesis, Oregon State University, Corvallis, Or. 256 pp.

Balster, C. A. and R. B. Parsons. 1969. Late Pleistocene Stratigraphy, Southern Willamette Valley, Oregon. Northwest Sci. 43:116-129.

Bartlett, R. J. and B. R. James. 1993. Redox Chemistry of Soils. Advances in Agronomy. 50:151-208.

Boersma, L., G.H. Simonson and D.G. Watts. 1972. Soil Morphology and Water Table Relations: II. Correlation Between Annual Water Table Fluctuations and Profile Features. Soil Sci. Soc. Am. Proc. 36:649-654.

Blaylock, M. J. and B. R. James. 1992. Oxidation - Reduction Behavior of Selenite in Soils. Soil Sci. Soc. Am. J. (submitted)

Blume, H. P. 1988. The Fate of Iron During Soil Formation in Humid-Temperate Environments. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Bretz, J. H. 1969. The Lake Missoula Floods and the Channeled Scabland. J. of Geology. 77:505--543.

Brewer, R. 1976. Fabric and Mineral Analyses of Soils. Robert E. Krieger Publishing. Huntington, New York.

Carter, V., M. S. Bedinger, R. P. Novitski and W. O. Wilen. 1979. Water Resources and Wetlands, in Wetland Functions and Values : The State of Our Understanding, P. E. Greeson, J. R. Clark, and J E. Clark, eds., American Water Resources Assoc., Minneapolis, Minn., pp. 344-376.

Carter, V. 1986. An Overview of the Hydrologic Concerns Related to Wetlands in the United States, Can. J. Bot. 64:364-374.

Cogger, C. G., and P. E. Kennedy. 1992. Seasonally Saturated Soils in the Puget Lowland I. Saturation, Reduction and Color Patterns. Soil Sci. Vol. 153, No. 6.

Cogger, C. G., P. E. Kennedy, and D. Carlson. 1992. Seasonally Saturated Soils in the Puget Lowland II. Measuring and Interpreting Redox Potentials. Soil Sci. Vol. 154.

D'Amore, D. V. 1995. The Stratigraphy, Hydrology, and Redoximorphic Character of the Jackson-Frazier Wetland. M.S. Thesis. Oregon State University, Corvallis, Or.

Diers, R., and J. L. Anderson. 1984. Part I, Development of Soil Mottling, in Soil Survey Horizons, winter 1984. pp. 9-12.

Drosdoff, M., and C. C. Nikiforoff. 1940. Iron-manganese Nodules in Dayton Soils. Soil Sci. 49:333-345.

Gallaher, R. N., and H. F. Perkins. 1973. Soil Nodules: I. X-ray Spectrograph and Electron Microprobe Analyses. Soil Sci. Soc. Amer. Proc. 37: 465-469.

Glasmann, J. R. 1982. Soil Solution Chemistry, Profile Development, and Mineral Authigenesis in Several Western Oregon Soils. Ph.D. Thesis, Oregon State Univ. Univ. Microfilms. Ann Arbor, Mich. (Diss. Abstr. 82:16636).

Glasmann, J. R. and G. F. Kling. 1980. Origin of Soil Materials in Foothill Soils of Willamette Valley, Oregon. Soil Sci. Soc. Am. J., 44:123-130.

Glasmann, J. R. and G. H. Simonson. 1985. Alteration of Basalt in Soils of Western Oregon. Soil Sci. Soc. Am. J. 49:262-272.

Glenn, J. L. 1965. Late Quaternary Sedimentation and Geologic History of the North Willamette Valley, Or. Ph.D. thesis, Oregon State University, Corvallis, Or.

Hansen, H. C. B., O.K. Borggard, and J. Sⓔrensen. 1994. Evaluation of the Free Energy of Formation of Fe(II) - Fe(III) hydroxide-sulphate (green rust) and its reduction of nitrite. Geochimica et Cosmochimica Acta, Vol. 58, No. 12, pp. 2599-2608.

Heller, P. L., Peterman, Z. E., O'Niel, J. R. and M. Shafiqullah. 1985. Isotopic Provenance of Sandstones from the Eocene Tyee Formation, Oregon Coast Range. Geological Soc. Am. Bull. 96:770-780.

Jackson, M. L. 1979. Soil Chemical Analysis-Advanced Course. 2nd ed., 11th Printing. Published by Author, Madison, WI 53705.

Knight, R. L., T. W. McKim, and H. R. Kohl. 1987. Performance of a Natural Wetland Treatment System for Wastewater management. J. Water Poll. Control Federation. 59:746-754.

Lawrence, J. R. and H. P. Taylor. 1971. Deuterium and Oxygen-18 Correlation: Clay Minerals and Hydroxides in Quaternary Soils Compared to Meteoric Waters

Lovely, D. R. 1993. Dissimilatory Metal Reduction. Annu. Rev. Microbiol. 47:263-290.

Marshall, J. 1985. A Value Assessment of the Jackson-Frazier Wetland. Unpublished MS thesis, Oregon State University, Corvallis, Or.

Mehra, O. P. and M. L. Jackson. 1960. Iron Oxide Removal from Soils and Clays by a Dithionite-Citrate System Buffered with Sodium Bicarbonate. Clays Clay Miner. 7:317-327.

Miller, D.M., T. Tang and D. W. Paul. 1993. Electrolytic Reduction of Soil Suspensions. Soil Sci. Soc. Am. J. 57:356-360.

Minerals in Soil Environments. 1989. SSSA Book Series: 1 (eds.) J. B. Dixon and S.B. Wood. p.393.

Mitsch, W. J. and J. G. Gosselink. 1993. Wetlands. Van Nostrand Reinhold Publishing, New York, New York. 698 p.

Moormann, F. R., and H. T. J. van de Wetering. 1985. Problems in Characterizing wetland soils. pp. 53-68. In Anonymous (ed.). Wetland Soils: Characterization, Classification, and Utilization. Proc. of a workshop held March 26 to April 5, 1984. Int. Rice Res. Inst., Los Banos, Phillippines.

Natural Resource Conservation Service. 1995. Wet Soils Monitoring, Benton County, Oregon. (CP93-OR076).

Norgren, J. A. 1962. Thin-section Micromorphology of Eight Oregon Soils. M.S. Thesis. Oregon State Univ., Corvallis, OR.

Parsons, R.B., C.A. Balster, and A.O. Ness. 1970. Soil Development and Geomorphic Surfaces, Willamette Valley Oregon. Soil Sci. Soc. Am. Proc. 34:485-491.

Phillippe, W. R., Blevins, R. L., Barnhisel, R. I. and H. H. Bailey. 1972. Distribution of Nodules From Selected Soils of the Inner Blue Grass Region of Kentucky. Soil Sci. Soc. of Amer. Proc. 36: 171-173.

Reckendorf, F. 1992. Geomorphology, Stratigraphy, and Soil Interpretations, Willamette Valley, Oregon. In: Proceedings of the Eighth International Soil Management Workshop: Utilization of Soil Survey Information for Sustainable Land Use. (ed. J. M. Kimble). July 11-24, 1992. May, 1993.

Rhoton, F. E., Bigham, J. M. and D. G. Schulze. 1993. Properties of Iron-Manganese Nodules from a Sequence of Eroded Fragipan Soils. Soil Sci. Soc. Am. J. 57:1386-1392.

Schwertmann, U. 1988. Occurrence and Formation of Iron Oxides in Various Pedoenvironments. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Schwertmann, U. land R. M. Taylor. 1989. Iron Oxides. pp.379-437 In: F.B. Dixon and S.B. Weed (eds.) Minerals in Soil Environments. Soil Environments. Soil Sci. Soc Am., Madison, WI.

Seter, L. M. and J. Baham. 1994. Geochemical Characteristics of Iron-Manganese Nodules in Seasonally-Flooded Soils in the Willamette Valley, Oregon. P.249. In Agronomy Abstracts. ASA, Madison, WI.

Snavely, P. D., N. S. MacLeod and H. C. Wagner. 1968. Tholeiitic and Alkalic Basalts of the Eocene Siletz River Volcanics, Oregon Coast Range. Am. J. Sci., 266:454-581.

Soil Survey Staff. 1992. Keys to Soil Taxonomy, fifth edition. SMSS Tech. Monogr. No.7. Virg. Polytech Inst. and State Univ., Blacksburg.

Somera, R. D. 1967. Iron and Manganese Distribution and Seasonal Oxidation Changes in Soils of the Willamette Drainage Sequence. Unpublished M.S. Thesis. Oregon State University, Corvallis, Oregon.

Stumm, W. and B. Sulzberger. 1992. The Cycling of Iron in Natural Environments: Considerations Based on Laboratory Studies of Heterogenous Redox Processes. Geochimica et Cosmochimica Acta. 56:3233-3257.

Tardy, Y. and D. Nahon. 1985. Geochemistry of Laterites, Stability of Al-Goethite, Al-Hematite, and Fe^{+3}-Kaolinite In Bauxites and Ferricretes: An Approach to the Mechanism of Nodule Formation. Am. J. of Sci. 285:865-903.

van Breeman, N. 1988. Long-term Chemical, Mineralogical, and Morphological Effects Of Iron-redox Processes In Periodically Flooded Soils. 1988. In: Iron in soils and Clay Minerals. J. W. Stucks et al., (eds). D. Reidel Publishing Co.

Vepraskas, M. J. and J. Bouma. 1976. Model Experiments On Mottle Formation Simulating Field Conditions. Geoderma. 15:217-230.

Vepraskas, M. J. 1992. Redoximorphic Features for Identifying Aquic Conditions. Technical Bulletin 301. North Carolina Agricultural Research Service, North Carolina State University, Raleigh, North Carolina.

Vepraskas, M. J. and L. P. Wilding. 1983. Albic Neoskeletans in Argillic Horizons as Indices of Seasonal Saturation and Iron Reduction. Soi Sci. Soc. Am J. 47:1202-1208.

von Gunten, U. and J. Zobrist. 1993. Biogeochemical Changes in Groundwater-infiltration Systems: Column Studies. Geochimica et Cosmochimica Acta. 57:3895-3906.

Wang, H. D., G. N. White, F. T. Turner and J. B. Dixon. 1993. Ferrihydrite, Lepidocrocite, and Goethite in Coatings from East Texas Vertic Soils. Soil Sci. Soc. Am. J. 57:1381-1386.

Zinn, J. A., and C. Copeland. 1982. Wetland Management, Congressional Research Service, The Library of Congress, Washington, D. C., 149 p.