

B51B-0728 0830h POSTER

Incorporation of arsenic in mammal bone: X-ray absorption spectroscopy

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X-ray absorption spectroscopy (XAS) of the distal tibia of a modern deer, *Odocoileus virginianus*, revealed that the energy position of the As K edge matched that of a reference arsenic(V) model compound. Comparison of the x-ray absorption near edge structure (XANES) of the deer spectrum to the spectra of model As compounds indicated a close match to arsenate(V), e.g., zinc orthoarsenate(5). This indicates that the nearest-neighbor shell of the arsenic in the bone consists of four oxygens in the tetrahedral arrangement typical of arsenic(V) oxyanions.

The XANES analysis demonstrates that the arsenic in the deer bone is not associated with an organic compound as a result of methylation. This suggests that the arsenic is associated with the mineral fraction of the bone, most likely with As substituting for P at the latter's structural site in the hydroxyapatite. The XAS data for the deer bone were very noisy due to the low level of arsenic present, just over 1 ppm. A total of 18 scans, taking nearly a full 8-hour beam shift, were averaged to obtain the spectrum studied. It is not clear that the second neighbor shell can be characterized sufficiently from these data to confirm that As substitutes for P in hydroxyapatite.

We conducted our XAS experiments on beam line 4-3 at the Stanford Synchrotron Radiation Laboratory. Data were collected in the fluorescence mode, using a solid state, 13-element Ge-detector. The energy reference was As(0) metal foil run parasitically in transmission mode during collection of the bone spectra. The edge shift seen in the experimental and As(V) model compound relative to the energy position of the arsenic(0) foil is consistent with the additional energy required to photoeject the 1-s electron of As(V), relative to that required for As(0). Arsenic content of the deer bone was determined by inductively coupled plasma mass spectrometry.

B51B-0729 0830h POSTER

Use of Synchrotron X-ray Fluorescence to Measure Trace Metal Distribution in the Brain

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X26A, National Synchrotron Light Source, was used to quantitatively evaluate the spatial distribution of trace metals, such as Zn and Cu, in brain tissue. X-ray microprobe techniques offer distinct advantages over other analytical methods by allowing analysis to be done in-situ with little or no chemical pretreatment and low detection limits (about 1 ppm). In the context of neuroscience, SXRF can provide non-destructive measurements of specific metal concentrations and distribution within nerve (brain) tissue. Neuronal tissue from organisms having undergone different normal or experimental conditions may be compared, with analytical capacities not limited by binding states of the metal (i.e., vesicular or enzymatic), as is the case with staining techniques. Whole regions of tissue may be

scanned for detectable trace metals at spatial resolutions of 10um or less using focused monochromatic x-ray beams. Here special attention has been given to zinc because it is the most common trace metal in the brain, and levels have been increasing in the environment. In this investigation, zinc concentrations present within the hilus of a rat hippocampus, and to a lesser extent in the cortex, have been shown to increase following long-term ingestion of zinc-enhanced drinking water that was associated with deficits in spatial memory. Concomitantly, copper concentrations in the internal capsule were comparatively lower. Other first order transition metals, Cr, V, Mn, and Co were not detected. In contrast, elevated levels of Zn, Cu, and Fe have been seen in amyloid plaques associated with Alzheimer's disease.

B51C MCC: 132 Friday 0830h

Mechanisms of Carbon Stabilization and Loss in Soils I (joint with GC)

Presiding: J Harden, U.S. Geological Survey; K O'Neill, USDA Forest Service

B51C-01 0840h INVITED

Thermally Altered Biomass (Black Carbon) in Soils: Formation, Analysis, Distribution, and Implications

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Black Carbon (BC), formed during biomass burning, is a chemically heterogeneous, biologically refractory class of carbon compounds (1, 5). BC is purely terrestrial in origin and occurs ubiquitously in soils and terrestrial sediments and is coupled to a common marine fate via atmospheric and fluvial transport, potentially representing a significant reservoir of extremely slowly cycling carbon (1). However, because of its physicochemical heterogeneity and a lack of established analytical techniques, the geochemistry and quantitative importance of BC in the global carbon cycle remains largely undescribed. Existing methods rely on operational definitions with clear-cut but different boundaries inherently designed to analytically determine different parts of the BC continuum (1, 2, 3).

In a set of German chernozem soils, BC from biomass burning makes up 15 to 45 percent of the soil organic carbon (SOC), as determined via UV-high energy photooxidation combined with ¹³C NMR (4, 6). High resolution microscopy and spectroscopy unambiguously confirmed the presence of submicron BC particles with short-range variability in elemental composition, and two sometimes coexisting modifications, i. e. amorphous char-BC from pyrolyzed cellulose and graphitic soot-BC. BC, up to 3990 years older than bulk SOC, is 1160 to 5040 carbon-14 years old, indicating significant residence times of BC in soils.

These results suggest three major implications: First, it seems that besides climate, vegetation and ioturbation, fire also plays an important role in the pedogenesis of Chernozems (4, 5). Second, BC can be a useful tracer for prehistoric human slash-and-burn activities, and thus represent a novel type of archaeological evidence (7). Third, the concept that BC from biomass burning is the source of the chemically stable aromatic components of soil organic matter, and point toward a different understanding of the large quantitative importance and longevity of BC in the terrestrial system (3, 4). BC provides a final sink for terrestrial organic carbon, removing substantial amounts of carbon from rapid circulation between the atmosphere, terrestrial and marine biosphere, and thus could be important to close the carbon budget in global biogeochemical models.

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B51C-02 0855h

The Sequestration and Protection of Organic Matter Within Mineral Mesopores

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Organic matter-mineral interactions may explain diverse phenomena such as sequestration of pollutants and preservation of organic matter in soils and sediments. Mineral mesopores (2-50 nm diameter) may sequester organic matter (natural and pollutant) and protect it from microbial and fungal enzymatic degradation in soils and sediments. To test this idea, we carried out batch aqueous experiments to examine adsorption of amino acid monomers and polymers onto synthetic mesoporous and nonporous alumina and silica with controlled intraparticle porosity with similar surface chemistry. All amino acid monomers and polymers smaller than about one-third the pore diameter exhibited significantly greater adsorption (on a surface area normalized basis) to mesoporous alumina (8.2 nm mean pore diameter) and silica (3.4 nm mean pore diameter) versus nonporous phases. Amino acid polymers (lysozyme, albumin, g-globulin) of sizes approaching and larger than the mesopores, however, exhibited greater adsorption to the nonporous phases indicating their exclusion from the internal surfaces of the mesoporous minerals. Further, we observed a sharp decrease in the surface area of the mesoporous materials after adsorption of these proteins indicating blockage of pore openings. These results provide a potential mechanism for the selective sequestration of sedimentary organic matter.

To test whether these pore-sequestered materials are likely to be preserved, we incubate mesoporous and nonporous minerals and sorbed organic matter (model amino acid compounds and natural organic matter extracts) in solutions containing bacterial or fungal derived enzymes. The amount of degradation of sorbed organic matter is detected by measuring sediment TOC before and after the experiment while qualitative changes are indicated by diffuse reflectance infrared Fourier transform (DRIFT) spectra. We expect that small organic compounds sorbed within pores will be protected from degradation while organic matter sorbed to nonporous mineral will be minimally protected. An overall bias toward the preservation of lower molecular weight organic matter is predicted. These results highlight the importance of particle surface morphology for organic matter preservation in soils and sediments.

B51C-03 0910h INVITED

Interactions between carbon and nitrogen mineralization and soil organic matter chemistry in Arctic tundra soils

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We used long term long-term lab incubations and chemical fractionation to characterize the mineralization dynamics of organic soils from tussock, shrub, and wet meadow tundra communities, to determine the relationship between soil organic matter (SOM) decomposition and chemistry, and to quantify the relative proportions of carbon (C) and nitrogen (N) in tundra SOM that are biologically available for decomposition. Despite large losses of soil C, respiration rates generally did not decline, and SOM chemistry was relatively unchanged after the incubation. The decomposition dynamics we observed suggest that tundra SOM, which is largely plant detritus, fits within existing concepts of the litter decay continuum. The lack of changes in organic matter chemistry indicates that this material had already decomposed to the point where the breakdown

of labile constituents was tied to lignin decomposition. Our results suggest that a large proportion of tundra SOM is potentially mineralizable, despite the fact that decomposition was dependent on lignin breakdown, and that the historical accumulation of organic matter in tundra soils is the result of field conditions unfavorable to decomposition, and not the result of fundamental chemical limitations to decomposition. Our study also suggests that the anticipated increases in shrub dominance may substantially alter the dynamics of SOM decomposition in the tundra.

B51C-04 0925h

Production of Dissolved Organic Matter During Fungal Wood Rot Decay

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Dissolved organic matter mediates numerous biogeochemical processes in soil systems impacting subsurface microbial activity, redox chemistry, soil structure, and carbon and nitrogen sequestration. The structure and chemistry of DOM is a function of the inherited chemistry of the source material, the type of microbial action that has occurred, and selective interaction with mineral substrates. The type of fungal decomposition imparted to woody tissue is a major factor in determining the nature of DOM in forest soils. In order to investigate the relationship between fungal decomposition and the nature of DOM in coniferous forest soils we conducted 32-week inoculation studies on spruce sapwood with basidiomycete brown-rot wood decay fungi where leachable dissolved and colloidal organic matter was separated from decayed residue. A detailed examination of the organic fractions was conducted using ¹³C-labeled tetramethylammonium hydroxide thermochemistry, solid-state ¹³C-NMR, and electrospray mass spectrometry. The progressive stages of microbial decay (cellulolytic and ligninolytic) were manifested in the chemical composition of the DOM which showed an evolution from a composition initially polysaccharide rich to one dominated by mildly oxidized and demethylated lignin. Upon removal of all polysaccharides at 16 weeks the DOM (up to 10% by weight of the original tissue) looked chemically distinct from the degraded residue

B51C-05 0940h INVITED

Quantifying Fine Root Carbon Inputs To Soil: Results From Combining Radiocarbon And Traditional Methodologies.

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Estimates of high belowground net primary productivity (50% or more) in forest ecosystems are often based on assumptions that almost all fine roots (< 2 mm in diameter) live and die within one year. Recent radiocarbon (¹⁴C) measurements of fine root cellulose in three eastern temperate forests of the United States show that at least a portion of fine roots are living for more than 8 years (Gaudinski et al. 2001) and that fine root lifespans likely vary as a function of both diameter and position on the root branch system. New data from

investigations under way in several different temperate forests further support the idea of large variations in root lifespans with radiocarbon-derived ages ranging from approximately one year to several years. In forests where both mini-rhizotron and ¹⁴C lifespan estimates have been made, the two techniques agree well when the ¹⁴C sampling is made on the same types of roots viewed by mini-rhizotron cameras (i.e. first and second order roots; the most distal and newest roots on the root branching system), and the ¹⁴C signature of new root growth is known. We have quantified the signature of new tree roots by taking advantage of locally-elevated ¹⁴C at Oak Ridge Tennessee, which shows that carbon making up new roots was photosynthesized approximately 1.5 years prior to new root growth. Position on the root branching system shows a correlation with age, with ages up to 7 years for 4th order roots of red maple. The method by which roots are sampled also affects the ¹⁴C-estimated age, with total fine root population, sampled via soil cores, showing longer lifespans relative to roots sampled by position on the root branch system (when similar diameter classes are compared). Overall, the implication of our studies is that assumptions of turnover times of 1 year result in underestimates of the true lifespan of a large portion of fine root biomass in temperate forests. This suggests that future calculations of belowground net primary productivity should take variation in fine root lifespan into account.

Reference: Gaudinski JB, Trumbore SE, Davidson EA, Cook A, Richter D (2001) The age of fine-root carbon in three forests of the eastern United States measured by radiocarbon, *Oecologia* 129:420-429.

B51C-06 0955h

Management-Induced Changes in Organic Carbon Pools of Temperate Soils: C-14 and C-13 Evidence

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Interpretation of soil organic carbon (SOC) dynamics has been difficult because SOC is a mixture of materials with vast different turnover times. This heterogeneous nature of SOC necessitates the differentiation of component pools in order to describe the turnover kinetics. Currently no satisfactory method is available to separate those SOC pools physically. Recent advances in bulk SOC methods using natural C-14 and C-13 signatures, however, have gained insights into the turnover of SOC in temperate soils. This paper presents the findings of SOC turnover dynamics in North America croplands by interpreting data from published literature using the bulk carbon paired-plot approach. The analysis indicates that management-induced changes in SOC are mainly in the active pools that have turnover time ranging from 15-93 y. The ages of the refractory pools are in the range of 899-5138 y. Management may change the sizes of active pools drastically but not their turnover times. The results suggest a bimodal distribution of SOC in temperate surface soils which can be approximated by two distinct SOC groups: active SOC pools turnover in decades or less and refractory pools turnover in hundreds of years or more. Temperate soils can be sources or sinks of atmospheric CO₂ depending on management which affects the sizes of active SOC. Active SOC will reach a new equilibrium in 30-200 y depending on the nature of soils and climates. The mechanism that preserves the refractory SOC is not clear at this point, however, certain aggregates formed by clay and organic matter may hold the key to the protection of refractory SOC.

B51C-07 1030h INVITED

Organic Matter Quality and its Influence on Carbon Turnover and Stabilization in Northern Peatlands

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Peatlands cover 3-5 % of the world's ice-free land area, but store about 33 % of global terrestrial soil carbon. Peat accumulation in northern regions generally is controlled by slow decomposition, which may be limited by cold temperatures and water-logging. Poor organic matter quality also may limit decay, and microbial activity in peatlands likely is regulated by the availability of labile carbon and/or nutrients. Conversely, carbon in recalcitrant soil structures may be chemically protected from microbial decay, particularly in peatlands where carbon can be buried in anaerobic soils.

Soil organic matter quality is controlled by plant litter chemical composition and the susceptibility of organic compounds to decomposition through time. There are a number of techniques available for characterizing organic quality, ranging from chemical proximate or elemental analysis to more qualitative methods such as nuclear magnetic resonance, pyrolysis/mass spectroscopy, and Fourier transform infrared spectroscopy. We generally have relied on proximate analysis for quantitative determination of several organic fractions (i.e., water-soluble carbohydrates, soluble nonpolars, water-soluble phenolics, holocellulose, and acid insoluble material). Our approaches to studying organic matter quality in relation to C turnover in peatlands include 1) ¹⁴C labelling of peatland vegetation along a latitudinal gradient in North America, allowing us to follow the fate of ¹⁴C tracer in belowground organic fractions under varying climates, 2) litter bag studies focusing on the role of individual moss species in litter quality and organic matter decomposition, and 3) laboratory incubations of peat to explore relationships between organic matter quality and decay.

These studies suggest that proximate organic fractions vary in lability, but that turnover of organic matter is influenced both by plant species and climate. Across boreal peatlands, measures of soil recalcitrance such as acid insoluble material (AIM) and AIM/N were significant predictors of decomposition. However, when limited to individual peatland features or bryophyte species, soluble proximate fractions were better predictors of organic matter decay. This suggests that decomposition within single litter or peat types is controlled by the size of relatively small, labile carbon pools. As peatlands store the majority of soil carbon in the boreal forest, the influences of peat quality on carbon storage and turnover should be considered in understanding the fate of carbon in northern ecosystems.

B51C-08 1045h

Peatland Responses to Varying Interannual Moisture Conditions as Measured by Automatic CO₂ Chambers

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Net ecosystem CO₂ exchange (NEE) was measured from June 2000 through October 2001 by ten automatic chambers at a peatland in southeastern New Hampshire. The high temporal frequency of this sampling method permitted detailed examination of NEE as it varied daily and seasonally. Summer of 2001 was significantly drier than the 30-year average, while summer of 2000 was wetter than normal. Although NEE varied spatially across the peatland with differences in plant species composition and biomass, maximum CO₂ uptake was 30-40% larger in the drier summer in evergreen and deciduous shrub communities, but the same or lower in sedge sites. Ecosystem respiration rates were 13-84% larger in the drier summer depending on plant growth form with water table and temperature as strong predictors. Ecosystem respiration was also correlated with maximum ecosystem productivity suggesting that plant processes, water table and temperature are tightly linked in their control of soil and plant respiratory losses. The ratio between maximum productivity and respiration declined for evergreen shrub and sedge sites between the wet and dry summer, but increased in deciduous shrub sites. A drier climate may reduce the CO₂ sink function of peatlands for some plant growth forms and increase it for others. Ecosystem carbon and climate models should account for differences in growth form responses to a drier climate when predicting the effects of climate change on ecosystem carbon balances.

B51C-09 1100h

Climate Controls on Carbon Sequestration in Eastern North America

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Mid-latitude forest ecosystems have been proposed as a "missing sink" today. The role of soils (including wetlands) in this proposed sink is a very important unknown. In order to make estimates of future climate change effects on carbon storage, we can examine past wetland carbon sequestration. How did past climate change affect net wetland carbon storage? We present long-term data from existing wetland sites used for paleoclimate reconstruction to assess the net carbon storage in wetland over the last 15,000 years. During times of colder and wetter climate, many mid-latitude sites show increases in carbon storage, while past warmer, drier climates produced decreases in storage. Comparisons among bog, fen, swamp, and tidal marsh are demonstrated for the Hudson Valley region.

B51C-10 1115h

On Farm Management and its Effect on Carbon Sequestration

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The interest in carbon sequestration in soils is increasing and how different farm management practices affect carbon is of interest to farmers and land managers. Much of the work in the past has been done on experimental plots and not in fields with the management found on producing or working farms. This work reports on studies on farms under normal management and not on research plots. Sites were studied in the grasslands of the central U.S. that were converted to CRP to look at the effect of various management practices on soil carbon. The effects of no-till were evaluated under a variety of management regimes in several different climatic zones. Native, no-till and conventional tilled sites on the same soil series were sampled in Ohio (long term no-till), Nebraska (irrigated fields) and Kansas (hog manure application both dryland and irrigated). Soils were sampled in 2-meter deep pits and laboratory measurements were made of the chemical and physical properties of the soil. Aggregate stability was one of the measured properties that was indicative of an improved soil structure and it clearly demonstrates that the aggregate stability improved rapidly under both CRP and also when no-till was used.

B51C-11 1130h

The Impact of Disturbance on Carbon Source and Sinks in Colorado Ecosystems

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During the past several decades, focus on terrestrial carbon sinks has been associated with forest regrowth and soil sequestration. The recent fire in the west (2000-2002) raises the question of what are the

net losses of carbon due to combustion losses, and the effect on the net biome carbon balance between fire events. Analysis of fire return intervals and changes in net ecosystem exchange during the succeeding years to evaluate the net uptake of carbon over these episodes of fire disturbances. Comparison of the forest net carbon exchange will be compared to agricultural soil sequestration to compare the net sink potentials and the implications of disturbance and agricultural management regimes. We will be making these assessments using a modified version of the DayCent model. This model allows us to combine the slow responses of earth system components associated with forest growth and soil organic matter development with the fast processes associated with daily and diurnal scales. The role of land management, agricultural prior disturbance and land use history, nutrient limitation, chronic and acute stress all feature prominently as mechanisms in recent US-wide estimates of carbon fluxes.

B51C-12 1145h

Effects of soil thermal dynamics on carbon cycling in extratropical terrestrial ecosystems of the Northern Hemisphere

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Evidence from a variety of analyses and sources confirms that the terrestrial biosphere became a larger carbon sink in the 1990s as compared to the 1980s. This recent sink can be largely attributed to the Northern extratropical areas (30°N-90°N), roughly split between North America and Eurasia. However, there are considerable uncertainties as to the magnitude of the sink in different regions and the contribution of different mechanisms. Here we used the Terrestrial Ecosystem Model (TEM 5.0) to estimate the influence of soil thermal dynamics, including permafrost dynamics, on carbon storage in the Northern extratropics by coupling the simulation of TEM with a Model of Atmosphere Transport Chemistry (MATCH). We found that the simulated seasonal atmospheric CO₂ concentrations match both the amplitude and timing of the observations at the monitoring stations of NOAA/CMDL network. We found that the TEM simulations generally captured the greening trend in the Northern extratropics as found by remote sensing data. We estimated that only 0.55 and 0.90 Pg C yr⁻¹ were stored in Northern extratropical ecosystems during the 1980s and the early 1990s, respectively. These values are lower than comparable estimates from inverse model calculations, remote sensing and forest inventory data. In the 1980s, this storage was almost equally distributed between North America and Eurasia. However, in the early 1990s, carbon sequestration was strikingly different with 0.27 and 0.63 Pg C yr⁻¹ stored in North America and Eurasia, respectively. Overall, the study suggested that, in addition to the soil thermal dynamics, other mechanisms, such as nitrogen deposition, air pollution, might also be responsible for these regional differences of terrestrial carbon storage in the Northern extratropics.

B52A MCC: Hall C Friday 1330h

Mechanisms of Carbon Stabilization and Loss in Soils II Posters (joint with GC)

Presiding: J Harden, U.S. Geological Survey; K O'Neill, USDA Forest Service

B52A-0730 1330h POSTER

Nitrogen Retention by Buried Coarse Woody Debris in Lowland Coniferous Forests of Olympic National Park, Washington

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The N retention mechanisms and capacities of old-growth forests are poorly understood and generally underestimated. We characterized the types of immobilization abiotic vs. microbial that occur during the winter in soils of an old-growth coniferous forest on the western Olympic Peninsula, Washington. In addition, we investigated the effect of substrate type on N-retention capacity and efficiency. Large carbon accumulations in old-growth forests, in the form of a thick forest floor and buried coarse woody debris (BCWD), can provide a significant energy source for microbial utilization and may provide a buffer against N saturation by creating zones where the microbial community is N limited. In the forest studied, BCWD was nearly 15% of the total soil volume. Buried coarse woody debris was chemically and physically distinct from fine litter and mineral soil and may be different from surface coarse woody debris. Despite this, BCWD is customarily excluded from studies of soil N cycling. In this study, BCWD was a significant sink for added inorganic N under cold temperatures, and the microbial community in BCWD utilized C and N in different ratios than in either mineral soil or fine litter.

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The Potential use of Soil-C Isotope Analyses to Evaluate Paleoclimate

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Soil profiles were sampled by horizon to about 2m depth from 12 native grassland sites extending along and across the US Great Plains. Ring samples of above-ground plant material were clipped and related to their own and to the 13C and 12C isotope ratios (expressed as delta 13C) of the soil organic carbon (SOC) for present-day frigid, mesic, and thermic soil temperature regime soils. We make the assumptions that: (1) the delta 13C of SOC with horizon age (using 14C dating) was directly related to the mixture of warm and cool season plants growing during the prehistoric time period during which that earlier SOC was sequestered, and (2) the ratio of warm to cool season species that existed prehistorically was related to soil temperature regimes in the same way that we observed for the present time. Carbon isotope analyses, determined by soil horizon, were evaluate by their 13C and 12C ratios to determine the possible temperature regimes that may have existed with increasing 14C ages ranging back to as long 13 thousand years before present (YBP) for each native grassland site. These data indicate that, especially within the present day mesic temperature zone, much cooler soil temperature regimes existed 8 to 12 thousand YBP, but had warmed by 2 thousand YBP. Also, older and younger soil horizons may have been intermixed during prehistoric times by soil erosion and deposition processes at several locations including in MT, MN, and TX.