Title: Paleomagnetism, Rock Magnetism and Diagenesis in Hemipelagic Sediments from the Northeast Pacific Ocean and the Gulf of California

Abstract approved: Shaul Levi, Associate Professor of Geophysics

Downcore magnetic profiles from undisturbed Kasten cores taken in rapidly deposited laminated sediments from the Gulf of California and in bioturbated hemipelagic muds on the Oregon continental slope give apparently reliable directions, but show dramatic decreases in the intensities of natural (NRM) and artificial (ARM, IRM) remanences with depth. Downcore porewater and solid sulfur analyses show concave-down decreases in porewater sulfate and systematic increases in pyrite and metastable monosulfides. The maximum curvature of the sulfide profiles occurs directly below the high magnetization zone. Combined with other compositional and mineralogic analyses, these data suggest that due to oxidative decomposition of organic matter, magnetites and other iron oxides become progressively reduced and subsequently sulfidized and pyritized with depth. Iron reduction seems to occur prior to sulfide formation. Changes in magnetic stability parameters are consistent with selective dissolution of the finer sized grains causing downcore coarsening of the magnetic fraction.
Paleomagnetic directions from the Oregon sediments show exceptional directional stability and provide a detailed record of geomagnetic secular variation for the past 3000 years. When compared to secular variation studies from other regions, directional fluctuations show good coherence and time delays consistent with a constant westward drift having a periodicity of 1200 years which has continued for at least the last 3000 years. A maximum correlation analysis with a zonal drift model of the present field lends support to this hypothesis.

Paleomagnetic measurements on a 152 m sedimentary section taken with a Hydraulic Piston Corer at DSDP Site 480 in the Gulf of California yield an almost continuous secular variation record for the past 200–300 Ky. Initial results show no major zones of reversed polarity and the core and site mean inclinations are not significantly different than the expected geocentric axial dipole inclination. The similarity of mean inclinations in laminated, homogeneous, and mottled sediment lithologies suggests that remanence was acquired below the active zone of bioturbation.
PALEOMAGNETISM, ROCK MAGNETISM, AND DIAGENESIS IN HEMIPELAGIC SEDIMENTS FROM THE NORTHEAST PACIFIC OCEAN AND THE GULF OF CALIFORNIA

by

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A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Completed 18 November 1983
Commencement June 1984
 APPROVED:

 Redacted for privacy

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 Date thesis is presented 18 November 1983

 Typed by Robert Karlin for Robert Karlin
ACKNOWLEDGEMENTS

Since this project encompassed several disciplines, much of the work would not have been possible without the unstinting support of many of the faculty, students, and staff at Oregon State University. I am indebted to my major adviser, Shaul Levi, who introduced me to paleomagnetism and provided constant encouragement and guidance in the course of my graduate studies. Ross Heath, Ken Scheidegger, Dale Bibee and Jim Ingle are sincerely appreciated for giving freely of their time, energy, and expertise as members of my committee.

I would especially like to thank Shaul, Ross, and Erwin Suess for their insights in helping to develop some of the ideas presented here. My warmest thanks are also extended to Hans Schrader for the opportunity to work in the Gulf of California.

The analytical aspects of this work benefited greatly from the time, expertise, and equipment unselfishly shared by several individuals: Sherman Gromme (USGS cryogenic magnetometer), H. Wickman (Mossbauer spectrometer), Ross Heath and Greg Camp1 (XRF), Andy Ungerer (LECO), Martin Goldhaber (sulfur analyses), and Minze Stuiver (C-14). I am also grateful to Becky Simpkins and Torrey Karlin for help in typing the initial draft.

One of the best aspects of my graduate tenure has been the warm, positive atmosphere created by my fellow co-workers, especially Dennis Schultz, Karin Schultz, Paul Loubere, Mitch Lyle, Dave Murray, and Haraldur Audunsson. Dennis also provided invaluable assistance in helping to obtain and measure some of the
paleomagnetic samples.

Finally, I would like to thank my wife, Torrey, whose patience, love and understanding made the effort worthwhile.

This work was supported in part by a Texaco Oil Fellowship and grants from the National Science Foundation.
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PALEOMAGNETISM, ROCK MAGNETISM, AND DIAGENESIS IN HEMIPELAGIC SEDIMENTS FROM THE NORTHEAST PACIFIC OCEAN AND THE GULF OF CALIFORNIA

INTRODUCTION

The study of variations in the Earth’s magnetic field is one of the oldest areas of scientific endeavor. In 1600, William Gilbert’s famous de Magnete marked the publication of one of the first studies utilizing the modern scientific technique. In this treatise, the dipolar nature of the geomagnetic field was compared to the properties of a uniformly magnetized sphere of lodestone. Soon afterward, H. Gellibrand in 1635 observed that the measurements of the magnetic declination in London changed with time. Since these early studies, the field has been observed to have drifted significantly westward with time. Despite extensive work, the nature of this geomagnetic secular variation is, as yet, poorly understood.

According to our present understanding, the magnetic field at the earth’s surface arises from the convective movements of conductive fluid in the earth’s core. Turbulent eddies and changing patterns of motion in the core dynamo result in spatial and temporal secular variation with unknown but probably variable time constants. The westward drift has been variously attributed to differential rotation between the core and mantle or the effects of Coriolis accelerations on upwelling and downwellings of molten iron in the core. Due to the shortness of the historical secular variation records, the time constants associated with the dynamo behavior are
poorly constrained.

This study concerns the paleomagnetism, rock magnetism, sedimentology, and geochemistry of marine sediments from the Oregon continental margin and the Gulf of California. The overall goal of this work has been to characterize the behavior of the secular variation in these areas on timescales of decades to millennia. In order to evaluate the fidelity and reliability of the sedimentary paleomagnetic record, careful study was made of the magnetic mineralogy and the sediments which carry the magnetic signal.

This dissertation is divided into seven sections. In the first chapter the downcore behavior of the natural remanent magnetization is examined in order to evaluate the potential of obtaining relative paleo-intensities from sediments. Rock magnetic, sedimentological, and geochemical analyses are combined to show that diagenesis of iron oxides, due to organic matter decomposition, causes reduction and dissolution of magnetic minerals and formation of pyrite with depth. This alteration changes the character of the original magnetic signal, thereby inhibiting relative paleointensity determinations. In the second chapter, the nature of the sediments, and the depositional chronology, are examined. The Oregon sediments are found to be a highly homogeneous mixture of material of complex lithology derived from several continental sources. The only anomalous downcore geochemical features are related to transformation of seawater sulfur into sedimentary pyrite. The Gulf of California sediments are found to be a mixture of a terrigenous source of remarkably constant mineralogy with biogenic silica in
diatoms. The relative propositions of these inputs is shown to be moderated by climatic influences. The third chapter describes pioneering efforts to determine the nature of the iron species in the sediments utilizing Mossbauer spectroscopy. The iron in the Oregon muds is found to reside mainly in detrital phyllosilicates, which show little variation in abundance downcore. Attempts to differentiate Fe sulfides from ferric oxides delineate limits of this technique in heterogeneous media.

Chapter IV concerns the rock magnetic experiments conducted to determine the nature of the sedimentary carriers. This section shows how certain systematic trends in rock magnetic properties can be explained as the result of progressive reduction and dissolution of magnetic oxides with depth.

In Chapter V, the secular variation of directions recorded in the Oregon sediments is examined. Our results, when compared to archaeomagnetic and sediment investigations from other regions, indicate the presence of a constant westward zonal drift of about 0.3°/yr for at least the past 3000 years. This finding is supported by a correlation analysis where the Oregon records are compared to a model of the present field drifting zonally at various rates back in time.

In Chapter VI, paleomagnetic measurements are reported from an ongoing study of a 152m Hydraulic Piston Core from the Gulf of California. The intent of this study is to examine, in detail, secular variation and possible geomagnetic excursions occurring in the past 200-300 Kyr. First results suggest that the sediment is a
reliable magnetic recorder and that the field has been primarily dipolar during this period when averaged over intervals of >10000 years.

The final chapter proposes a vector statistic for examining pairwise correlations of vector time series and presents a test for significance from a hypothesis of null correlation. In the appendices the various equations used in paleomagnetism are discussed and comments are made on the use (and misuse) of the associated statistics.
CHAPTER I

DIAGENESIS OF MAGNETIC MINERALS IN RECENT HEMIPELAGIC SEDIMENTS

ABSTRACT

Downcore magnetic profiles from undisturbed Kasten cores taken in rapidly deposited laminated sediments from the Gulf of California and in bioturbated hemipelagic muds on the Oregon continental slope give apparently reliable directions, but show dramatic decreases in the intensities of natural (NRM) and artificial (ARM, IRM) remanences with depth. Downhole profiles show monotonic decreases in porewater sulfate and systematic increases in solid sulfur, presumably in pyrite and metastable monosulfides. The maximum rate of change of the sulfide profiles occurs directly below the high magnetization zone. Combined with other compositional and mineralogical analyses, these data suggest that due to oxidative decomposition of organic matter, magnetites and other iron oxides become progressively reduced and subsequently sulfidized and pyritized with depth. Iron reduction seems to occur prior to sulfide formation. Changes in magnetic stability parameters are consistent with selective dissolution of the finer sized grains causing downcore coarsening of the magnetic fraction.

INTRODUCTION

Rapidly deposited sediments from marine and lake environments are being used increasingly to study decadal to millenial fluctuations
in the Earth's magnetic field. The objectives of these secular variation studies are to gain more fundamental understanding of the geodynamo and perhaps to develop a dating technique for sediments. While lacustrine sections are generally restricted to temperate latitude glacial lakes (<20 Ky. in age), rapidly deposited marine sediments along continental margins potentially offer continuous high resolution, yet long term records of geomagnetic secular variation in many parts of the world. However, to interpret the sedimentary magnetic record accurately, geochemical processes that affect the reliability of the magnetic signal must be understood. Here we discuss an important early diagenetic process occurring in marine sediments—the oxidative decomposition of organic matter, reduction of iron minerals and the formation of pyrite. Using examples from anoxic laminated sediments in the Gulf of California and suboxic bioturbated muds from the Oregon continental slope, we demonstrate how, in these two contrasting depositional regimes, iron reduction causes dramatic downcore decreases in remanence intensity and changes in stability, consistent with progressive dissolution of the finest grains and downcore coarsening of the remaining iron oxides.

Early Diagenesis

The ultimate cause of early diagenesis in marine sediments is the decomposition of organic matter by microbial oxidation. The rates of decomposition and effects on the substrate depend mainly on the availability and reactivity of both organic matter and
reductants and the competitive efficiency of microbial populations. Microbes tend to reduce those chemical species which produce the most energy. Thus, in pore waters, reduction tends to occur according to a well defined sequence determined by the free energies of the reactions (Stumm and Morgan, 1970, Reeburgh, 1982). In the pore waters of suboxic sediments, Froelich et al., (1979) found a systematic succession of downcore diagenetic reactions proceeding from direct oxidation (by \( O_2 \)) to manganese reduction, nitrate reduction and ammonia formation. After consumption of labile \( MnO_2 \) and \( NO_3 \), iron oxides are reduced, imparting the characteristic olive grey-green color to many hemipelagic muds. If sufficient metabolizable organic matter is still present, sulfate reduction begins, followed eventually by fermentation and concomitant methane production. At depths where sulfate is reduced, ferrous iron in the pore waters becomes sulfidized, first forming metastable monosulfides (e.g. mackinawite) and subsequently pyrite (Berner, 1964, Rickard, 1975, Goldhaber and Kaplan, 1974).

Sources of Iron For Reduction and Sulfidization

In the marine environment, reactive iron is present in detrital minerals, as Fe-oxide coatings, in exchangeable Fe-hydroxide interlayers in clays, and to a minor extent, as Fe-organic chelates. Authigenic iron carbonates and phosphates such as siderite (\( FeCO_3 \)) and vivianite (\( Fe_3(PO_4)_2 \cdot 8H_2O \)), while common in some lakes, are generally not found in marine sediments because of alkaline condi-
tions and the presence of calcium carbonate (Rickard, 1973).

In reducing environments, well crystallized iron oxides usually have been considered to be relatively inert (Berner, 1970). However, recent recalculation of phase equilibria in the Fe-S-H₂O system (Henshaw and Merrill, 1980) suggest that the common ferrimagnetic oxides (magnetite, hematite and maghemite) may not be thermodynamically stable in the Eh-pH conditions found in the porewaters of some anoxic sediments.

Among the detrital mineral phases, potentially reactive iron can be found in oxides (hematite, αFe₂O₃, maghemite, γFe₂O₃, magnetite, Fe₃O₄), hydroxides (Fe(OH)₃, Fe(II)Fe(III)(OH)ₓ), and oxyhydroxides (goethite, FeOOH) and various iron silicates, especially clays. The extent of reaction appears to depend on surface area as well as crystallinity. Berner (1970) found that sand or silt sized grains of magnetite, hematite, goethite, hornblende, augite, and biotite released iron much less readily in both HCl and H₂S than fine-grained hematites, goethites, and chlorites. In studying the reaction kinetics involved in the sulfidization of goethite, Rickard (1975) found that the reaction rate was a strong function of surface area, hence particle size. Indeed, the reaction rate was so rapid that he suggested that goethite sulfidation was not the rate controlling step in pyrite formation. Rather, in agreement with Berner (1970), he suggested that the rate of sulfate depletion was the controlling factor in pyritization.
Sulfide Mineral Phases

In the marine environment, the primary source of sulfur to sediments is seawater sulfate. Organically bound sulfur usually amounts to less than 10% of the total sediment sulfur content (Goldhaber and Kaplan, 1974). From laboratory syntheses, sulfide mineral phases include: 1) 'amorphous' iron sulfide, FeS<9>; 2) mackinawite, FeS; 3) cubic iron sulfide, FeS; 4) hexagonal pyrrhotite, FeS<1.1>; 5) griegite, Fe<3>S<4>; 6) smythite, Fe<3>S<4>; 7) marcasite, orthorhombic FeS<2>; and 8) pyrite, cubic FeS<2>.

Smythite, which is formed by sulfidization of siderite, (Rickard, 1973) and cubic FeS are not observed under natural sediment conditions, (Goldhaber and Kaplan, 1974). Marcasite, which can form authigenically or as a pseudomorph after pyrite, is formed under acid conditions (pH < 6.5) (Rickard, 1973).

Amorphous iron sulfides with compositions between FeS<0.87> and FeS<0.92>, are the initial black, acid soluble product of the reaction of ferrous iron with H<2>S or HS- (Berner, 1964). X-ray determinations by Rickard (1969) have found that this phase has peaks characteristic of poorly crystalline mackinawite. Upon aging in anoxic conditions, the 'amorphous' FeS can convert to well crystallized mackinawite, pyrrhotite or pyrite.

Mackinawite is a non-magnetic, acid soluble, sulfur-deficient tetragonal monosulfide. It is metastable at most Eh-pH and converts to pyrite in anoxic conditions, or griegite, if oxidized (Rickard, 1969, 1973). For marine conditions of pH 7.0-8.6, extensive work has shown that mackinawite is a necessary metastable precursor to pyrite.
Griegite is a metastable black, acid soluble cubic iron sulfide, Fe$_3$S$_4$, with an inverse spinel structure (Goldhaber and Kaplan, 1974). Forming a sulfur analogue to magnetite, it is strongly ferrimagnetic and has a Curie point of 580°C (Vaughn and Craig, 1978). In acid conditions, upon sulfidization of ferrous iron, griegite can coprecipitate with mackinawite; although in alkaline conditions, only mackinawite is observed. The transformation of mackinawite to griegite is an oxidation, thus oxygen or elemental sulfur are required. Griegite is metastable, and upon oxidation, converts to pyrite, marcasite or pyrrhotite (Rickard, 1969, 1973). As reviewed by Goldhaber and Kaplan (1974), griegite has been identified in recent muds of the Black Sea and Lake Superior. More recently, it has been found in brackish water sediments of an English tidal flat (Suttill et al., 1981).

The magnetic properties of griegite should be helpful in its identification in sediments. Since Rickard (1969) has shown that griegite transforms to pyrrhotite upon heating above 180°C, in a magnetite-griegite mixture, thermomagnetic measurements in vacuum or in a reducing environment may show an irreversible decrease in magnetization with a minimum at 300°C -320°C (the Curie point of pyrrhotite). In a similar manner to magnetite, griegite can readily oxidize upon heating in air, thus thermomagnetic measurements in air are unlikely to be diagnostic.

Pyrrhotite, with a composition of Fe$_{(1-x)}$S, is a stable end member, along with pyrite, in the iron sulfide system (Rickard,
1969). If lattice vacancies are present, the hexagonal structure of pyrrhotite can deform to monoclinic, giving rise to a net ferromagnetism with a spontaneous moment of 13.5 emu/gm and a Curie point of 320 °C (Stacey and Banerjee, 1974). Pyrrhotite can be synthesized from aqueous solutions with high heat or prolonged aging (Rickard, 1973). There appears to be little data on its distribution in sediments, although Kobayashi and Nomura (1972) reported pyrrhotite from sediments in the Sea of Japan. However, their reported thermomagnetic and X-ray data could not rule out the possibility of greigite or a co-existing mixture of maghemite and pyrite.

The other stable end member, pyrite, FeS₂, has a cubic structure and is acid insoluble. Pyrite is a common authigenic mineral in many lacustrine and marine sediments. It can occur either as single microscopic crystals, usually 1-10 μm in diameter, or as raspberry-shaped frambois (Goldhaber and Kaplan, 1974).

Formation of Pyrite

The reduction of iron oxides and liberation of hydrogen sulfide during organic matter decomposition are conducive to the formation of pyrite. If magnetic minerals are being reduced or if authigenic phases are formed, the paleomagnetist must be concerned with the pathways of pyrite formation.

The routes of pyritization are complex and controversial because of the many valence states of sulfur and their possible interactions with ferrous and ferric iron. As summarized by Goldhaber and Kaplan (1974), laboratory syntheses show that at low pH,
non-framboidal pyrite can form directly from ferrous iron and polysulfides, or co-precipitate with acid soluble phases, such as mackinawite and griegite. The acid soluble phases are metastable and can, in turn, transform to pyrite. In alkaline conditions such as found in the marine environment, it is generally accepted that the formation of pyrite requires the initial formation of intermediate, acid soluble monosulfides (Berner, 1970, 1981, Rickard, 1969, 1973, 1975, Goldhaber and Kaplan, 1974). In reactions of goethite with hydrogen sulfide at pH>6.5, Berner (1964) and Rickard (1969) found that mackinawite and elemental sulfur were the only products. Through the reaction \( \text{FeS} + \text{S}_0 \rightarrow \text{FeS}_2 \), pyrite can be formed (Berner, 1970).

Based on the results of Sweeney and Kaplan (1973), Goldhaber and Kaplan (1974) suggested that framboidal pyrite was formed when the initial "amorphous" FeS precipitate transformed into griegite, which has a spherical texture. As the griegite converted to pyrite, either the spherical texture was retained or framboids were developed. Thus, two distinct pathways for pyrite formation may exist, as evidenced by non-framboidal individual crystals or framboids.

These findings may have some significance to paleomagnetists. Since griegite formation is an oxidation process, the occurrence of griegite in anoxic, alkaline marine sediments might not be expected. However, after sampling or in laboratory drying experiments, mackinawite can oxidize to griegite when exposed to air, resulting in anomalous magnetizations with time and a spurious remanence. As the griegite converts to framboidal pyrite, magnetizations would
decrease. The occurrence of framboids in dried sediments or magnetic separates and their absence in fresh, wet sediments would be presumptive evidence for the formation and transformation of griegite.

Marine Areas Suitable For High Resolution Paleomagnetic Studies

Oceanic regimes which are amenable to high resolution paleomagnetic studies are those with high terrigenous sedimentation rates. These areas, generally adjacent to continental margins, also contain large amounts of organic matter in most cases because of 1) increased fluvially derived terrigenous carbon input, 2) upwelling-induced high oceanic carbon input, and 3) enhanced preservation due to rapid burial (Heath et al., 1977). As a consequence of the high carbon input, direct oxidation (by $O_2$), if present at all, is confined to the upper few cm of sediment, although this layer generally thickens going offshore (Reeburgh, 1982). If sufficient organic matter is present, the remainder of the sediment column is anoxic, since sulfate is abundant in seawater. This model for hemipelagic sediments contrasts with the deep sea pelagic 'red' clay regime, where due to low organic input and slow sedimentation, oxidizing conditions can prevail throughout the entire sediment column. (Sayles and Manheim, 1975)

RESULTS

We have made a detailed comparative study of the magnetic, geochemical and sedimentological properties of sediments from two con-
trasting depositional environments, the Gulf of California and the Oregon continental margin. BAM-80 El7 (27° 35.2' N, 111° 36.6' W, depth = 625 m) is a 4.5 m Kasten core taken in the Guaymas Basin where the oceanic O_2 minimum intersects the slope. The sediments are composed of undisturbed, finely laminated couplets of light colored diatom-rich ooze alternating with darker organic-terrigenous-diatom muds. Varve chronologies and three ^14C dates give sedimentation rates between 140 and 160 cm/Ky (see Chapter II). Major element chemistry shows high correlations (r > 0.9) between the terrigenous elements Al, K, Fe and Ti, suggesting downcore mixing of a single terrigenous assemblage, such as from the nearby Rio Yaqui, with Si-rich material, presumably diatoms (see Chapter II). This simple model is also supported by X-ray mineralogy (Chapter II) and Mossbauer studies (Chapter III).

Downcore magnetic profiles with replicated sampling give stable and apparently reliable directions. The core mean inclination of 41.1° (± 5° = 2°) is comparable to the expected geocentric axial dipole (EGAD) inclination of 46.3°. However, the striking feature of downcore natural (NRM) and laboratory-produced anhysteretic (ARM) remanent magnetization profiles, partially demagnetized at 100 Oe AF (Figure I-la), is the precipitous decrease in magnetic intensity by over an order of magnitude from the surface to 20-30 cm, whereupon intensities become relatively constant. The stabilities of NRM and ARM, as measured by the median demagnetizing field (MDF), also show a steplike decrease at this depth (Figure I-lb).

X-ray powder diffraction patterns of magnetic mineral separates
Figure I-1. Downcore magnetic properties and sulfur profiles of Kasten Core BAM 80-E17, Guaymas Basin, Gulf of California.

a) Magnetization intensities, partially demagnetized at 100 AF, and b) median demagnetizing fields of NRM (●) and ARM (○);
c) sulfate-corrected solid sulfur concentrations of total (●), and acid volatile (▲) fractions; d) porewater sulfate in millimoles/liter. Total sulfur was determined by X-ray fluorescence and LECO analyzer; acid insoluble sulfur was measured by LECO. Acid volatile is total minus acid insoluble sulfur, as obtained from LECO.
indicate that the top 30 cm consist mainly of pure magnetite \( (a_0 = 8.39 \text{ Å}) \) with minor amounts of hematite. Ferrimagnetic griegite \( (\text{Fe}_3\text{S}_4) \) was not observed. Below 30 cm, the only magnetic species present in the concentrates is pure magnetite. Isothermal remanence acquisition curves (Dunlop, 1972), as well as the X-ray results and ARM stabilities, suggest that the remanence throughout the core is controlled by magnetite. The ARM stabilities \( (250-450 \text{ Oe MDF}) \) suggest that the magnetic material is very fine grained. (Levi and Merrill, 1976) (see Chapter IV).

Core W7810 28 is a 3.9 m Kasten core \( (44° 50.1' \text{ N}, 125° 7.5' \text{ W}, \text{ water depth} = 1825 \text{ m}) \) taken in a small depositional basin on the lower Oregon continental slope. The sediment consists of heavily bioturbated, mottled to homogeneous olive-green hemipelagic mud. A red-brown surficial oxic layer was not observed, and a 30 cm boxcore at the same site contained numerous worms, tubules and burrows. Correlation with another \(^{14}C\) dated core at the same site indicates that the sedimentation rate is \( \sim 125 \text{ cm/Ky} \).

Downcore X-ray determinations and chemical analyses (Chapter II) suggest complex mineralogic assemblages which show no coherent variations with subbottom depth. Mossbauer studies (Chapter III) of bulk material show a remarkable downcore consistency in the chemical properties of the dominant iron-rich species (mainly detrital phyllosilicates).

Magnetic directions are stable and replicable within horizons. The core mean inclination of \( 60° \) \( (\alpha = 95 \pm 2°) \) closely approximates the EGAD inclination of \( 63° \). However, like the Guaymas Basin
Figure 1-2. Downcore magnetic properties and sulfur profiles of Kasten Core W7710-28, Oregon continental slope. a) Magnetization intensities, partially demagnetized at 150 Oe AF, and b) median demagnetizing fields of NRM (●) and ARM (○); c) solid sulfur concentrations of total (●), and acid insoluble (▲) fractions on a sulfate-free basis, as measured by X-ray fluorescence.
sediments, these muds also show a strong downcore decrease in NRM and ARM intensities ('cleaned' at 150 Oe AF) and decrease in MDF with depth (Figure 1-2 a,b), with the maximum change occurring between 70 and 100 cm. Magnetic concentrates contain only magnetite ($a_0 = 8.39 \text{ A}^\circ$) throughout the core.

Analyses of sedimentary sulfur in the Guaymas and Oregon sediments (Figures I-1c, I-2c) show an inverse relation between sulfur and magnetic intensity. For the Guaymas sediments, profiles of sulfate-free fractions of 1) total, 2) acid insoluble in 0.1 N HCl (pyrite + organic S), and 3) acid volatile (metastable monosulfides) sulfur show systematic increases downcore, reaching relatively constant values at 100-150 cm. The maximum rates of increase occur directly below the zone of high magnetization. In contrast, the porewater sulfate profile (Brumsack, pers. comm., 1981) shows an exponential downcore decrease, indicating sulfate reduction to a depth of ~300 cm (Figure I-1d).

Downcore sulfur profiles for the Oregon suboxic muds show analogous trends. Acid insoluble sulfur, presumably in pyrite, and total sulfur increase downcore, reaching relatively constant values at 110-130 cm, directly beneath the zone of high magnetization. An appreciable acid volatile fraction is not present.

DISCUSSION

In light of the models of iron and sulfur diagenesis described earlier, these diverse analyses yield a consistent picture of Fe diagenesis. In the 20-30 cm of the anoxic muds of the Guaymas Basin,
the iron in fine grained magnetic oxides (as well as other iron minerals) becomes reduced by reaction with organic matter. Changes in NRM and ARM intensities and stabilities are consistent with selective dissolution of the smaller grains, leading to downcore coarsening of the magnetic fraction.

Iron reduction must occur separately from and prior to sulfide formation since intermediate metastable sulfides are not produced in the top 20-30 cm and the various sulfide maxima occur at 50-100 cm, well below the iron reduction zone. This conclusion is in accord with laboratory experiments which have found that 1) iron reduction is independent of sulfate reduction and 2) nitrate reducing rather than sulfate-reducing bacteria appear to be responsible for iron reduction (Sorensen, 1982). Thus, reduced iron must either diffuse downward or form an unstable ferrous oxyhydroxide, silicate or Fe-organic chelate which is eventually moved into the zone of sulfidization and pyritization. The ferrous iron then reacts with hydrogen sulfide, derived from sulfate reduction, to form mackinawite (FeS) which inverts to pyrite upon reaction with elemental sulfur. Since the concentration profiles of the sulfide species are not mirror images of the porewater sulfate profile, the rates of monosulfide formation and pyritization must be controlled by the availability of both sulfide and reactive iron.

Similar processes can be recognized in the sub-oxic to anoxic Oregon muds, except that iron reduction and pyritization begins deeper in the sediments, probably as a result of more oxidizing conditions in the water column and bioturbation in the surficial sediments.
The reduction and dissolution of iron oxides is important to paleomagnetists studying rapidly deposited sediments in both lacustrine and marine environments. Since iron reduction is not directly coupled to sulfide formation, Fe oxides in lake sediments might also undergo reduction with accompanying decreases in remanence and other changes in magnetic properties with depth. Rather than forming sulfides, ferrous iron may accumulate to appreciable levels in the porewaters of lake sediments, eventually reacting to form authigenic minerals, such as siderite (FeCO$_3$) or vivianite (Fe(PO$_4$)$_2$·8H$_2$O) (Berner, 1981).

Although Fe reduction seems to have little effect on the reliability of paleomagnetic directions (see Chapter V), questions arise as to the validity of relative paleointensity determinations in diagenetically altered sediments. Such estimates rely on the assumptions that the distribution of remanence carriers is uniform throughout the section and that magnetic mineral concentration and field are the only independent variables responsible for the primary remanence (Levi and Banerjee, 1976). Unless 1) NRM stabilities remain constant downcore, and 2) concentration normalizing parameters (e.g. ARM) respond in an identical manner as NRM to dissolution-induced grain size changes, the above assumption(s) will be violated and relative paleointensity determinations will give erroneous estimates of paleofield behavior.

In both oceanic and lacustrine sediments, the extent of Fe diagenesis and consequent effects on magnetic properties will depend upon the degree to which reducing conditions are established, as well as the initial grain size distribution and crystallinity of the mag-
netic species. Since the redox potential is primarily controlled by the organic matter accumulation rate, the effects of iron reduction will be magnified in regions such as continental borderlands where sedimentation rates are high and the magnetic fraction is fine grained.

Downcore variations in magnetic properties (e.g. NRM, ARM, IRM or $\chi$, low field susceptibility) may provide rapid, non-destructive diagnostic tools for the geochemist in identifying zones where iron reduction has occurred. Moreover, the rate of change of remanence properties downcore might be used to model the effects of bioturbation. In the sedimentary record, where changing climate and oceanic parameters may induce fluctuating redox conditions in the surficial sediments, variations in pyrite concentrations, or conversely, drastic changes in remanence intensity and stability may provide fingerprints of ancient geochemical boundaries. The recognition of these diagenetic processes may become increasingly important as the Deep Sea Drilling Project's Hydraulic Piston Corer provides more long undisturbed sedimentary sections for paleomagnetic study.
CHAPTER II
GEOCHEMISTRY, SEDIMENTOLOGY AND CHRONOLOGY OF OREGON AND GULF OF CALIFORNIA SEDIMENTS

INTRODUCTION

Hemipelagic muds from the Oregon continental margin and laminated diatomaceous ooze from the Guaymas Basin in the Gulf of California are deposited in distinctly different depositional regimes, yet both types of sediments show drastic changes in magnetic properties with depth. To assess whether the downcore magnetic variations were caused by changes in sediment provenance or the effects of early diagenesis, geochemical and sedimentological analyses were undertaken on three cores from the Oregon continental slope (W7710-28, W7710-26 and W7809-27) and one core in the Guaymas Basin (BAM 80 E17) (Figures II-1 and II-2).

The objectives of this work were:

- to characterize the major element chemistry and mineralogical composition of the different sediments in order to better evaluate factors which may have influenced rock magnetic properties
- to develop a chronology and establish sedimentation rates for each area using C14 age determinations and varve counts where applicable
- to determine whether characteristic downcore elemental variations in the Oregon cores could be used as stratigraphic markers for intercore correlation, independent of their
Figure II-1. Location of study area on the Oregon continental slope.
Figure II-2. Location of study area in the Guaymas Basin of the Gulf of California.
paleomagnetic signatures.

The results suggest a surprising downcore uniformity in major geochemical properties from both areas, making these sediments well suited for paleomagnetic work.

On the Oregon continental margin, the sedimentology of surface sediments deposited has been extensively studied (Krissek, 1982, Karlin, 1980, Duncan 1968), but to date, no downcore geochemical profiles have been reported. The study area (Figure II-1) is a small basin on the lower continental slope off central Oregon. The surface sediments are typically olive green, heavily bioturbated, suboxic hemipelagic muds composed of 30-40% clay, 40-60% silt with minor amounts of sand.

The sediments are complex mixtures of terrigenous material derived from four dominant sources. In the clay sized fraction, Karlin (1980) found that the southerly Klamath Mountain (KM) and northern California Coast Range (NCR) rivers contribute significant amounts of chlorite and illite to the sediments, while the Columbia River (CR) and nearby Oregon Coast Range streams (OCR) donated principally smectite with minor amounts of illite. Krissek (1982) confirmed Karlin's results for the clay fraction and showed that in the 2-20 μm fraction, the KM contribution could be characterized by its high hornblende and subequal abundances of chlorite and illite; the NCR by its equal amounts of chlorite, illite, quartz, and plagioclase; the CR by its high plagioclase, illite and quartz and the OCR by it's smectite content. By a linear programming approach, Krissek showed that on the central Oregon slope near our study area,
the KM accounted for 50-75%, while the NCR and CR made up 25-50% and <25% of the sediment, respectively.

Krissek also conducted extensive chemical analyses of the various size fractions. For the entire Oregon margin, Krissek apparently found very uniform major element compositions in each size class. For the 2-20 μm fraction, his factor analysis showed Fe and Mg patterns corresponding to a southerly source area (NCR and KM), Ca and Sr trends associated with plagioclase from the CR and high offshore variability in K which he could not relate to a specific area. The sediments in our study area are thus a complex assemblage of material with distinct mineralogical signatures of their source areas, but with chemical characteristics that are not well defined.

The sediments in our study area (Figure II-2) in the Gulf of California (27° 58.5'N, 111° 37.5'W, 622 m water depth) are finely laminated diatomaceous oozes, underlying a zone where the oceanic oxygen minimum intersects the slope (Schrader et al., 1980). Strong seasonal upwelling alternating with periods of heavy rainfall and high terrigenous input produces fine submillimeter couplets of light-colored diatom rich and darker organic terrigenous-diatom layers (Schrader et al., 1980, Calvert, 1964). DeMaster (1979) showed that the chronologies based on laminae counts and 210Pb decay curves match closely, implying that the couplets represent annual varves, at least for the past 200 years. At present, downcore geochemical or sedimentological analyses have not been reported for the laminated sediments of the Gulf, although sulfur diagenesis in the porewaters
and solid phases has been well documented (Berner, 1964; Goldhaber and Kaplan, 1980). A major research effort to define the biostratigraphy, chemistry, and sedimentology of the Gulf of California is presently underway (Schrader, pers. comm.).

In a classic work on the distribution of sands in the Gulf, Van Andel (1964) found that distinctive assemblages of heavy minerals were found proximal to their source areas. Our study area is in his Yaqui Province, which is characterized by high augite, amphibole, lesser epidote and low amounts of basaltic hornblende and hypersthene. From the sharp boundaries of the heavy mineral provinces, Van Andel concluded that in most of the central Gulf, redistribution of sediments by longshore transport was minimal and most fluvial material was carried directly offshore to deep basins.

METHODS

Coring, storage and sampling techniques are described in the paleomagnetism section. Samples from all levels in the Kasten and box cores were taken from the interiors of the cores to avoid disturbances and contamination. At each horizon in the cores, several grams of material were freeze dried, disaggregated in a ball mill for 5 minutes then split into fractions for X-ray fluorescence spectroscopy (XRF), organic carbon, LECO sulfur, X-ray diffraction and Mossbauer studies. Separate bulk density measurements were made using standard techniques. For Oregon Core 28 and the Gulf of California Core E17, XRF measurements were made on splits of
unwashed dry sediments, desalted material and acid treated samples. Material from Oregon Cores 26 and 27 were desalted. The desalting and acid treatments consisted of dissolving and shaking the dry sediment in distilled water or hot 0.1N HCL for 15 minutes, centrifuging and pouring off the supernatant fluid. The material was resuspended in distilled water, recentrifuged and decanted. The washing process was repeated three times. The treated sediment was then freeze dried and disaggregated. Planchettes for XRF analysis were prepared by placing the dry powder in a piston and compacting the material with a backing of cellulose using a hydraulic ram. Washed and acid treated samples for Cores El7, 26 and 27 required dilution with 10-15% cellulose to maintain structural integrity.

Initial sulfur determinations were made on a LECO analyzer by M. Goldhaber at the USGS, Denver. These measurements were then used to calibrate XRF sulfur counts from splits of the same samples \((R^2 = 0.99)\) so that more detailed sulfur profiles could be obtained.

Organic carbon and carbonate for Cores El7 and 28 were measured using the wet oxidation technique of Weliky (1982) as well as the standard burning method. The wet oxidation method involves treating the samples with hot phosphoric acid then dichromic acid to obtain independent determinations of carbonate \((\text{CO}_3\) \)) and organic carbon \((\text{OC})\). The evolved \(\text{CO}_2\) gas is then measured on a LECO carbon analyzer. In the burning technique the sample is heated to \(>1200^\circ\) C, and the \(\text{CO}_2\) gas is measured by LECO. Comparison of total carbon \((\text{TC} = \text{CO}_3 + \text{OC})\) by the two techniques showed that the wet oxidation method gave consistently lower values of TC, especially for high OC
samples of E17. This suggests that the dichromic acid caused incomplete oxidation of the organic carbon. Thus for this study, values of carbonate by wet oxidation and organic carbon values by burning were used.

Age determinations were made using laminae counts on E17 and $^{14}$C dates on 3 levels from E17, 9 levels from Core 26 and 2 levels from Core 27. $^{14}$C ages were kindly provided by M. Stuiver of the University of Washington for the Oregon cores and S. Robinson of the USGS on the Gulf of California Core E17.

Preliminary X-ray diffraction determinations of the mineralogy of five levels each from Cores 28 and E17 were made to assess whether any gross changes in mineralogy occurred downcore. Random mounts of bulk sediment, solvated in ethylene glycol, were prepared and analyzed using the same techniques as Krissek (1982). A 10% boehmite internal standard was employed to facilitate comparison of mineral peak areas between samples. Samples were analyzed on a Norelco diffractometer using Cu-Kα radiation from 3-60 ° 2θ in 0.02 steps.

Laminae counts were performed on each of the nine trays of BAN 80 E17 using a magnifying lens. Replicate counts were made between prominent laminae at intervals of approximately 2.2 ± 0.7 cm. Precision was within 6%. Out of 196 intervals, 8 were uncountable due to indistinct layering. For these intervals and for sections between trays, counts were interpolated from the mean number of laminae per cm over the surrounding 50 cm. Average sedimentation rates over 10 cm intervals were derived by summing the laminae counts over the entire core, interpolating the cumulative counts as varves at even 5 cm intervals.
and taking a finite difference derivative over each 5 cm section. Absolute age calibration was made by pegging the varve count at 17.3 cm (a 2 cm homogeneous band with foram flecks) to a correlative 1910 horizon (Schrader, 1983, pers. comm.)

To estimate counting bias, trays 2 (46-96 cm) and 3 (96-146 cm) were recounted with Hans Schrader. For tray 2, a well laminated section, internal agreement between my first count and the recount was within 2%, as were comparisons with my counts and Schrader's. Tray 3 contained two 15 cm intervals with alternating packets of very fine black laminae and faint indistinct laminae. For these intervals initial and recount were systematically 17% higher than Schrader's. This discrepancy was mostly due to subjectivity in defining varves in faintly banded sections.

RESULTS

Age Determinations

Carbon 14 ages for the 9 levels of Oregon Core 26 and two levels of the Reineck box Core 27 are shown in Figure II-3. As Core 26 over-penetrated by ~30 cm, Cores 27 and 26 are spliced together in the figure. The $^{14}$C ages increase linearly with depth, yielding a mean sedimentation rate of 123 ± 8 cm/ky with a surface intercept at 2035 ± 94 yrs. Deviations from linearity might be due to minor fluctuations in sedimentation rates. Alternatively, the $^{14}$C variations may be caused by non uniform mixing of new and old carbon from active and dead carbon reservoirs. The old surface age is
Figure II-3. Age-depth curve for Oregon slope Cores W7710-26 (>30 cm depth) and W7809-27 (<30 cm depth).
consistent with other reported 14C surface ages in the NE Pacific. For purposes of establishing a chronology for Cores 26-27, we have assumed that the surface age represents the present and have applied age corrections based on dendrochronology (Stuiver, pers. comm.) to the raw 14C ages. The recalculated ages cause no change in sedimentation rate and we assume a linear age-depth relation throughout the core.

The remarkable fine scale structure of the laminations in Core E17 allow us to construct a detailed varve chronolgy. The cumulative age-depth curve, as derived from laminae counts at 2.5 cm intervals, is shown in Figure II-4, along with available carbon 14 dates. According to the varve counts, the base age of the core is about 3340 years, yielding an overall sedimentation rate of 135 cm/ky for the entire 450 cm core.

Carbon 14 determinations give ages of 770 ± 60 yrs at 15-28 cm, 1700 yr at 147-159 cm and 3000 ± 50 yr at 298-308 cm. The overall slope of the 14C ages is 126 cm/ky with a surface intercept of 560 yrs BP. For the first two 14C dates, agreement is excellent between the sedimentation rates determined from the 14C (141 cm/ky) and varve counts (142 cm/ky). However, in the interval from 150-300 cm, the sedimentation rates based on the 14C ages (115 cm/ky) differs by 27% from the varve rate (158 cm/ky).

The extrapolated 14C surface age is consistent with surface dates of 765 yr reported in the laminated sediments of the nearby Carmen Basin (DeMaster, 1979) and 620 yr ages for recent clam and snail specimens in the area (Berger et al., 1966). However, DeMaster
Figure II-4. Age-depth plot of Gulf of California Core BAM 80 E17, based on varve chronology, and three ¹⁴C dates.
(1979) found $^{14}$C downcore profiles yielded sedimentation rates that, while internally consistent, can be appreciably lower than concordant $^{210}$Pb and varve rates. He suggested that the $^{14}$C activity in the surface waters might vary considerably both temporally and spatially due to variable mixing between atmospherically equilibrated carbon in the photosynthetic zone and 'old' dissolved carbon from upwelled deep Pacific waters with an apparent age of 2000 years. Thus, changes in rates of upwelling or storminess, which influence the air-sea gas exchange rate, can cause local variations in $^{14}$C activity in the surface waters, leading to unreliable $^{14}$C profiles.

Sedimentation rates derived from the varve counts are shown in Figure II-5. Overall, the data show high frequency oscillations superimposed on a ramped, quasi-sinusoidal slowly varying component with a wavelength of ~125 cm. The pronounced decrease in rates below 350-360 cm coincides with a color change in the sediment and a slight increase in wet bulk density. No evidence was found for an unconformity near this depth. The spike in sedimentation rates at 290-300 cm is real; however, the high rates in the top 20 cm might be influenced by conservative counting in an area of probable core top disturbance, warped laminae and complex structure (particularly lenticular wedgeouts).

Accumulation rates (Figure II-6), in gm/cm$^2$-Ky, were derived by multiplying dry bulk densities (Figure II-25b) by sedimentation rates, each interpolated at 1 cm intervals. The dry bulk densities are variable, but generally increase downcore,
Figure II-5. Sedimentation rates (in cm/Ky) of BAM 80 E17, based on varve chronology.
Figure II-6. Accumulation rates (in gm/cm$^2$/ky) of BAM 80 El7, based on varve chronology.
presumably due to compaction. Much of the variability is due to the relative proportions of thick diatom + thin dense, dark laminae packets compared to packets of couplets of subequal thickness. The resulting accumulation rate profile, with a mean of ~25 gm / cm²-Kyr, shows oscillatory behavior, suggesting a long term moderating influence such as climate.

The reliability of the varve chronology and associated rate determinations is difficult to evaluate without additional cores and radiometric dates for correlation. Although replicate counts give good internal agreement, investigators must decide on what constitutes a laminae couplet particularly in finely laminated zones where much time is represented. However, if subseasonal laminae are present and counted, then ages are overestimated. Alternatively, hiatuses, erosional unconformities, or extremely fine (apparently homogeneous) laminae result in underestimation of the true age. Moreover, the relatively common lenticular wedges of laminae packets in the upper sections of the core must be assumed to represent passive deposition in microtopography rather than erosion, redeposition, or post depositional slumping. In any event, most sources of error cause the ages to be underestimated (sedimentation rates too high), thus this varve chronology must be considered as a lower estimate on the age of the material.

X-ray Diffraction

Stacked diffractograms from five levels of Core 28 are presented
in Figure II-7. The bulk sediment was mixed with an internal standard of 10% boehmite to facilitate intercomparison of the random mounts. For all levels, major peaks, in order of decreasing dominance, included quartz, chlorite, illite, montmorillonite (smectite), plagioclase, amphibole, and olivine. Minor peaks of pyrite were detected in the samples from 130 and 237 cm. Overall, the mineralogy and relative peak heights showed very little variance downcore, suggesting that the relative inputs of the different terrigenous sources did not vary significantly with time.

X-ray diffractograms of five levels from the Gulf of California core El7 (Figure II-6) gave relatively poor diffraction patterns due to high background counts and a broad hump of opal from 10° - 30° 2θ. The major diffraction peak was from quartz. Minor, but recognizable reflections included pyrite, montmorillonite, illite, chlorite, and plagioclase. The diffractograms showed some downcore variability, but due to the poor quality of the patterns, differences could not be quantified.

Elemental Abundances

Oregon Sediments

The sediments from Kasten Cores 28 and 26 and the 30 cm Reineck Box Core 27 (from the same location as Core 26) show uniform profiles in their major element chemistry (Figures II-9 to II-17). Since Core 26 overpenetrated and the top 30 cm were not recovered,
Figure II-7. Stacked X-ray diffractograms of five levels from Core 28. Glycolated random mounts included a 10% boehmite standard. The x-axis is the diffraction angle in degrees 2θ. Diffraction peak identification is Mo - montmorillonite (smectite), Chl - chlorite, IL - illite, Bo - boehmite, Qtz - quartz, Plag - plagioclase and feldspars, Cal - calcite, Amph - amphibole, Ol - olivine, and Pyr - pyrite.

Figure II-8. Stacked X-ray diffractograms of five levels from Core 28. Peak identifications are the same as in Figure 7.
Figure II-7.
Figure II-8.
Cores 27 and 26 will henceforth be considered together.

The mean values and variability for 11 major elements (normalized as oxides to 100%) are summarized in Table II-1 for Core 28 and Table II-5 for Cores 26 and 27. As an index of variability, the percent variation, $V$, was calculated as $100 \times$ standard deviation/mean for each element (Snedecor and Cochran, 1980). Analytical precision, based on calibration of standards, is estimated to be $<3\%$ for Mg, Si, K, Ca, Ti, Fe and S; $<5\%$ for Al, Mn, and $<6\%$ for P and Ba. From replicate samples from the same horizon and duplicated measurements, the estimated uncertainty due to sample variability is $<2\%$ of the sample mean value.

For the washed samples in Core 28, with the exception of S,CaO, org C and BaO, the remainder of the elements showed downcore variabilities of less than 5%. Inter-element correlations for the washed samples (top half of Table II-2) show strong positive associations of sulfur with depth ($r = 0.84$) and weaker positive correlations of Al with Ti (0.65), Mn (0.68), Fe (0.61) and P (0.62). Negative correlations are found between Si and Ti (-0.67), Mg (-0.73), and Mn (-0.70) as well as P with depth (-0.69) and S (-0.75). The associations between depth, sulfur, and P can be attributed to oxidative decomposition of organic matter and the formation of sulfides with depth (see Chapter I). The correlations between the terrigenous elements Al, Ti and Mn are probably due to their association with clay minerals. Since Si is found in biogenic opal as well as terrigenous silicates, the weak negative Si correlations might reflect fluctuations in biogenic vs terrigenous input and may be partly an artifact of a closed data set.
Figure II-9. Oregon Core 28 - downcore profiles of SiO2, CaO and Al2O3 in percent dry weight. Abundances are corrected for seawater concentrations and have been normalized so that the sum of the oxides of the 12 major elements equals 100%. Desalted samples are denoted by squares connected by solid lines; 0.1N HCl acid-treated samples are shown with circles connected by dashed lines.
Figure II-10. Oregon Core 28 - downcore profiles of Fe2O3, TiO2 and MnO2 in percent dry weight. Symbols are the same as in Figure 9.
Figure II-11. Oregon Core 28 - downcore profiles of K2O, MgO and Phosphorus in percent dry weight. Desalted samples are denoted by squares connected by solid lines; 0.1N HCl acid-treated samples are shown with circles connected by dashed lines.
Figure II-12. Oregon Core 28 - downcore profiles of BaO, Sulfur in percent dry weight and sum of oxides per level. Desalted samples are denoted by squares connected by solid lines; 0.1N HCl acid-treated samples are shown with circles connected by dashed lines.
Figure II-13. Oregon Core 28 - downcore profiles of organic C, CaCO$_3$ in percent dry weight and water content at time of sampling.
### Table II - 1.

**Oregon Core 28**

Summary of mean values and variability in oxide abundances of Core 28 samples.

Abundances are normalized to sum = 100% of oxides. Samples were desalted prior to treatment. The percent variation, %V, is a measure of variability and is defined as 100 * standard deviation/mean.

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<th>Mean</th>
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<th>%V</th>
<th>Mean</th>
<th>St.Dev.</th>
<th>%V</th>
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<td>0.00076</td>
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TABLE II - 2

Oregon Core 28 - Correlation Matrix of Oxide abundances

Oxides are salt adjusted and normalized to sum = 100%, N = 26
Correlations shown are significant at a 0.05 significance level (r > .40)
Upper triangular matrix is interelemental correlations of oxides
Lower triangular matrix contains correlations of oxides/Al2O3

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### Table II - 3.
Oregon Core 28 - Acid Treated

Summary of mean values and variability in oxide abundances of acid-treated Core 28 samples.

Abundances are normalized to sum = 100% of oxides. Samples were desalted prior to treatment with 0.1N HCl. The percent variation, %V, is a measure of variability and is defined as 100 * standard deviation/mean. The last column, which is 100 * (acid-washed)/washed, is the relative amount of each oxide removed as a result of the acid treatment.

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<tr>
<th>Oxide</th>
<th>Mean</th>
<th>St.Dev.</th>
<th>%V</th>
<th>Mean</th>
<th>St.Dev.</th>
<th>%V</th>
<th>100*(A-W)/W</th>
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<td>66.634</td>
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<td>4.3340</td>
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<td>0.0497</td>
<td>0.00076</td>
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Table II - 4

Oregon Core 28 Correlation Matrix of Oxide abundances -acid treated
Oxes are salt adjusted and normalized to sum = 100%
Correlations shown are significant at a 0.05 significance level (r > .4)
Upper triangular matrix is interelemental correlations of oxides
Lower triangular matrix contains correlations of oxides/Al2O3

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<td>+</td>
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<td>--</td>
<td>--</td>
<td>--</td>
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</tbody>
</table>

depth     Na  | Mg  | Al  | Si  | P   | K   | Ca  | Ti  | Mn  | Fe  | Ba  | S   | Sum |

51
Figure II-14. Oregon Core 26 - downcore profiles of SiO2, CaO and Al2O3 in percent dry weight. Abundances are corrected for seawater concentrations and have been normalized so that the sum of the 12 major elements equals 100%.
Figure II-15. Oregon Core 26 - downcore profiles of Fe$_2$O$_3$, TiO$_2$ and MnO$_2$ in percent dry weight.
Figure II-16. Oregon Core 26 - downcore profiles of K20, MgO and Phosphorus in percent dry weight.
Figure II-17. Oregon Core 26 - downcore profiles of BaO, Sulfur in percent dry weight and sum of oxides per level.
Table II - 5.
Oregon Cores 26+27

Summary of mean values and variability in oxide abundances of Cores 26+27 samples.

Abundances are normalized to sum = 100% of oxides. Samples were desalted prior to treatment. The percent variation, %V, is a measure of variability and is defined as 100 * standard deviation/mean.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Mean</th>
<th>St.Dev.</th>
<th>%V</th>
<th>Mean</th>
<th>St.Dev.</th>
<th>%V</th>
</tr>
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<td>TiO₂</td>
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Table II - 6

Oregon Core 26 Correlation Matrix of Oxide abundances
Oxides are salt adjusted and normalized to sum = 100%
Correlations shown are significant at a 0.05 significance level (r > .40)
Upper triangular matrix is interelemental correlations of oxides
Lower triangular matrix contains correlations of oxides/Al2O3

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<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Ba</th>
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<td>+</td>
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<td>0.55</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>--</td>
</tr>
</tbody>
</table>

depth Na Mg Al Si P K Ca Ti Mn Fe Ba S sum
Q-mode factor analysis of the Core 28 washed samples produced two factors, each accounting for 49.9% of the variance. The first factor is composed predominantly of sulfur and downcore factor loadings essentially mimicked the sulfur profile (Figure II-18). The second factor contains roughly equal abundances of all of the other elements and an absence of sulfur. Due to orthogonality of the eigenvectors, the profile of downcore factor loadings necessarily mirrors the factor 1 curve.

Upon acid treatment of the Core 28 samples, downcore trends (Figures II-9 to II-12), mean values, and variability (Table II-3) remained unchanged for Si, S, and the terrigenous elements Al, K, Ti, Mn, and Fe. However, 46% of the Ca, 42% of total P, 22% of Ba and 8% of the Mg were removed. Two fluctuations in Ca at 100 and 130 cm were not evident in the acid treated Ca profile, suggesting that these variations were caused by changes in biogenic carbonate. Interestingly, Al shows an inverse pattern to Ca at these depths and acid treated P (organic P) also shows a high at 100 cm. This seems to indicate that while most of the core had a constant terrigenous/biogenic ratio, a rapid, though minor change in biogenic input occurred at 100-130 cm.

Acid treatment caused an improvement in certain interelemental correlations (lower half of Table II-4), although factor analyses of the acid treated samples showed identical results to the desalted samples. Associations between the terrigenous elements Al, Mg, and Mn as well as their negative correlation to Si improved, possibly as a result of removal of biogenic carbonate, amorphous silica and
Figure II-18. Downcore profile of factor loadings from Q-mode factor analysis of Oregon Core 28 major element chemistry. This factor, explaining 49.9% of the variance, was composed principally of sulfur. The other factor contained the rest of the elements and forms an inverse profile to the first factor.
acid soluble Mg in magnesian calcites, Ca-Mg phosphates and/or proto-dolomites (Suess, 1979). Upon acid treatment an Fe to P relation developed and the negative correlation of P to S was lost. However, the significance of these associations is difficult to evaluate, since the organic carbon/acid treated P ratio of about 80:1 is less than the expected Redfield C/P ratio of 106:1, suggesting that the mildness and brief duration (15 minutes) of the HCl treatment may have left some of the more resistant inorganic phosphates such as apatite (Lindsay and Vlek, 1972) undisturbed.

If the organic carbon were readily metabolizable and only sulfate reduction occurred, we would expect that oxidative decomposition of organic matter should result in organic carbon curves which mirror the sulfur profiles. Although organic carbon generally decreases downcore (Figure II-13a) and sulfur increases (Figure II-12b) the overall trends in the curves do not match closely. Interestingly, some of the fluctuations in the two curves seem to show a direct, rather than inverse correspondence, suggesting that where there is high carbon input, sulfide formation is intensified and vice versa. Nevertheless, the lack of overall inverse correspondence implies that the reservoir of metabolizable carbon utilized in sulfate reduction is not simply related to the total residual carbon in the system.

Since the Core 28 profiles show anomalies in Ca and to a lesser extent Al at 100-130 cm, chemical analyses of Cores 26 and 27 were undertaken to examine whether intercore correlations could be made, independent of the paleomagnetism of the sediments. Downcore profiles for Core 26 and 27 are shown in Figures II-14 to II-17.
Summary statistics and interelement correlations are given in Tables II-5, II-6. Overall, downcore variabilities are similar between Cores 26 and 27 and Core 28, although means are slightly different, particularly for Al, Mg, Si, and to a lesser extent, Mn. This also holds true when only samples from similar depths are compared. Moreover, downcore trends in Cores 26 and 27 with the exception of S, show no obvious correlation to Core 28. While variability in Ca in both data sets is on the order of 10% and fluctuations occur at similar levels, a definitive correlation based on Ca is equivocal.

Interelement correlations are generally better in Cores 26+27 than in 28. This is caused mainly by highly correlated enhancements of the oxides of Al, Mg, K, and Fe and deficiencies in Si and Ca in the top 30 cm of Core 27. If the data is normalized to Al2O3, (Tables II-1, II-3, & II-5) only S, SiO2 and CaO show significant variations downcore. The remainder of the elements are essentially constant downcore and most correlations disappear (lower halves of Tables II-2, II-4, & II-6). Thus, it would seem that downcore changes are largely a result of fluctuating biogenic input and perhaps minor differences in grain size.

The lack of definitive downcore chemical correlation between cores 28 and 26 + 27 (which are within 1 mile of each other) is problematic and, at present, poorly explained. Since the variability for most elements in both cores is less than 5%, an obvious conclusion from the chemistry is that, with the exception of diagenetic S and biogenic carbonate the sediments are very homogeneous. The monotony of the sediment chemistry is a mixed blessing. While making
these cores excellent for paleomagnetism, the homogeneity also inhibits stratigraphic correlation.

Minor variations in the elemental abundances might be due to locally variable biogenic input and/or small shifts in grain size distributions in the terrigenous fractions. Lateral differences in grain size distribution could be due to source-related effects, hydraulic sorting, or more likely, incomplete homogenization of the sediment brought about by burrowing of benthic fauna. Since all of the Oregon sediments were heavily mottled and worms and tubules were observed in the surface sediments, lateral inhomogeneities in grain size might not be unexpected. Further analyses of within-horizon variability might permit evaluation of this hypothesis.

Comparison of the washed samples from Cores 28 and 26 + 27 gives some indication, albeit limited, as to the nature of the mineral species in the sediment. Of all of the elements, sulfur shows the strongest concentration gradient with depth in both cores. As discussed in Chapter I, the downcore sulfur increase can be related to the formation of sulfides due to the progressive oxidative decomposition of organic matter and the reduction of iron and seawater sulfate with depth. When compared to porewater sulfate sulfur (0.1-0.2% dry weight for 60% water content) and similar surface solid sulfur values, the downcore solid sulfur for Cores 28 (0.6%) and 26 (0.5%) show an excess, suggesting cycling of seawater sulfate through the sediments. This excess downcore solid sulfur has often been observed in other anaerobic marine sediments (Goldhaber and Kaplan, 1974, Berner, 1981).
In marine sediments, commonly occurring sulfur minerals include pyrite (FeS\(_2\)), mackinawite (FeS) barite (BaSO\(_4\)) and Mn sulfide (Goldhaber and Kaplan, 1974; Berner, 1981; Suess, 1979 a,b). In core 28, the lack of change of S and Fe upon acid treatment suggests that acid soluble monosulfides, such as the metastable species mackinawite, were not present in measurable quantities. The Mn profile showed no effects due to acid treatment implying that the Mn was in a reduced state. Further, the correlation of Mn with Al and lack of association with S or Fe seems to indicate that the Mn is tied into clay minerals such as smectites, rather than Fe-rich chlorite or sulfide phases. Moreover, even if all of the Mn were in a sulfide form, the Mn sulfide would account for less than 5% of the total downcore solid sulfur.

Barium occurs in hemipelagic sediments in exchangeable sites on clays and as barite. Suess (1979a) found barite micronodules in reduced sediments in the Baltic Sea and showed that sorbed Ba was readily exchanged for seawater cations upon mixing of Ba saturated smectites with salt water. He proposed that the exchangeable Ba reacts with seawater sulfate forming barite microcrystals attached to clay surfaces. For Core 28, if the barium occurred solely as barite, the average Ba value of 0.067 ± .002% would correspond to sulfur percentages of 0.016 ± .002%. Sulfur associated with barite thus can account for about 6% of the total sulfur in the top meter, and only about 3% in the deeper parts of the core.

The above calculations suggest that 90-95% of the solid sulfur occurs in the form of pyrite (organically bound S is assumed negli-
gible). By a combination of chemistry, X-ray diffraction and Mossbauer studies, we can attempt to partition the iron found in the Core 28 sediments into different phases. Through XRD, Fe-rich trioctahedral chlorite was identified by its basal 00% reflections (Brindley and Brown, 1980) as the dominant iron bearing detrital mineral. This was confirmed in Mossbauer studies (Chapter III) which allowed us to separate the recoil-free Fe fraction into chlorite and pyrite + Fe(III) oxide phases. (No appreciable ferric iron was assumed in the chlorite). Pyrite iron can be estimated by assuming the solid sulfur is composed solely of pyrite and barite.

The resulting profile of iron phases downcore (Figure II-19) shows the essential constancy of total Fe and chlorite with depth. Although the top few cm of Core 28 (as well as 26) are missing, the lack of a downcore concentration gradient in Fe implies in situ reduction of iron oxides and transformation to acid insoluble pyrite, rather than upward diffusion of porewater Fe(II) and reprecipitation near the oxic/anoxic boundary. While chlorite makes up about 55% of the total Fe, pyrite iron accounts for about 3-5% in the top meter and 10-14% deeper in the core. The remaining Fe (25-40%) must be in the form of resistant oxides (e.g., spinels, magnetite) and other detrital silicates (e.g., pyroxenes, amphiboles, olivines).

Gulf of California Core BAM 80 E 17

The chemistry of the laminated diatomaceous ooze of the Guaymas Basin Core E17 contrasts sharply with abundances found in the hemi-
Figure II-19. Oregon Core 28 - Partitioning of total Fe into chlorite, pyrite, and residual phases.
pelagic Oregon muds. Downcore profiles of normalized oxides (corrected for porewater Ca, Mg, S), CaCO₃, and organic carbon (Figures II-20 to II-23) as well as the statistical summary (Table II-7) show a predominance of silica and large variability among the other elements. CaO values (mostly as carbonate), over 5% at the surface, decrease to about 1% below 10 cm depth. Total organic carbon decreases from over 6% at the surface to 4.7% at 10 cm, suggesting that CO₂, produced as a result of oxidative decomposition of organic matter, caused extensive carbonate dissolution in <30 years, as determined from the varve counts. Sulfate reduction can inhibit dissolution and preserve carbonate in completely anoxic waters (Dunbar and Berger, 1981); thus the Ca, carbonate, and organic carbon curves, as well as the porewater sulfate profile (Figure I-2), suggest that completely anoxic conditions and the onset of sulfate reduction do not begin until below 10 cm depth. This agrees with foraminifera distributions for this core as studied by Schrader et al. (man. in prep.). With the exception of S and Ba, the remaining elements show substantial variability downcore, but no obvious trends with depth.

Interelement correlations (Upper half of Table II-8) show very high correlations (r > 0.9) between the terrigeneous elements Al, Mg, Ti, K, Mn, and Fe with slightly lower inverse correlations (r = 0.7-0.8) to Si. These associations suggest mixing between a terrigenous source, such as the nearby Rio Yaqui, and a silicous biogenic assemblage, presumably composed mostly of diatoms. The terrigenous source apparently retains a remarkably constant composition through time.
Figure II-20. Gulf of California Core BAM 80 E17 - downcore profiles of SiO2, CaO and Al2O3 in percent dry weight. Abundances are corrected for seawater concentrations and have been normalized so that the sum of the 12 major elements equals 100%.
Figure II-21. Gulf of California Core BAM 80 E17 - downcore profiles of Fe$_2$O$_3$, TiO$_2$ and MnO$_2$ in percent dry weight.
Figure II-22. Gulf of California Core BAM 80 EL7 - downcore profiles of $K_2O$, $MgO$ and Phosphorus in percent dry weight.
Figure II-23. Gulf of California Core BAM 80 E17 - downcore profiles of BaO. Sulfur in percent dry weight and sum of oxides per level.
Figure II-24. Gulf of California Core BAM 80 E17 - downcore profiles of organic C, CaCO₃ in percent dry weight and water content at time of sampling.
Figure II-25. Gulf of California Core BAM 80 EL7 - downcore profiles of porosity (%), dry bulk density (gm/cc), and wet bulk density (gm/cc).
## Table II - 7.

**Gulf of California Core E17**

Summary of mean values and variability in oxide abundances of Core E17 samples.

Abundances are normalized to sum = 100% of oxides and adjusted for salt concentrations. The percent variation, %V, is a measure of variability and is defined as 100 * standard deviation/mean.

<table>
<thead>
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<th>Oxide</th>
<th>Mean</th>
<th>St.Dev.</th>
<th>%V</th>
<th>Mean</th>
<th>St.Dev.</th>
<th>%V</th>
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</thead>
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<td>-</td>
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<td>14.7</td>
<td>0.1690</td>
<td>0.01115</td>
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<td>P</td>
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<td>12.4</td>
<td>0.0301</td>
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<td>0.015</td>
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<td>23.1</td>
</tr>
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<td>S</td>
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<td>0.278</td>
<td>31.4</td>
<td>0.1027</td>
<td>0.03022</td>
<td>29.4</td>
</tr>
</tbody>
</table>
### Table II - B.

Gulf of California Core EL7 Correlation Matrix of Oxide abundances

Oxides are salt adjusted and normalized to sum = 100%
Correlations shown are significant at a 95% confidence level \( r > 0.40 \)
Upper triangular matrix is interelemental correlations of oxides
Lower triangular matrix contains correlations of oxides/Al2O3

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Ba</th>
<th>S</th>
<th>Sum</th>
<th>Water</th>
<th>BulkD cm/Ky</th>
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<td>depth</td>
<td>+ 0.52</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.41</td>
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<td>--</td>
<td>--</td>
<td>0.71</td>
<td>--</td>
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<td>-0.65</td>
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<td>0.56</td>
<td>0.70</td>
<td>0.78</td>
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<tr>
<td>Mg</td>
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<td>-0.93</td>
<td>--</td>
<td>0.95</td>
<td>0.56</td>
<td>0.93</td>
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<td>-0.86</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>K</td>
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<td>0.75</td>
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<td>--</td>
<td>+</td>
<td>--</td>
<td>0.98</td>
<td>0.89</td>
<td>0.94</td>
<td>0.56</td>
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<td>-0.84</td>
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<tr>
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<td>--</td>
<td>-0.42</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>--</td>
<td>0.64</td>
<td>0.47</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ti</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.75</td>
<td>--</td>
<td>+</td>
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<td>0.96</td>
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<td>0.54</td>
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<td>--</td>
<td>+</td>
<td>0.94</td>
<td>0.48</td>
<td>--</td>
<td>0.50</td>
<td>-0.73</td>
</tr>
<tr>
<td>Fe</td>
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<td>0.57</td>
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<td>--</td>
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<td>+</td>
<td>0.57</td>
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<td>0.55</td>
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<tr>
<td>Ba</td>
<td>0.73</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>--</td>
<td>--</td>
<td>0.50</td>
<td>-0.43</td>
<td>0.69</td>
<td>-0.55</td>
</tr>
<tr>
<td>S</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.46</td>
<td>-0.50</td>
<td>0.51</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>--</td>
<td>0.50</td>
<td>--</td>
<td>-0.52</td>
<td></td>
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<tr>
<td>sum</td>
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<td>--</td>
<td>-0.54</td>
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<td>--</td>
<td>0.53</td>
<td>--</td>
<td>--</td>
<td>+</td>
<td>--</td>
<td>0.71</td>
<td>-0.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Correlation coefficients are significant at a 95% confidence level. 

Water depth: -0.46 to -0.83
BulkD cm/Ky: -0.65 to +0.59

Water: -0.46 to -0.83
BulkD: 0.90 to 0.59

Correlation coefficients are significant at a 95% confidence level.
When the data are normalized to Al to remove the effects of aluminosilicates (Table II-7 and lower half of Table II-8) most of the variability and high correlations for Ti, Fe and K disappears. Thus these elements must be associated with aluminosilicates, possibly as illites. However, Mg and Mn, show a 0.9 correlation and each element retains a high downcore variability upon normalization to Al. Ca shows a moderate association with these elements suggesting that some of the Ca, Mg, and Mn may occur in the form of rhodochrosite and/or protodolomite (Suess, 1979). High negative correlations with Si (0.8-0.9) might be due to dilution of these authigenic minerals by biogenic silica.

A Q-mode factor analysis of the normalized, salt corrected oxides reveals three factors, explaining 99% of the data variance (Figure II-26 a,b). Factor 1, with 45% of the variance, contains high Mg and Mn, subequal proportions of Al, K, Ti, Fe, Ba and S and a lack of Si, P, and Ca. Because of the lack of silica and high factor scores for the terrigenous elements, this factor appears to reflect a terrigenous assemblage. Factor 2 showed high Si and P and lower subequal amounts of the remaining elements, with the exception of low or negative scores for Mg, Ca and Mn. The factor scores, explaining 37% of the variance, seem to indicate a mixed biogenous/terrigenous assemblage. Factor 3, with 16.5% of the variance, probably represents a biogenic carbonate component, since factor scores show mainly Ca and only minor amounts of Mn, Mg, and P.

The nature of the factor scores suggests climatically moderated influences. Since the terrigenous elements are very highly
Figure II-26. a) Downcore profiles of factor loadings and b) scores for each factor from Q-mode analysis of E17 major element chemistry.
correlated to each other, a very constant source mineralogy is indicated. The partitioning of the terrigenous elements into factors with and without silica might imply that factor 1 represents times of high terrigenous input, but little or no upwelling, thus low biogenic silica, on the eastern side of the Gulf. This would correspond to enhanced input during July-September rainy season, when winds are southeasterly and upwelling occurs mostly on the western Gulf side (Schrader, 1982). The second factor, with high silica and a significant terrigenous signal, could reflect periods when biogenic and terrigenous input covary; i.e., when northwesterly winds during January to June cause both upwelling and precipitation to occur on the mainland side of the Gulf.

Downcore profiles of the normalized loadings for the three factors are shown in Figure II-26a. The behavior of the factor loadings can be divided into 3 zones. From the surface to ~30 cm, the carbonate factor shows a strong decrease, probably caused by extensive carbonate dissolution, as mentioned earlier. From 30 to about 300 cm the carbonate factor remains constant, but deeper it shows an increase with depth. Below ~30 cm, factors 1 and 2, in general, are inversely related. However, below 300 cm the silica/terrigenous factor decreases with depth.

If factors 1 and 2 are indeed climatically related, their inverse correlation is to be expected. Fluctuations in the silica-rich factor are highly correlated to sedimentation rates below ~30 cm, perhaps suggesting that variability in long term wind patterns controls sediment accumulations through linked changes in
upwelling and precipitation-induced fluvial input. A significant increase in dry bulk density (Figure II-25b) and decreases in sedimentation rates (Figure II-5) and factor 2 loadings below 360 cm (Figure II-26a) could indicate either a major climate change ~2300 yrs BP or enhanced silica dissolution.

In studying silicoflagellates from El7, Murray (1982) found that *Octactis pulchra*, a high productivity indicator, decreased in abundance from ~350 cm downwards. Starting at the same level, downcore increases were noted for *Dictyocha messanensis*, a cosmopolitan species. He also noted no signs of increased silica dissolution with depth. Thus the major drop in sedimentation rates and the change in chemistry must be related to a major climatic shift commencing about 2300 years ago. After this time, northwesterly winds in January to June became relatively more important in the seasonal wind regime, leading to relatively enhanced upwelling on the mainland side of the Gulf.

Although sulfide sulfur is derived principally from seawater, in the Q mode analysis, sulfur was partitioned evenly between Factors 1 and 2 with the terrigenous elements. The lack of a separate diagenetic sulfide factor indicates that sulfide formation is not controlled by sulfate reduction, but rather by the amount of available reactive iron in the terrigenous fraction. This conclusion is consistent with relations found between magnetic intensities and the various sulfide and sulfate fractions as discussed in Chapter I.

Using some of the same techniques as with the Oregon sediments, we can roughly partition the iron in the El7 sediments into a
sulfide and non-sulfide fractions. Preliminary Mossbauer analyses showed that only 10-15% of the total Fe was in a reduced state in clay minerals. We assume that all of the sulfur is present as pyrite and that organically bound S is negligible. The Ba concentrations suggest that <2% of the sulfur could be tied up as barite. The sulfide iron estimation must be regarded as a lower limit if iron monosulfides are present.

The Fe partitioning (Figure II-27) shows that sulfide iron increases in the top 60-120 cm, then fluctuates about a relatively constant value below this depth. Below 60 cm the fluctuations in pyrite iron generally covary with total iron, again suggesting that the availability of reactive iron controls sulfide abundance. The proportion of pyrite iron varies from less than 20% in the top few cms, to 50-70% throughout most of the core. These high percentages attest to the pervasiveness of diagenesis in these highly reducing sediments.
Figure II-27. Gulf of California Core BAM 80 E17 - Partitioning of total Fe into chlorite, pyrite and residual phases.
CHAPTER III

MOSSBAUER STUDIES

ABSTRACT

Mossbauer spectroscopy has been used to characterize the nature and form of iron occurring in bulk sediments and clay separates from the Oregon continental slope and the Gulf of California. For the Oregon sediments, Mossbauer parameters indicate that iron occurs mainly in detrital chlorite and proportions of chlorite/total iron do not vary downcore. The Gulf of California spectra are poorly resolved due to low total iron contents and apparently reflect a complex mineralogy. Attempts to resolve overlapping pyrite and ferric oxide peaks in bulk sediments and synthetic chlorite/pyrite mixtures were unsuccessful.

INTRODUCTION

Downcore variations in the magnetic properties of the Oregon and Gulf of California sediments suggest that either the source and amounts of Fe bearing minerals have changed through time or that diagenesis has altered the iron species due to reaction with decomposing organic matter. To distinguish between these two possibilities, Mossbauer studies of the bulk sediment and clay fraction were undertaken to better define the nature of the iron bearing species in the sediments.

Mossbauer spectroscopy is based on the quantum mechanical effects of recoil-free emission and resonant absorption of radiation, first discovered by Rudolf Mossbauer in 1957. Due to energy quantiza-
tion, an excited nucleus decays to its ground state by emitting energy at characteristic frequencies. In the case of a free atom, conservation of momentum requires that part of the emitted energy is imparted to the recoiling nucleus, so that the energy of the emitted radiation is less than the excitation energy. Thus an emitted gamma ray has insufficient energy to excite another nucleus, thereby inhibiting absorption. However, if a nucleus is locked in a crystal lattice, three other possibilities exist (Wertheim, 1964). 1) If the free atom recoil energy is greater than the atom's bonding energy, the atom will be dislodged from its lattice site. 2) If the free atom recoil energy is less than the displacement energy but greater than the characteristic lattice vibrational (phonon) energy, the lattice will dissipate the recoil energy by vibration and heating. 3) Finally, if the recoil energy is less than the phonon energy, since allowable lattice energies are quantized, in a certain fraction of events, the entire lattice recoils as a rigid body when a gamma ray is emitted or absorbed. Because the lattice is massive, in the third case, the recoil energy is negligible and resonant absorption occurs, giving rise to the Mossbauer effect.

The Mossbauer effect is valuable because the effective line width (i.e., overlap between the frequency range of absorption and emission energies) is extremely small, allowing very fine resolution of the gamma ray energy. For an energy of 100 KeV and an excited half life of $10^{-7}$ sec., the gamma ray energy can be defined to 1 part in $10^{13}$ (Wertheim, 1964). However, practical considerations limit study to only certain isotopes with suitable combinations of excitation
energies and lifetimes. Of the commonly occurring isotopes, $^{57}$Fe is the only isotope with an appropriate half life (10^-7 sec) and gamma ray energy (14.4 KeV).

Since the line width is smaller than the characteristic energies associated with nuclear magnetic and electronic interactions, the hyperfine structure of electronic configurations, oxidation state, chemical bonding and magnetic interactions can be studied with Mossbauer spectroscopy. Since the nucleus is affected by its immediate environment, energy must be added to or subtracted from an emitted gamma ray to excite an absorbing nucleus. Changes in energy can be obtained by vibrating the source (or absorber). When an emitted gamma ray energy coincides with a characteristic energy level of the absorber nucleus, resonant scattering takes place in all directions. When viewed from the detector, absorption occurs.

Since the difference in velocity corresponds to a Doppler shift in frequency or energy in the emitted gamma ray, the resulting absorption spectrum as a function of velocity is a measure of the transitional energies in the absorber as affected by the chemical environment surrounding the nucleus.

In Mossbauer spectroscopy, three parameters (IS, QS, H[eff]) commonly are used to describe the absorption spectrum. The isomer [IS], or chemical shift, is the deviation of a peak (or the mean of a peak-pair, if the nuclear levels are split) from zero velocity, as measured in mm/sec. The shift arises from a change in nuclear radius between the excited and ground state, caused by coulombic interaction
between the nucleus and s electron cloud (Wertheim, 1964). Quadrupole splitting \( QS \) is the velocity difference between pairs of peaks. \( QS \) arises when nuclear levels in the absorber are split (i.e., have different spin) in the excited state. The splitting is the result of the interaction between the nuclear quadrupole moment and the electric field gradient surrounding the nucleus. The gradient is due to deviations of the nucleus from spherical symmetry and is caused by a non-cubic lattice or asymmetry in the electronic configuration. For iron, both the isomer shift and quadrupole splitting are very sensitive to oxidation state, anion coordination number and crystal symmetry.

A third parameter, the effective internal field, \( H_{\text{eff}} \), is used if the absorber is magnetic. Interaction between the nuclear magnetic dipole moment and the internal field due to the atom's electrons splits the nuclear levels in both the excited and ground states. This gives rise typically to six-peak spectra. The spacing between the two outermost peaks is directly related to the effective internal field around the nucleus.

Because of the sensitivity of Mossbauer parameters to magnetic properties, oxidation state, chemical bonding and crystal structure, Mossbauer spectroscopy has considerable potential as a tool for understanding the nature and genesis of Fe-bearing minerals in different sedimentary environments. Iron in well crystallized silicate minerals (Bancroft et al., 1967, Gibb, 1967) and clays (Weaver et al., 1967, Taylor et al., 1968, Bowen et al., 1969) has been characterized intensively. Iron oxides in soils, (Gangas et al., 1973, Goodman and Berrow, 1976, Kodama et al., 1977, Bigham et al., 1978), lake
sediments (Coey et al., 1974, Readman et al., 1976, Papamarinopoulos et al., 1982), brackish sediments (Suttill et al., 1982) and manganese nodules (Gager, 1968, Johnston and Glasby, 1978) have also been studied. However, to date, with the exception of a study of Fe oxides in western Pacific hemipelagic sediments (Johnston and Glasby, 1982), almost no Mossbauer work on marine sediments has been reported. This is rather surprising, since Mossbauer spectroscopy seems well suited to examining the effects of iron oxide alteration in the the sediment column.

In this section, we describe Mossbauer spectra of bulk material from 12 levels from Core 28 and 6 levels of E17, as well as in six clay separates from the cores (3 samples per core). Our intent is to characterize the dominant iron bearing species and to determine whether a downcore change in oxidation state in iron due to organic matter decomposition can be detected.

METHODS

Mossbauer spectra were obtained from a conventional constant acceleration spectrometer, utilizing a $^{57}$Co source diffused in rhodium. All analyses were performed at room temperature and calibrations were made using natural iron foil. Mossbauer parameters were computed in a non linear least square fitting program. Facilities were kindly provided by H.H. Wickman of the chemistry department at OSU. Counts on freeze-dried samples (~80-120 mg) in a lucite disk holder (2.2 cm x .025 cm) were obtained for periods ranging from 1-5 days depending on iron content.
RESULTS

Oregon Sediments

Typical Mossbauer spectra for samples from 12 levels of Oregon core 28 are presented in Figures III-1 and 2. As the sediments had iron contents of over 4% dry weight, all samples gave well resolved spectra with good signal to noise ratios. A surprising result from these analyses is that samples from all depths of Core 28 gave essentially identical spectra, with a large absorption peak occurring at -0.2 mm/sec, a distinct shoulder at 0.6 mm/sec and a prominent secondary peak at 2.44 mm/sec. No evidence of magnetic hyperfine splitting was observed, suggesting that the magnetic fraction constitutes less than 5% of the total iron present in the bulk sediment. With all parameters unconstrained, the spectra could be well fitted with two Lorenzian couplets, giving peak pairs with comparable heights and widths. Attempts to fit the spectra with two peak pairs constrained to have equal areas gave essentially identical results to the unconstrained fits.

The relevant Mossbauer parameters for unconstrained fits for the Oregon sediments are listed in Table III-1. Doublet I, with an average $IS = 0.36 \pm 0.01$ mm/sec, $QS = 0.62 \pm 0.02$ mm/sec and half width $= 0.65 \pm 0.04$ mm/sec, could be due to either high spin Fe(III) or low spin Fe(II) (Coey et al., 1974). Minerals with similar IS and QS values include ferric gel (Mathalone et al., 1970) poorly crystalline goethite (van der Kraan, 1972), pyrite (Morice et al., 1969), illite (Bowen et al., 1969), and smectite (Rosenson and Heller-Kallai, 1977). The broad half width and asymmetry in peak
Figure III-1. Mössbauer spectra of 6 levels of Oregon Core 28. Vertical axis is percent absorption. Smooth curve is the fitted spectra using two unconstrained Lorenzian peak pairs. The heights and line widths of each peak are shown by vertical and horizontal bars. Note the essential similarity of the spectra.
Figure III-2. Mossbauer spectra of 6 levels of Oregon Core 28. Symbols are the same as in Figure 1.
Table III - 1.

Summary of parameters from Mossbauer spectra of Core 28 bulk sediments and clay separates.

Derived from Non-linear least Squares Fitting of Spectra using fit of two peak pairs with heights of each peak pair not constrained.

**Bulk Sediments**

<table>
<thead>
<tr>
<th>Sample depth</th>
<th>Isomer shift (cm)</th>
<th>PEAK II</th>
<th>PEAK I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Isomer line shift (mm/sec)</td>
<td>Quadr. split width (mm/sec)</td>
</tr>
<tr>
<td>8</td>
<td>1.12</td>
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</tr>
<tr>
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<td>1.12</td>
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<td>1.12</td>
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</tr>
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</tr>
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<td>1.12</td>
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<td>0.45</td>
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<td>1.12</td>
<td>2.65</td>
<td>0.45</td>
</tr>
<tr>
<td>208</td>
<td>1.12</td>
<td>2.65</td>
<td>0.46</td>
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<tr>
<td>277</td>
<td>1.13</td>
<td>2.64</td>
<td>0.45</td>
</tr>
<tr>
<td>387</td>
<td>1.12</td>
<td>2.65</td>
<td>0.42</td>
</tr>
</tbody>
</table>

**Clay Separates** (peak heights constrained)

<table>
<thead>
<tr>
<th>Sample depth</th>
<th>Isomer shift (cm)</th>
<th>PEAK II</th>
<th>PEAK I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Isomer line shift (mm/sec)</td>
<td>Quadr. split width (mm/sec)</td>
</tr>
<tr>
<td>48</td>
<td>1.13</td>
<td>2.65</td>
<td>0.35</td>
</tr>
<tr>
<td>178</td>
<td>1.13</td>
<td>2.66</td>
<td>0.35</td>
</tr>
<tr>
<td>347</td>
<td>1.14</td>
<td>2.65</td>
<td>0.36</td>
</tr>
</tbody>
</table>
heights (~1.25) suggest that this couplet may be the sum of several minerals with slightly different peak velocities. However, attempts to further resolve this region with various combinations of constrained and unconstrained peak pairs resulted in no systematic trends nor improvement of the $\chi^2$ value. Fe(III) in illite is the most promising candidate for Doublet I because of a prominent 10A peak in the X-ray diffraction patterns of the bulk sediments. Pyrite iron, constituting <15% of the total iron, may contribute up to 20% of the absorption area of Doublet I. The contribution of amorphous iron oxides and poorly crystalline hydroxides (e.g. goethite) cannot be established at present. However, leaching experiments, Mossbauer analysis of heavy mineral separates and low temperature work might isolate the fraction of these species in Doublet I.

For the 12 levels, Doublet II has an average IS = 1.12 ± 0.005 mm/sec, QS = 2.65 ± 0.01 mm/sec and a half width of 0.44 ± 0.01 mm/sec. These values, consistent with a high spin Fe(II) couplet, correspond closely to parameters characteristic of chlorite (Blaauw et al., 1980) and vivianite (Forsyth et al., 1970), but are significantly different from reported values for pyroxenes, olivines and amphiboles (Bancroft et al., 1967). As 14 A Fe-rich chlorite was the dominant mineral identified in the X-ray diffractograms (vivianite was not detected), doublet II can be unambiguously identified as chlorite. The proportion of Doublet II to the total absorption area (0.557 ± 0.014) is remarkably constant for all levels of Core 28.
Since the absorption peak areas in a Mossbauer spectrum are proportional to iron content, the iron present in each couplet can be assessed quantitatively. For all levels of Core 28, the ratio of Doublet II/I is 1.26 ± 0.07. Given the total iron content and the II/I ratio for each sample, the average iron content in Doublet II (chlorite) is 2.42 ± 0.06%, while 1.93% is present in Doublet I as illite, smectite, ferric oxides and/or pyrite. Since the average acid insoluble sulfur content is 0.42 ± 0.16%, this yields an average pyrite iron content of about 0.49%. Thus 20-25% of Doublet I is present as reduced iron in pyrite. If we assume that the remainder of Doublet I is due to Fe(III) in clays and oxides, the ferrous/ferric ratio for the core is (2.91/1.44) = 2.02. This indicates that about 2/3 of the iron minerals in this core are in a reduced state, with the major phase being in detrital chlorite. The invariance of the chlorite fraction downcore suggests that the nature of the detrital fraction in at least the structurally stable iron oxides has not changed through time.

The Mossbauer parameters of the three clay separates from Core 28 (Figure III-3, Table III-2) have essentially identical isomer shifts and quadrupole splitting as the bulk sediments. Magnetic hyperfine splitting was not observed. The total absorption area of the clay separates was ~90 vs. ~120 for the bulk sediments. This suggests that about 75% of the iron oxides in the sediments are found in the clay-sized fraction. Similarly, the chlorite Fe(II) couplet constitutes about 49% of the total absorption area in the clay separates compared to 56% for the bulk sediments. Since
Figure III-3. Mossbauer spectra of 3 < 2 μm clay separates from Oregon Core 28. Velocity scale is twice that of the bulk sediments in Figures III-1 and III-2.
chlorite tends to be more abundant in the 4-22 μm size fraction in surface sediments off Oregon (Krissek, 1982), the lower chlorite abundance in the clay separates is probably an artifact of its size distribution in the sediments.

Gulf of California core E17

Mossbauer spectra for 6 samples from Core E17 are presented in Figure III-4. The spectra show a broad central absorption area from -0.5 to 1 mm/sec, which can be readily distinguished as two overlapping peaks of sub-equal height. A very minor secondary plateau extends to about 2.7 mm/sec. In contrast to the Oregon sediments, these sediments showed a maximum relative absorption of <2% and took several days to run. This is consistent with a total iron content of only 1-1.5% dry weight as determined by XRF.

To fit the spectra, several combinations of constrained and unconstrained peaks were tried. If peak areas were totally unconstrained or if more than two peak pairs were used, no unique solution could be found. The best solution was obtained by constraining the heights and areas for two peak pairs. Relevant Mossbauer parameters for this fit are listed in Table III-2. Doublet I is a strong absorption peak pair with IS = 0.33 ± 0.005 mm/sec, QS = 0.60 ± 0.02 mm/sec and a half width = 0.62 ± 0.09 mm/sec. This peak accounts for >80% of the total absorption area of the spectra.

The broad line width, but narrow range of IS and QS, suggest a mixture of species with one dominant component. The IS and QS
Figure III-4. Mossbauer spectra of 6 levels of sediments from the Gulf of California Core BAM 80 E17.
Table III-2

Summary of parameters from Mossbauer spectra of Core El7 bulk sediments and clay separates.

Derived from Non-linear least Squares Fitting of Spectra using fit of two peak pairs with heights of each peak pair constrained to be equal.

<table>
<thead>
<tr>
<th>Sample depth (cm)</th>
<th>%Fe</th>
<th>PEAK II Isolem</th>
<th>Quad. shift (mm/sec)</th>
<th>Quad. split (mm/sec)</th>
<th>line width (mm/sec)</th>
<th>Area (mm/sec)</th>
<th>PEAK I Isolem</th>
<th>Quad. shift (mm/sec)</th>
<th>Quad. split (mm/sec)</th>
<th>line width (mm/sec)</th>
<th>Area (mm/sec)</th>
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<tbody>
<tr>
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<td>1.57</td>
<td>1.09</td>
<td>2.36</td>
<td>0.66</td>
<td>5.47</td>
<td>0.34</td>
<td>0.57</td>
<td>0.64</td>
<td>26.29</td>
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<td>2.49</td>
<td>0.56</td>
<td>5.39</td>
<td>0.33</td>
<td>0.61</td>
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<td>0.35</td>
<td>0.57</td>
<td>0.76</td>
<td>22.50</td>
<td>24.87</td>
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</table>

Clay Separates

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<th>%Fe</th>
<th>PEAK II Isolem</th>
<th>Quad. shift (mm/sec)</th>
<th>Quad. split (mm/sec)</th>
<th>line width (mm/sec)</th>
<th>Area (mm/sec)</th>
<th>PEAK I Isolem</th>
<th>Quad. shift (mm/sec)</th>
<th>Quad. split (mm/sec)</th>
<th>line width (mm/sec)</th>
<th>Area (mm/sec)</th>
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<td>8</td>
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<td>2.48</td>
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<td>0.36</td>
<td>0.55</td>
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<td>0.29</td>
<td>2.51</td>
<td>0.33</td>
<td>0.66</td>
<td>0.63</td>
<td>24.19</td>
<td>26.70</td>
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</table>
values are very similar to reported values for pyrite (Vaughn and Craig, 1978). As previously concluded from the sulfur and total iron analyses (see Chapter II), the expected proportion of iron in pyrite ranges from <20% in the top 20 cm to 55-75% of total iron below 49 cm. The Mössbauer spectra are then consistent with the presence of pyrite. However, systematic downcore variations in the peak/total area ratio are not observed as expected. Thus, because of spectral peak overlap, quantitative estimation of pyrite percentages using Mössbauer spectra are not possible.

Doublet II, accounting for 10-17% of the total absorption shows considerable variability in its Mössbauer parameters. The IS varies from 1.09-1.19 mm/sec; QS from 2.36-2.56 mm/sec and half width from 0.33-0.66 mm/sec. The large IS and QS imply a high spin Fe(II) compound. The values are within a range reported for octahedrally coordinated Fe(II) in certain amphiboles (Bancroft et al., 1969), but are too low to be associated with commonly occurring clays or pyroxenes (Bancroft et al., 1967, Rosenson et al., 1979, Bowen et al., 1969, Rosenson and Heller-Kallai, 1977). Because of the dominance of opal and poor reflections in the X-ray diffractograms, verification of this identification from X-ray patterns was not possible.

Mössbauer spectra of three clay separates from the Gulf of California (Figure III-5, Table III-2) were poorly resolved, probably due to low total iron abundances, but yielded similar parameters to the bulk sediment. The total absorption area (% relative absorption/velocity channel * total number of channels) was
Figure III-5. Mossbauer spectra of 3 <2 μm clay separates from Gulf of California Core BAM 80 E17. Velocity scale is twice that of the bulk sediments in Figure III-4.
somewhat larger than in the bulk material (38-52 vs 26-38), suggesting that the iron is concentrated in the fine-grained fraction.

DISCUSSION

In the Oregon sediments, the proportion of high spin Fe(II) in chlorite is invariant at all levels, suggesting that the nature and amount of the detrital fraction is essentially constant downcore. However, to evaluate the effects of diagenesis in sediments from both regions, it is necessary to resolve the broad central absorption area into components due to low spin Fe(II) in pyrite (IS = 0.3 mm/sec, QS = 0.6 mm/sec) and other Fe(III) compounds with similar velocities. To evaluate the possibility of resolving the central area, mixtures of a chlorite standard (var. ripidolite, Clay Minerals Society C Ca-1) and a ground pyrite cube were prepared. The resulting spectra and Mossbauer parameters are summarized in Figure III-6. The pure chlorite spectra showed a strong high spin Fe(II) doublet (IS = 1.13 mm/sec, QS = 2.62 mm/sec) and a lesser Fe(III) peak pair (IS = 0.40 mm/sec, QS = 0.74 mm/sec) which constituted 16% of the total absorption area. As expected, with increasing pyrite content, the central peak pair grew in area and height at the expense of the Fe(II) chlorite doublet. Using two doublet fit with peak pair areas constrained to be equal, the values of the chlorite Fe(II) IS and QS parameters remained unchanged. However, the IS of the Fe(III)/pyrite Fe(II) doublet shifted toward the pyrite value, though in a nonlinear manner. A plot of the relative peak area of the chlorite Fe(III)/pyrite Fe(II) doublet versus pyrite content (Figure III-7)
Figure III-6. Mossbauer spectra of various mixtures of chlorite (var. ripidolite) and pyrite standards.
Figure III-7. Peak area percentages of pyrite/(chlorite+pyrite) plotted against proportion of pyrite in chlorite/pyrite mixture. Squares are measured values and circles are measured values with the chlorite ferric iron peak area subtracted.
shows a reasonably linear trend ($r^2 = 0.99$) with a slope of 1.22 and an intercept of -0.22. If the amount of Fe(III) chlorite is subtracted, a good linear relation ($\%_{pyr} = 0.01 + 1.02 \times$ area; $R^2 = 0.99$) is seen between pyrite content and peak absorption area. However, all attempts to fit the spectra with three peak pairs resulted in a lack of convergence of the fit. (Note that a more rigorous treatment should take into account the differing mass absorption characteristics of chlorite and pyrite). Fe(II)-rich trioctahedral chlorite is a common constituent of marine sediments derived from the weathering of low grade metamorphic rocks (Weaver and Pollard, 1975). The amount of Fe(II) can often be estimated by XRD from the position of the 060 reflection, in the absence of kaolinite or vermiculites (Brindley and Brown, 1980). However, the amount of Fe(III), though usually less than 4%, is often quite variable due to oxidation (Weaver and Pollard, 1975) and can be estimated only through wet chemical analyses of pure separates, which is very difficult.

The lack of resolvable fit in the pure mineral mixtures suggests caution in estimating the amount of pyrite iron in natural sediments in the presence of goethite and clay Fe-hydroxides (e.g. Suttill et al., 1982). Since the central absorption area of the Mossbauer spectra of a pure mixture could not be resolved into separate Fe(III) and Fe(II) components, we must conclude that quantitative estimation of pyrite in complex sedimentary mixtures is ambiguous by this technique. However, by first using selective leaching techniques (Gangas et al., 1973) and/or heavy mineral separates, pyrite iron
might be estimated after amorphous iron oxides and interlayer Fe hydroxides have been removed.
CHAPTER IV

ROCK MAGNETISM AND PALEOINTENSITIES IN RECENT HEMIPELAGIC SEDIMENTS

ABSTRACT

Downcore profiles of NRM, ARM and IRM in suboxic hemipelagic muds off Oregon and anoxic laminated diatomaceous ooze from the Gulf of California show dramatic decreases in intensity with depth. Magnetic properties are controlled by magnetite in both environments, with perhaps a minor contribution of hematite in the topmost parts of the Gulf of California sediments. The intensity decreases and systematic downcore changes in various magnetic parameters are consistent with reduction and dissolution of ferrimagnetic iron oxides with depth due to early diagnosis of organic matter. The overall magnetic grain size distribution appears to rapidly coarsen downcore as the smallest and most abundant particles are removed, then slowly grow finer as the remaining grains begin to dissolve. After the initial dissolution of the finest grains, the NRM seems to reside in only a portion of the coarser grain sizes. In such diagenetically altered sediments, relative paleointensity determinations based on simple normalizations of NRM to concentration related parameters give false estimates of paleofield behavior.

INTRODUCTION

This paper discusses detailed rock magnetic measurements on rapidly deposited marine sediments from a small basin on the Oregon
continental slope and in the Guaymas Basin of the Gulf of California. Our overall objectives in this project have been to obtain high resolution secular variation and relative paleointensity records, allowing us to evaluate characteristic trends for the past several millenia. As part of these goals, the utility of the various relative paleointensity techniques has been evaluated. In Chapter I, I showed that downcore magnetic intensity decreases and sulfide enhancements were consistent with magnetic mineral reduction, dissolution and subsequent pyrite formation as a result of oxidative decomposition of organic matter. In this chapter, I expand on this work and show how early diagenesis in these two contrasting depositional environments affects the magnetic properties of the sedimentary column.

Estimates of paleofield intensities from continuously deposited sediments in various areas of the world would be particularly desirable to evaluate field behavior during transitions and the global vs. regional nature of apparent quasi-sinusoidal cyclicities in the last 10 Ky found in lavas and archaeologic artifacts (Barton et al., 1979). Due to the field's shielding effect against $^{14}\text{C}$-producing radiation, $^{14}\text{C}$ activity is a strong inverse function of the Earth's dipolar field (Elsasser et al., 1956; Bucha, 1970). Thus, knowledge of paleofield intensities could permit calibration of the $^{14}\text{C}$ time scale beyond presently available tree ring chronologies. Furthermore, reliable paleofield estimates would be particularly desirable for examining speculated magnetic field and climate links (King, 1974; Wollin et al., 1971, 1973, 1977, 1978; Harrison and Prosp-
pero, 1974). These links, while plausible, have not yet been substantiated (Pittock, 1978, Sternberg and Damon, 1979, Chave and Denham, 1979).

Attempts to reliably determine ancient geomagnetic intensities from sediments have not been notably successful (Chave and Denham, 1979; Turner and Thompson, 1981). Absolute paleointensities in sediments cannot be obtained by conventional thermal methods (Thellier and Thellier, 1959, Shaw, 1974) because the TRM does not duplicate the DRM acquisition process. Various relative paleointensity methods have been proposed based on normalization of NRM to a concentration related parameter such as initial susceptibility ($\chi$), saturation remanence (SIRM), isothermal remanence (IRM) or anhysteretic remanence (ARM) (Nakajima and Kawai, 1973; Thompson, 1975; Johnson et al., 1975; Levi and Banerjee, 1976). Unfortunately, all of these parameters are grain size dependent (Day, 1976, for review) and the problem becomes one of matching NRM coercivity spectra to the spectra of a laboratory-produced remanence.

Laboratory-produced remanences activate magnetite particles in different ways. $\chi$, and IRM are strongly influenced by domain wall movements in coarse multidomain (MD) grains (>4-15 $\mu$m in diameter). Since $\chi$ is measured in the presence of an external field, this parameter is also sensitive to submicron super-paramagnetic (SPD) grains and paramagnetic species. In contrast, ARM is controlled mainly by shape and stress anisotropies in single domain (SD) and pseudosingle domain (PSD) particles (Bailey, 1975; Levi and Merrill, 1976). Because of unknown effects of crystal defects, dislocations
and shape irregularities, there is considerable controversy over the specific limits associated with the SD/PSD and PSD/MD boundaries (Day, 1976, Moskowitz and Banerjee, 1979). However, it is generally accepted that SD particles of magnetite fall in a range of 0.05 to ~0.1-0.4 μm, while grains >15 μm show MD characteristics, with PSD particles falling somewhere between ~1 and 15. μm.

The NRM in sediments is assumed to be due to a portion of detrital magnetic grains aligning preferentially in the direction of the ambient field as they settle into the sediment matrix. The remanence in sediments contrasts to the remanence found in igneous rocks and ancient artifacts which is presumed to be of thermal origin. Despite intensive work, depositional (DPM) and postdepositional (pDRM) remanence acquisition processes are complex and poorly understood (Verosub, 1977, for review). The alignment efficiency and lock-in depth seem to depend on porosity and the relative grain size distributions of the magnetic population and matrix. Fixation of remanence appears to be abrupt and a function of a critical water content for a given sediment. Inclinations in bioturbated sediments can faithfully record the expected field direction, thus remanence often must be locked in below the zone of mixing (see Chapter VI).

In a sedimentary mixture, the NRM is commonly carried by a fraction of the SD and PSD sized grains. These particles originally acquired their magnetization as a TRM, therefore the magnetic concentration should be proportional to some measure of the amount of TRM in the material. Since ARM and TRM are similar in many respects (Bailey, 1975; Levi and Merrill, 1976), Levi and Banerjee (1976)
proposed that NRM/ARM ratios might give good estimates of relative paleointensities in homogeneous sedimentary sections where remanence resides in the fine-grained fraction. Alternatively, in cases where the remanence is carried by MD particles, NRM/IRM might be more suitable. The criteria of homogeneity (i.e., no change in NRM and ARM coercivities downcore) is necessary to avoid a dependence of these ratios on the chosen cleaning field and to minimize any grain size related effects. Such estimates are relative because the proportionality factor between ARM (or IRM) and the concentration of magnetic species responsible for NRM is unknown, as is the response of NRM to applied field. Also, ARM/TRM ratios are grain size dependent (Levi and Merrill, 1976; Kono, 1978), thus a downcore change in the magnetic size distribution would introduce a distortion in paleofield estimates.

METHODS

Sediments from both areas were collected with a 3-5 m Kasten corer with a 15 cm square cross section. Barrel tops were sealed with polyurethane to prevent loss of surface sediment. Cores were slabbed into 5 cm x 15 cm x 50 cm trays and kept wet and refrigerated during transport and storage. Paleomagnetic sampling was done with a thin walled square stainless steel tube mounted in an orienting frame from which material was extended into 6.5 cc sample boxes. Care was taken to keep samples wet, cold and in a low field environment prior to and between measurements in order to minimize drying and viscous remanence effects.
Remanence measurements were made either on a Schoenstedt DSM-1 spinner magnetometer or on a SCT cryogenic magnetometer for the NRM of the Gulf of California samples. All stepwise alternating (AF) demagnetizations were done with a single axis Schoenstedt AF demagnetizer up to at least the sample's median demagnetizing field (MDF). The MDF is the peak AF field at which the remanence falls to one half of its original value. ARM's were given along one axis with 1000 Oe AF and D.C. biasing fields of 0.5 Oe for the OR sediments and 0.25 Oe for the GC sediments. No ARM anisotropy was observed along different axes and ARM acquisitions were linearly proportional to applied bias field up to 2 Oe with no change in stability. Fourteen samples from OR Core 28 and 12 samples from GC core BAM 80 E17 were also given stepwise IRM acquisitions to 10 kOe followed by AF demagnetization to 1000 Oe AF in 50-100 Oe steps.

The magnetic components of seven samples from cores W7710-28, W7809-27 and BAM 80 E17 were separated using a continuous flow-through separation technique. Prior to separation, bulk samples were weighed, diluted in distilled water and sonified for 10 minutes. The sample slurry was then continuously stirred and pumped past a 3 K Gauss electromagnet. At regular intervals, the tubing was flushed with water to clear the slurry. The magnet was then turned off and the magnetic concentrate on the tubing walls was flushed into a separation tank. Periodically, both the slurry and concentrate were filtered through a 0.25 μm ceramic filter to remove excess water. Complete separation in most cases took 4-7 days. Despite the exhaustive removal procedure, apparently only about 60%
of the IRM and 30% of the ARM was lost after separation. The remaining sediment showed higher ARM and IRM MDFs than the untreated material suggesting that physical separation tends to extract coarser magnetic components.

The mineralogical characteristics of the seven magnetic separates were analyzed using a conventional Debye-Scherrer X-ray powder diffraction camera with Co radiation (35KV, 18 mA) and an Fe filter. Due to the small sample size, 0.3mm capillary tubes were used and an exposure time of 11-22 hours was necessary. Upon developing the film strip, the mean effective radius of the film was calculated using all pairs of readable back and forward diffraction ellipses. For all peak pairs, 'd' spacings were calculated using standard equations (Klug and Alexander, 1954). Peaks and their associated lattice parameters were identified from the ASTM powder Diffraction file. A minimum of three peaks were considered necessary for positive mineral identification. For the magnetite lines, the unit cell parameter, $a_0$, and associated errors were calculated from the equations (Klug and Alexander, 1954):

$$a_0 = d \times \sqrt{h^2 + k^2 + l^2}$$

$$\frac{\Delta a}{a_0} = a_0 \times \cot \Theta \ d\Theta$$

where $d \Theta = \text{minimum resolvable spacing ( } \sim0.25 \text{ degrees).}$

The texture and qualitative composition of the magnetic separates was examined using a scanning electron microscope (SEM) with an attached energy dispersive X-ray unit (EDAX).
RESULTS

Oregon (OR) Sediments

Magnetic Mineralogy

Results of XRD on the magnetic separates for three levels each from cores 28 and E17 and one sample from core 27 are summarized in Table IV-1. For the OR sediments, the only ferrimagnetic species identified at all levels was pure magnetite with a unit cell parameter of $a_0 = 8.39 \pm 0.01 \text{ Å}$. Other nonmagnetic minerals identified included chlorite, quartz, plagioclase and possibly hornblende. Reflections from magnetic sulfides such as pyrrhotite and gregite were not observed.

SEM photomicrographs of core 28 magnetic separates from 40-50 cm and 333-343 cm (Figures IV-1, IV-2) showed, in order of abundance, clay platelets ($\langle 2-20 \mu \text{ m} \rangle >$ large ($>20 \mu \text{ m}$) silicious biogenic fragments (mostly diatoms) $>$ plagioclase, quartz $>$ magnetite dipyramids and unidentified anhedral grains. Clumps of detrital particles with very small ($\langle 2 \mu \text{ m} \rangle$) subhedral to euhedral magnetite crystals were common, especially in the 40-50 cm sample. EDAX scans of the surfaces of diatom and quartz fragments showed Fe and Si peaks, while clay platelets gave high Fe as well as Al and Si peaks. This suggests that the surfaces of the non-magnetic particles were covered with an iron film whose colloidal particles were too fine to resolve due to magnetic defocussing of the electron beam. EDAX scans of magnetite euhedra showed only Fe, consistent with the cell parameters of a pure $\text{Fe}_3\text{O}_4$ magnetite, as determined by XRD.
### Table IV-1

X-ray diffraction identifications of minerals from magnetic separates from Cores E17 and 28.

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<tr>
<th>Core</th>
<th>Sample depth</th>
<th>Magnetic Species</th>
<th>N</th>
<th>Mean unit cell parameter</th>
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<tr>
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Figure IV-1 a) and b). SEM photomicrographs of magnetic separates from Core 28, depth 40-50 cm. Note the large number of ≤ 2 micron particles affixed to larger grains.

Figure IV-2 a) and b). SEM photomicrographs of magnetic separates from Core 28, depth 333-343 cm. The overall grain size is generally coarser than in the separates from 40-50 cm. Large 10-50 µm magnetite octahedra are deeply eroded in the upper left corner of a) and in the center of b).
Figure IV - 1.
Figure IV - 2.
An obvious feature of the core 28 SEM photos was that the grain size distribution of the 40-50 cm sample was very much finer than that of the 333-343 cm sample. Whereas the top sample contained many fine grains <1-2 μm in diameter as clusters and affixed to larger fragments, the deeper sample had a more uniform distribution with numerous individual 5-20 μm magnetite euhedra and few obvious micron sized particles.

Another way in which to assess the magnetic mineralogy is to apply a stepwise IRM and observe the approach to saturation. Magnetite, with a high spontaneous moment (93 emu/gm) due to cubic symmetry, approaches saturation by 2-3 KOe. Hematite, in contrast, has a low spontaneous magnetization (0.4 emu/gm) and strong anisotropy which gives rise to very high coercivities and slow approach to saturation (Stacey and Banerjee, 1974). Thus, remanence due to magnetite or hematite are readily distinguishable. IRM acquisition experiments on several samples from core 28 (Figure IV-3) showed saturation by 3 KOe, indicating that the magnetic properties of the Oregon sediments was controlled by magnetite.

Rock Magnetism

Downcore profiles of NRM intensities, demagnetized at 150 Oe AF, for Oregon cores 28 (Figure IV-4) and 26+27 (Figure IV-5) show very similar characteristics. (Cores 26 and 27 are spliced together because core 26 overpenetrated by 30 cm and Reineck box core 27 came from essentially the same location.) In the top 60 cm of cores 28 and 26 as well as in the 30 cm of core 27, intensities are high (2.5 to
Figure IV-3. SIRM acquisition curves of Core 28 sediments.
4.5 x 10^{-5} \text{ emu/cc}) and somewhat variable. Between 60 and \sim 120 \text{ cm}, NRM intensities decrease monotonically by almost an order of magnitude. Below 120 \text{ cm}, intensities continue to decrease but at a much slower rate and variability is much less. This precipitous decrease in NRM is obviously not related to changes in the Earth's field since concentration dependent ARM (Figure IV-4) and IRM profiles show similar but even more pronounced behavior.

The stability of the remanence can be roughly characterized by the median demagnetizing field (MDF). For magnetite, higher MDFs, corresponding to more stable remanence, generally indicate a lesser contribution of large (>5 \mu \text{ m}) MD particles (Day, 1976). As in the intensity profiles, all of the Oregon sediments show similar downcore trends in MDF values of NRM, ARM, and IRM (Figure IV-6). In Core 28, NRM MDFs decrease from 300-400 \text{ Oe} in the top 60 \text{ cm} to values of 225-275 \text{ Oe} below this depth. ARM MDFs are higher than corresponding NRM or IRM MDF values. The core 28 ARM MDF profile shows high values (350-450 \text{ Oe}) in the top 60 \text{ cm}, lower values (275-300 \text{ Oe}) from 60-160 \text{ cm}, and slightly higher values (300-370 \text{ Oe}) deeper in the core. The ARM MDFs of cores 26+27 show an identical pattern. Overall, the high NRM and ARM stabilities in the Oregon sediments imply that much of the remanence is controlled by SD and PSD particles (Levi and Merrill, 1978).

AF demagnetization curves of NRM, ARM, and IRM are shown for three representative levels of Oregon core 28 in Figure IV-7 and stabilities for the various levels are summarized in Table IV-2. The samples show consistent trends with depth. For the highly
Figure IV-4. NRM and ARM profiles of Core 28 sediments. NRM (solid) and ARM (open) values have been AF demagnetized to 150 Oe AF.
Figure IV-5. NRM, ARM and MDF profiles of Cores 26+27 sediments. NRM and ARM values have been AF demagnetized to 150 Oe AF.
Figure IV-6. Downcore profiles of NRM, ARM, and IRM Median Demagnetizing fields. IRMs were given at 5 Koe and ARM was acquired at 1000 Oe AF with a biasing field of 0.500 Oe.
Figure IV-7. Demagnetization curves of NRM, ARM and IRM for Core 28 sediments. IRMs were given at 5 kOe and ARM was acquired at
Table IV-2
Remanence Stabilities of NRM, ARM and IRM for selected levels of Oregon Core 28 and Gulf of California Core E17.

Median demagnetizing fields (MDF) are in units of Oersteds (Oe). Intensities of ARM and IRM have 1000 Oe AF intensity subtracted.

**CORE 28**

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<th>IRM MDF</th>
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**Gulf of California Core E17**

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magnetized samples in the top 60 cm, ARM and to a lesser extent NRM, are much harder than IRM. The high NRM stabilities suggest that the DRM initially lies predominantly in fine SD and PSD grains. In the intermediate intensity region between 70 and 150 cm, the MDFs of all three remanences decrease. ARM and NRM curves are still more stable than IRM. For the low intensity samples below 150 cm, ARM and IRM curves are similar and their MDFs show an apparent increase with depth whereas the NRM MDFs remain essentially unchanged. On the basis of these trends it would seem that the DRM is controlled by coarser particles with depth.

Gulf of California (GC) Core BAM 80-E17

Magnetic Mineralogy

For the Gulf of California sediments, XRD spectra of magnetic separates from 8-12 cm and 15-21 cm show intense magnetite lines and fainter hematite lines. The sample from 197-202 cm contained magnetite, but no hematite. Non-magnetic species included quartz, opal, plagioclase, and possibly clinopyroxene, ilmenite, hypersthene, illite and chlorite. No sulfides were positively identified, although pyrite may have been present. The magnetite unit cell parameter of 8.39 ± .005 Å suggests that the majority of the magnetite contains little Ti in solid solution.

SEM photos of the magnetic separates from 15-21 cm (Figure IV-8) show abundant siliceous debris (mostly diatoms), coarse clays, possibly hematite rhombs and numerous agglomerates composed
of diatom tests, clay booklets, and fine (<1-10 μm) magnetite euhedra. EDAX scans of the surfaces of diatom tests give Fe peaks, again suggesting surficial iron coatings. Magnetite dipyramids are well crystallized and showed little evidence of mechanical abrasion or solution pitting.

Photomicrographs of the 197-202 cm separate showed a coarser texture than either the top EL7 samples or the OR core 28 material. Magnetite grain sizes are variable but most commonly were in the range of 1 - 30 μm. Many of the magnetite grains show striking evidence of surface acid etching and solution pitting (Figures IV-9, IV-10). The extent of surface dissolution is variable, ranging from minor surface etching along fractures (Figure IV-9a), enhanced roughness of surface topography (Figure IV-10a) to deep solution pits and almost complete grain destruction (Figure IV-10b). Interestingly, only magnetite grains seem to have been attacked since in Figure IV-9a, a nearby rare chromite grain shows no evidence of dissolution.

IRM acquisition curves for sediments from core EL7 are shown in Figure IV-11. Samples below 30 cm reach saturation by 3 kOe, while specimens in the top 30 cm showed low remanence coercivities but slower approach to saturation. This is consistent with a dominant magnetite component throughout the core and a minor hematite contribution in the top few cms, in agreement with the XRD and SEM results.

Rock Magnetism
Figure IV-8. SEM photomicrographs of magnetic separates from Core E17, depth 15-21 cm.
   a) Closeup of clay booklet with numerous magnetite octahedra, plagioclase (?) rhombs, and siliceous debris attached. Note the mixture of grain sizes and well crystallized octahedra.
   b) Separates contained numerous conglomerates of clay booklets with affixed magnetite octahedra; centric and pennate diatom fragments, spores, and bristles; and plagioclase (?) rhombs.

Figure IV-9. SEM photomicrographs of magnetic separates from Core E17 depth 198-202 cm.
   a) Octahedron of magnetite (lower left) with etched surface. A nearby chromite octahedron (upper right) shows no evidence of acid attack.
   b) Closeup of surface etching on magnetite grain seen in a). Note the submicron particles affixed to the surface. Their fuzzy appearance is probably due to magnetic defocussing of the electron beam.

Figure IV-10. SEM photomicrographs of magnetic separates from Core E17 depth 198-202 cm.
   a) Large (50 μm) magnetite particle showing surface etching and solution pitting indicative of acid attack.
   b) Partially dissolved and deeply pitted magnetite particle. Note submicron particles attached to the surface.
Figure IV - 8.
Figure IV - 9.
Figure IV - 10.
Figure IV-11. SIRM acquisition curves of Core E17 sediments.
For the laminated sediments from GC core E 17, intensity profiles of NRM, ARM (Figure IV-12) and IRM show a very steep decrease in magnetization from the surface to about 30 cm. Below this depth, NRM intensities continue to decrease slowly while ARMs and IRMs are relatively constant or slightly variable with depth. NRM MDFs, shown in Figure IV-13, also decrease sharply from the surface to ~20 cm, then remain relatively constant downcore. Both ARM and IRM MDFs, (Figure IV-13) also show an initial decrease from the surface, but then again slowly increase downcore.

NRM, ARM and IRM AFD curves for the E 17 core shows similar, but even more pronounced behavior than the Oregon sediments (Figure IV-14, Table IV-2). In the top 30 cm, while intensities for all three remanences decrease dramatically, NRM stabilities drop from about 350 Oe to 150 Oe, then stay relatively constant with depth. The high ARM and IRM stabilities in the top 20 cm indicate a dominant fine-grained component in the surface sediments. ARM and IRM stabilities initially decrease from the surface to 20 cm, then increase slowly downcore. These trends suggest an initial coarsening of the distribution followed by a gradual fining with depth.

The NRM is initially more stable than IRM in the top 30 cm, but with depth, NRM stabilities are significantly lower than either of the laboratory-produced remanences. The NRM stabilities imply that the DRM is initially held mostly in SD and PSD grains, but with depth, only a small fraction of the original detrital remanence survives and this is carried by relatively more MD particles, which have lower stabilities. Because of the striking differences between
Gulf of Cal. Core BAM 80 E17

Magnetic Intensity ($\times 10^{-7}$ emu/gm(wet))

Figure IV-12. NRM and ARM profiles of Core E17 sediments. NRM (solid) and ARM (open) values have been AF demagnetized to 100 Oe AF.
Figure IV-13. Downcore profiles of NRM, ARM and IRM Median Demagnetizing fields. IRMs were given at 5 Koe and ARM was acquired at 1000 Oe AF with a biasing field of 0.250 Oe.
Figure IV-14. Demagnetization curves of NRM, ARM and IRM for Core E17 sediments. IRMs were given at 5 KOe and ARM was acquired at 1000 Oe AF with a biasing field of 0.250 Oe.
the NRM coercivities and those of the artificial remanences, it is obvious that the ARM and IRM activate different parts of the magnetic spectrum than the residual DRM.

DISCUSSION

Possible causes for the downcore trends in NRM intensity include fluctuations in magnetic field and changes in the mineralogy, concentration and/or size distribution of the magnetic fraction. Intensity changes in the Earth's magnetic field can be discounted immediately because the geomagnetic field has changed by only a factor of three in the last 10 kyr (Barton, et al., 1980), whereas the observed NRM decreases by factors of 10-20 from the surface. Moreover, the parallel trends in laboratory-produced remanences suggest a profound change in rock magnetic properties.

Fundamental differences in magnetic mineralogy with depth can also be ruled out since magnetite was the only magnetic mineral found in the magnetic separates of the Oregon cores and at depth in E17. Although hematite as well as magnetite was found in the top 20 cm of E17, the rapid saturation of IRM at 2-3 KOe, the NRM MDFs, and the low spontaneous moment of hematite suggest that the remanence near the surface was dominated by magnetite.

Changes in the relative concentration and perhaps size distribution of the magnetic fraction can be due to diagenesis, authigenesis, or variations in the detrital sediment source with time. In most sediments of heterogeneous lithology, probably the most
common cause of downcore fluctuations in natural and artificial remanence is due to variations in terrigenous input and detrital source mineralogy. As discussed in the Geochemistry and Mossbauer sections, the Oregon sediments display constant downcore profiles in major element chemistry, X-ray mineralogy and Mossbauer characteristics. Moreover, at least for Core 26, sedimentation rates are constant downcore implying uniform detrital input with time. For the Gulf of California sediments, the high covariance of terrigenous elemental abundances suggests a surprising constancy in source mineralogy with time. Accumulation rates in E17 are quite variable downcore; however, the trends in magnetic properties show no correspondence. We must then conclude that the observed trends in remanence are not caused by changes in provenance of the terrigenous material.

Unlike highly oxidized pelagic sediments where authigenic Mn-Fe hydroxides have been reported at depth in the sediment column (Johnson et al., 1975, Henshaw, 1978, Henshaw and Merrill, 1980), rapidly deposited hemipelagic sediments such as found along many continental margins are typically sub-oxic to reducing so that oxidized authigenic minerals would not be expected. Magnetic sulfides such as pyrrhotite ($\text{Fe}_{1-x}\text{S}$) which have been reported in the Sea of Japan (Kobayashi and Nomura, 1972) or griegite ($\text{Fe}_3\text{S}_4$) were not observed here. Such authigenic sulfides seem to require acid conditions (Rickard, 1975) which are normally not found in marine sediments (Berner, 1981).

In the OR and GC sediments, authigenic magnetite could be formed in surficial layers either as a result of partial reduction
and conversion of ferric oxides or from the oxidation and precipitation at the redox boundary of diagenetically remobilized porewater Fe(II) from below. From thermodynamic considerations, Henshaw and Merrill (1980) suggested that under suitable Eh-pH conditions, magnetite could be a stable equilibrium mineral. However, as they also note, such calculations make the dubious assumption of equilibrium and are critically dependent on the choice of reactive end members. In sediments, iron occurs in many phases and determination of the reactive species is notoriously difficult. Moreover, convincing evidence of authigenic magnetite has not yet been reported in marine sediments. Although this authigenic magnetite formation hypothesis cannot be readily dismissed, we consider this possibility to be unlikely in these sediments since drying and storage experiments (Levi and Karlin, man. in prep.) show no increase in remanence with time or upon exposure to air. (Indeed, the opposite was observed.) Furthermore, authigenic Fe$_3$O$_4$ formation in the present polarity field would be expected to increase, rather than decrease the NRM.

As discussed in Chapter I, the most likely cause of downcore decreases in remanence is due to reduction of magnetite and subsequent formation of pyrite. This occurs as a result of microbial decomposition of organic matter utilizing the ferric/ferrous transition as a source of metabolic energy.

The behavior of the natural and artificial remanences upon demagnetization yields some interesting insights into the nature of the dissolution process. The large decrease in NRM, ARM and IRM
near the surface suggests that a substantial portion of the magnetic fraction is rapidly dissolved when anoxic conditions commence. The depth where anaerobic decomposition begins is probably mostly a function of the amount of organic input and secondarily, the total accumulation rate (Berner, 1981). In the highly reducing GC sediments, it appears that Fe reduction starts in the top 10 cm, while in the sub-oxic OR muds, anoxia is delayed until ~60 cm.

The high NRM and ARM MDFs in the surface sediments indicates that the initial magnetic fraction is composed mainly of very fine SD and PSD particles. The NRM and ARM are also more stable than the IRM. In the transitional intensity zone, MDFs of all remanences drop sharply as the intensities decrease, consistent with downcore coarsening of the remaining magnetic material and a larger relative contribution of MD grains. Note that the response of MDFs to particle dissolution depends on the initial particle size distribution. Because of the humped shape of the theoretical curve of relaxation time (i.e., coercivity) versus grain size (Merrill, 1975), it is possible that for a particular distribution, the stabilities could first increase then decrease due to progressive grain dissolution.

With depth, the MDFs of the laboratory-produced remanences increase again, although intensities remain about the same or decrease slightly. There is a tendency for ARM stabilities to increase relative to the IRM stabilities with depth. These trends suggest a downcore fining of the remaining grain size distribution. NRM stabilities show no obvious corresponding trend. The low NRM
MDFs relative to IRM suggest that the remaining detrital remanence is controlled by coarser MD grains.

The downcore increase in relative stability of ARM and IRM is peculiar, but can be readily understood by examining the SEM photos of the magnetic separates (Figures IV-9, IV-10). The large MD sized magnetite grains show signs of extensive surface etching and solution pitting. This leads to large increases in specific surface area and formation of many small segregated SD and PSD sized regions. Since ARM is more sensitive to PSD sized grains whose moments are controlled by surface stress anisotropies and domain wall pinning about dislocations (Bailey, 1975, Dunlop and West, 1969), these large, partially dissolved particles should yield relatively large and stable ARM moments.

In contrast, one would expect that the original NRM would be progressively destroyed. After initial dissolution of the finest grains, the residual DRM would be carried mainly by larger PSD and MD sized grains. This would lead to an effective decrease in the 'lock-in' depth and range over which remanence is fixed, since coarser particles would be locked into the matrix closer to the surface. With depth (and time), the DRM moment carried by PSD grains would diminish as the initial grain surfaces are destroyed, stresses are relieved and domain walls become unpinned. Since the MD moment is a volume magnetization and MD particles are larger, DRM carried by MD particles would remain until grains are extensively pitted and/or destroyed.

With regard to relative paleointensities based on concentration
normalization, Levi and Banerjee's (1976) criteria of homogeneity is violated in sediments which have undergone diagenetic alteration. In a practical sense, since NRM MDFs change in a different manner than ARM or IRM, there is a dependence of the NRM to ARM (or IRM) ratios on the chosen 'cleaning field'. More importantly, at least for the GC sediments, the DRM appears to be controlled by SD and PSD sized particles near the surface and by a small portion of the MD grains at depth. ARM may be a suitable normalizing parameter at the surface but inappropriate at depth. The converse is true for IRM. Thus, no single 'concentration' normalizing factor may be applicable to the entire core.

CONCLUSIONS

1. In the Oregon sediments, magnetite is the mineral responsible for the magnetic properties of the sediments. In the Gulf of California sediments, magnetite is the dominant magnetic mineral throughout the core, although hematite is found near the surface. The hematite is apparently destroyed by diagenesis downcore.

2. In both the OR and GC sediments, the magnetic properties are modified by diagenetic processes through the reduction and dissolution of magnetite. Initially, the smaller magnetite particles are dissolved either completely or to superparamagnetic sizes. This causes a precipitous drop in the intensities of the various remanences and an accompanying decrease in the stabilities. Dissolution continuing further
downcore causes shifts in the particle size distribution to smaller grain sizes, reflected in relatively increased remanence stabilities downcore.

3. Because of the effects of grain size selective dissolution and the activation spectrum of DRM versus remanences produced in the laboratory, relative paleointensity estimates in diagenetically altered sediments will not give reliable results.
INTRODUCTION

Observatory records of the geomagnetic field for the past 300 years have established in detail how the field varies on time scales of decades to centuries. Through the use of spherical harmonic analyses and comparison of isoporic foci, it has been well established that the field has drifted westward at about $0.3^\circ/yr$ for the main field and $0.2^\circ/yr$ for the non-dipole field (Bullard et al., 1950, Yukatake, 1962, 1968, Yukatake and Tachinaka, 1968).

From dynamo theory, it is widely accepted that non-dipole fields at the Earth's surface originate from large scale turbulent motions of conductive fluid near the core/mantle boundary. The moving fluid interacts with the main toroidal field, producing electric currents which, in turn, give rise to secondary field components with time constants of decades to millenia. Upwelling and downflow of the limbs of these convective eddies can cause westward drift of individual non-dipole features on a local or regional scale. If the core spins at a relatively slower rate than the mantle, then the entire field will appear to drift westward as viewed from the Earth's surface. Since the growth and decay rates of these core perturbations are unknown but likely to be highly variable, distinguishing between local and global drift is difficult given the short span of available records.

Deciphering patterns of secular variation (SV) are relevant to
understanding the time scales of fluctuations of the geodynamo and the effects of the mantle's conductive shielding. As important, SV studies can help answer some nagging problems in paleomagnetism. To a first approximation, extensive early work in paleomagnetism of basalts and deep sea sediments has shown that the long term behavior of the field is that of a geocentric axial dipole. A common assumption is that the oscillations in the field directions are random, allowing the use of Fisher statistics to place confidence intervals about paleopoles and permitting spatial and temporal comparisons of pole positions. However, as originally observed in Tertiary Ice-landic lavas (Wilson, 1970) and later found in lavas from many parts of the world over the past 5 My (Merrill and McElhinny, 1977), inclinations are often slightly shallower than expected for a geocentric axial dipole. Wilson (1970) first proposed that this second order ('far-sided dipole') effect might arise from an off-centered dipole. Recently, Creer (1983) showed that certain plausible patterns of secular variation and westward drift can cause time averaged directions NOT to average exactly to a geocentric dipole when directions are treated as unit vectors. Thus, if non-dipole drift is not random, or if anomalies are persistent over long periods, inferences based on Fisher statistics may be inappropriate. This would place severe limitations on the resolution that can be achieved in global or regional tectonic reconstructions.

Until recently, the major impediment to evaluating global vs regional patterns of secular variation has been the shortness (<2 Ky) and limited spatial coverage of reliable archaeomagnetic records.
In the past few years, paleomagnetic studies of wet sediments from glacial lakes and uplifted dry sedimentary sections have attempted to extend the SV record back to 10-30 Ky. However, because of the proximity and diversity of nearby sediment sources, sedimentation rates in lakes are often highly variable and the mixture of old and new carbon reservoirs leads to large uncertainties in radiocarbon ages.

Marine sediments are another potentially useful recorder of secular variation. Hemipelagic muds deposited along continental margins have the advantages of wide distribution, high sedimentation rates and a more uniform depositional environment than found in continental limnic regimes. This study was undertaken to examine the feasibility of using marine sediments to obtain detailed SV trends. Two 3 m Kasten cores and one 0.3 m box core were taken in a small basin on the Oregon lower continental slope at a depth of 1820m. The sediments were subjected to extensive paleomagnetic, rock magnetic and geochemical analyses to determine the character of the material, the nature of the remanence carriers and the reliability of the magnetic signal. In this chapter, directional results for the two cores are reported. The resulting secular variation curve, spanning the last 3.1 Ky, is compared to other relevant studies and a model of the geomagnetic field based on present behavior. The results suggest a regional coherence to SV trends and a tentative correlation to westward drift of the present field at a rate of 0.3°/yr, yielding a 1200 year periodicity.

METHODS
Sediments from the Oregon continental slope were collected with a 3 m Kasten corer with a 15 cm square cross section. The Kasten corer is a gravity corer with a titanium barrel and detachable L-shaped sides. This corer is superior to conventional piston or gravity devices because the large cross section allows multiple horizontal sampling, core twisting is not a problem and coring disturbance is minimized.

Cores W7710-26 and 28 were both retrieved with full barrels. The top 30 cm of Core 26 was lost in core handling due to overpenetration. In Core 28, the top 88 cm penetrated into the weight stand and was recovered by extruding the mud into a plastic tray with a piston. Cores were slabbed for storage into 5 cm x 15 cm x 50 cm trays. Trays were kept wet and refrigerated during transport and storage. Paleomagnetic sampling was done with a thin-walled square stainless steel tube mounted in an orienting frame from which material was extended into 6.5 cc sample boxes. Two to four samples were obtained from each horizon in the central portion of the core. Care was taken to keep samples wet and cold and in a low field environment prior to and between measurements in order to minimize drying and viscous remanence effects as much as possible.

Remanence measurements were made on a Schonstedt DSM-1 spinner magnetometer. Stepwise alternating field demagnetizations were done with a Schonstedt single axis AF demagnetizer up to at least the sample's median demagnetizing field (MDF) for Core 28 and 200 Oe or more for Core 26. Two to four pilot samples from several horizons in
Core 26 were 'cleaned' in steps of 50-100 Oe to 1000 Oe AF in order to examine the stability of remanence and rock magnetic properties.

RESULTS

Stability of the Magnetic Signal

Alternating field demagnetization (AFD) characteristics of several samples for Oregon (OR) Core 26 are shown in Figure V-I. For all of the Oregon sediments, directions show exceptional directional stability and smooth decay upon AFD to at least 400 Oe peak field. Overall, the angular mean standard deviation between the 100, 150 and 200 AF levels averages 1.5 and 1.4 degrees per sample for Cores 28 and 26, respectively. NRM median demagnetizing fields (MDFs) of >200 Oe, as well as rock magnetic measurements (see Chapter IV) suggest that the NRM throughout the cores is controlled by single domain and pseudosingle domain magnetite particles. Viscous remanence acquisition experiments (Levi and Karlin, man in prep) show that VRM acquired in the Earth's field for periods over one year is readily demagnetized by 150 Oe, thus wet storage has little effect on the NRM. Drying experiments show a diminution of the remanence, but essentially no change in original direction after drying and AFD.

Paleomagnetic Directions

Downcore profiles of inclination (I), relative declination (D), and angular deviations are shown in Figures V-2 for OR core 28 and Figure V-3 for Core 26+27. At each horizon, mean directions were
Figure V-1. AF demagnetization curves and stereonet of NRM directions for 4 samples from 268 cm depth level in Core 26.
obtained by vector averaging the directions from the 100, 150 and 200 AF levels for each sample then combining samples into a horizon average. The bands surrounding each horizon encompass the range of all AFD measurements at that depth level.

For Core 28, the core mean inclination (Ic) is 62.6° with an a.95 of 2.7° and k of 65.5. For Core 26, Ic is 60.6° with an a 95 of 1.8° and k of 202. Given the sedimentation rate of 123 cm/Ky determined from 9 C14 dates for Core 26 and 2 dates in the top 25 cm of Core 27 (r = 0.97) (see Chapter II), the base of Cores 28 and 26 represent 3155 and 2440 years, respectively, assuming a zero age at the surface. The expected geocentric axial dipole (EGAD) inclination at this latitude is 63°. Given the within-horizon uncertainty, the EGAD inclination and the mean inclinations from both of these highly bioturbated cores are in fairly close agreement. This observation and the relatively modest within-horizon scatter (~5°) suggests that remanence must be fixed below the 10-15 cm zone of intense bioturbation. Moreover, no inclination error is evident as has been found in studies of dry sedimentary deposits (Verosub, 1977, for review).

The lack of inclination error in these sediments as well as wet sediments from the Gulf of California (Karlin and Levi, 1982), Minnesota lakes (Banerjee et al., 1979) and muds from several pelagic areas (Opdyke and Henry, 1969) suggest that inclination error, when present, must be a postdepositional feature associated with drying and compaction rather than a primary remanence attribute as has been commonly postulated.

For core 28, the average within-horizon standard deviation,
Figure V-2. Downcore profiles of inclination and declination for Core 28. Bands encompass all AF measurements at 100, 150, and 200 Oe for every sample at each horizon. Solid circles are the means for each level.
Figure V-3. Downcore profiles of inclination and declination for Core 26. Bands encompass all AF measurements at 100, 150, and 200 Oe for every sample at each horizon. Solid circles are the means for each level.
\(s(w)\), is \(5.0 \pm 2.9^\circ\). The top 30 cm show anomalously high scatter of \(~10^\circ\), which is probably an artifact of coring disturbance when the top 88 cm were extruded from the core barrel. Core 26 has a similar \(s(w)\) of \(4.1^\circ\). Since these sediments are mottled and showed little evidence of bedding, it is not possible to determine whether the within-horizon scatter is due to deformation upon sampling or a real manifestation of variability in the sedimentary recording process, as proposed by Verosub (1979).

Because of the problems in recovery of the top 30 cm of the Kasten cores, a 50 x 50 x 30 cm Reineck box core W7710-27 was obtained at the same location as Core 26 to examine within-horizon variability and remanence acquisition in the surface sediments. Upon recovery, the box core showed numerous live polychaetes, worm burrows, and tubules in the top 20 cm, attesting to active mottling and bioturbation of the surface sediments. A thixotropic gel, similar to that reported by Stober and Thompson (1979) was present in the top 5 cm and proved impossible to sample. The core was extensively sampled aboard ship and sediments were kept cold and wet in a low field box to minimize VRM and drying effects prior to storage and VRM experiments. A summary of within and between horizon statistics is presented in Table V-1.

The results from the box core indicate that remanence is acquired at within 5 cm of the sediment surface, since inclinations of \(~60^\circ\) are very similar to the present field. However, the relatively large within-horizon variability suggests that remanence may not be completely fixed in the top 20-30 cm for all particle
Table V-1

Summary of mean directions and average NRM and ARM intensities for Core 27. Samples have been partially demagnetized at 150 Oe AF. Intensities are in units of 1.E-5 emu/cc.

<table>
<thead>
<tr>
<th>Level (cm)</th>
<th>Mean Incl</th>
<th>s</th>
<th>Mean Decl</th>
<th>s</th>
<th>N</th>
<th>Mean NRM Int.</th>
<th>s</th>
<th>Mean ARM Int.</th>
<th>Mean ARM MDF</th>
<th>Mean NRM MDF</th>
<th>Mean ARM MDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. 59.8</td>
<td>151.6</td>
<td>1</td>
<td>1.943</td>
<td>--</td>
<td>1</td>
<td>15.9</td>
<td>195</td>
<td>393</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. 66.3</td>
<td>155.1</td>
<td>4.5</td>
<td>2.381</td>
<td>.26</td>
<td>3</td>
<td>18.8</td>
<td>276</td>
<td>395</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. 60.6</td>
<td>158.1</td>
<td>13.5</td>
<td>2.663</td>
<td>.89</td>
<td>3</td>
<td>18.1</td>
<td>270</td>
<td>423</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15. 61.0</td>
<td>156.5</td>
<td>19.0</td>
<td>3.129</td>
<td>.43</td>
<td>4</td>
<td>19.0</td>
<td>300</td>
<td>428</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20. 57.1</td>
<td>154.8</td>
<td>9.4</td>
<td>3.519</td>
<td>.01</td>
<td>3</td>
<td>17.7</td>
<td>295</td>
<td>450</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To better examine the effects of secular variation, the within and between horizon variability can be partitioned using a two-tier analysis of variance (ANOVA) approach (Watson and Irving, 1957). This technique assumes that within-horizon variability is Fisherian and independent of depth. Because of suspected sampling disturbance, level 147 of Core 26 was excluded from the analysis. Table V-2 summarizes the ANOVA results for both cores. Ratios of between and within mean squares yield F ratios of 6.2 for Core 28 and 4.1 for Core 26. These values far exceed the table F value at 0.01 significance level for the appropriate degrees of freedom. This suggests that the between horizon SV significantly exceeds the within-horizon variability due to the sedimentary recording process and random errors in sampling. By equating the mean squares to their expectation values and solving for $k_w$ and $k_b$, the within and between horizon angular standard deviations ($s(w)$ and $s(b)$) can be estimated from $s = 81./\sqrt{k}$ (McElhinny, 1973). For cores 28 and 26, $s(w)$ is $5.5^\circ$ and $4.5^\circ$, respectively. These values may represent the maximum resolution of the sedimentary recorder. The between level variability, $s(b)$, is $7.7^\circ$ for Core 28 and $4.4^\circ$ for Core 26 (which spans a lesser interval). The present variability in a band about $45^\circ$ latitude is about $7.3^\circ$. Whether the lower variability in Core 26 is a geomagnetic phenomenon or an artifact of the sedimentary averaging process is unclear.

To examine the variability between cores, Cores 28 and 26 were combined in Figure V-4, after first removing the mean
Table V-2

Directional Statistics and analysis of variance within and between horizons for Cores 28 and 26.

CORE 26

Summary statistics for 30 horizons (30-300 cm). AF levels of 100, 150 and 200 AF have been vector averaged for each sample.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>avg. I</th>
<th>avg. D</th>
<th>α 95</th>
<th>K</th>
<th>R</th>
<th>s avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>By horizon</td>
<td>30</td>
<td>60.8</td>
<td>165.3</td>
<td>1.8</td>
<td>205.2</td>
<td>29.859</td>
<td>5.7</td>
</tr>
<tr>
<td>Combined</td>
<td>93</td>
<td>60.4</td>
<td>165.5</td>
<td>1.2</td>
<td>159.9</td>
<td>92.424</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Analysis of Variance within and between horizons for Core 26, 120-300 cm

<table>
<thead>
<tr>
<th></th>
<th>df</th>
<th>mean square</th>
<th>F</th>
<th>K</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within horizon</td>
<td>126</td>
<td>1.58E-3</td>
<td>4.09</td>
<td>315.7</td>
<td>4.6</td>
</tr>
<tr>
<td>Between horizons</td>
<td>58</td>
<td>6.48E-3</td>
<td>338.4</td>
<td>4.4</td>
<td></td>
</tr>
</tbody>
</table>

CORE 28

Summary statistics for 100, 150 and 200 AF levels (16-388 cm). AF levels of 100, 150 and 200 Oe have been vector averaged for each sample.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>avg. I</th>
<th>avg. D</th>
<th>α 95</th>
<th>K</th>
<th>R</th>
<th>s avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>By horizon</td>
<td>42</td>
<td>62.6</td>
<td>253.1</td>
<td>2.7</td>
<td>65.5</td>
<td>35.594</td>
<td>5.0</td>
</tr>
<tr>
<td>Combined</td>
<td>90</td>
<td>61.1</td>
<td>251.1</td>
<td>1.8</td>
<td>71.5</td>
<td>88.756</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Analysis of Variance within and between horizons for Core 28 (16-388 cm)

Six horizons with single samples are excluded.

<table>
<thead>
<tr>
<th></th>
<th>df</th>
<th>mean square</th>
<th>F</th>
<th>K</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within horizon</td>
<td>108</td>
<td>2.30E-3</td>
<td>6.2</td>
<td>217.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Between horizons</td>
<td>70</td>
<td>1.42E-2</td>
<td>110.3</td>
<td>7.7</td>
<td></td>
</tr>
</tbody>
</table>
declination of each core. Following a suggestion of Verosub (pers. comm.), declinations were scaled by a factor of \( \cos(I_c) = 0.5 \) so that angular differences in D and I are comparable. Depths were matched on a 1:1 correspondence since the large intensity decrease at 70-120 cm occurs at the same levels in both cores. It can be seen that below 120 cm, directions in both cores match fairly closely, given the within-horizon uncertainty. The average angular deviation between core directions in this interval is 6.4°. In contrast, the core directions above 120 cm diverge markedly, showing an average angular deviation of 14.6°. It is entirely possible that the top 110 cm of Core 28 was disturbed when the top 88 cm section overpenetrated, was extruded from the core barrel, emplaced in trays and the core barrel was capped. For this reason, the top 110 cm of Core 28 was excluded from further analysis.

To examine dispersions associated with the recording process compared to secular variation (SV), the intervals from 120-300 cm in both cores were subjected to another two-tier ANOVA (Table V-3). The resulting F ratio of within to between core variance is 2.11 which is significant at a 0.02 level. For the 19 levels between 120-300 cm, the average inclination is 60.3° with a \( k = 267, \alpha_{95} = 2.1° \).

Master curves of downcore D and I (Figure V-5 a,b) were obtained by vector averaging the two cores between 120-300 cm, adding the Core 26 30-120 cm and Core 28 300-388 cm intervals and assuming a constant sedimentation rate of 123 cm/ Ky. As before, D values are scaled by \( \cos(I) = 0.5 \) for direct comparison.

As seen in Figures V-5 a,b, downcore fluctuations in D and I show
Table V-3.
Directional Statistics and analysis of variances of Cores 28 and 26.

Summary statistics for cores 28 and 26, levels 120-300 cm.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>avg. I</th>
<th>avg. D</th>
<th>α 95</th>
<th>K</th>
<th>R</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core 28</td>
<td>19</td>
<td>59.6</td>
<td>164.6</td>
<td>2.0</td>
<td>294.4</td>
<td>18.939</td>
<td>avg.</td>
</tr>
<tr>
<td>Core 26</td>
<td>19</td>
<td>61.0</td>
<td>246.4</td>
<td>3.0</td>
<td>130.3</td>
<td>18.862</td>
<td></td>
</tr>
<tr>
<td>By level</td>
<td>19</td>
<td>60.3</td>
<td>0.0</td>
<td>2.1</td>
<td>266.8</td>
<td>18.933</td>
<td>5.0</td>
</tr>
<tr>
<td>Combined</td>
<td>38</td>
<td>60.3</td>
<td>0.0</td>
<td>1.7</td>
<td>183.3</td>
<td>37.798</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Analysis of Variance for cores 28 and 26, levels 120-300 cm.

<table>
<thead>
<tr>
<th></th>
<th>df</th>
<th>mean square</th>
<th>F</th>
<th>K</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within</td>
<td>38</td>
<td>1.77E-3</td>
<td>2.11</td>
<td>282.5</td>
<td>4.8</td>
</tr>
<tr>
<td>Between</td>
<td>36</td>
<td>3.74E-3</td>
<td>507.7</td>
<td>3.6</td>
<td></td>
</tr>
</tbody>
</table>
CORES 26 and 28

Figure V-4. Downcore profiles of horizon means of inclination and declination for Cores 28 (squares) and 26 (circles). Core mean declinations were set to zero.
good serial correlation, except for the 2840 year horizon. Swings average ± 5° in I and ± 10° in D. A Bauer plot of D and I (Figure V-6) shows rather complex behavior. The dominant mode of looping is clockwise from 2470 to the present. Trends are generally consistent among adjacent points with the exception of sharp spikes at 1600 and 1850 yr BP. From the bottom of Core 28 at 3150 yr to 2740 yrs, a large anticlockwise loop occurs. According to Runcorn's Rule (Runcorn, 1959), clockwise looping is often associated with westward drift. However, Dodson (1979) pointed out that the converse is not necessarily true, since certain configurations of non-dipole fields can give rise to anticlockwise looping, even though the dominant mode of drift is westward.

DISCUSSION

Comparison with other Secular Variation studies in North America

One way of assessing the geomagnetic secular variation is to compare the Oregon site with records of comparable time control and resolution elsewhere. In North America, numerous paleomagnetic studies have been undertaken on wet and dry lake sediments and lavas deposited during the Holocene epoch (Lake Erie - Creer et al., 1976; Lake Michigan - Creer et al., 1976, Vitorello and Van der Voo, 1977, Dodson et al., 1977; Lake Superior - Mothersill, 1979; Lake Huron - Mothersill, 1981; Lake Tahoe - Palmer et al., 1979, Denham, 1981; Wyoming lakes - Shuey et al., 1977; Minnesota lakes - Lund, 1981, Banerjee et al., 1979, Western U.S. lavas - Champion,
Figure V-5. Master profile of inclination and declination with time for Oregon sediments.
Figure V-6. Bauer plot of declination versus inclination for Oregon sediments. Solid lines indicate clockwise looping with time while dashed lines refer to counterclockwise looping.
However, many of these studies suffer from poor chronological control, complex lithology and highly variable sedimentation rates. Of the available work, the only data covering the same window as our sediments with good resolution and time control are the sediments from Lake Ste Croix (LSC) in Minnesota (Banerjee et al., 1979; Lund, 1981). Unfortunately, only inclination records are reliable, since each section was obtained in azimuthally unoriented 1-3 meter segments.

A cross correlation analysis (Davis, 1973) was used to compare the Oregon (OR) profile with the records from LSC Core 75B (Lund, 1981). Inclinations were first interpolated to even 100 year intervals. This spacing was considered optimum because it was slightly greater than the sampling period (81 years) of the OR records. The profiles were then successively shifted against each other in 100 year increments and conventional Pearson correlation coefficients were computed for each lag. The cross correlation analysis has advantages over standard spectral analysis in that individual segments can be matched and no assumptions are necessary as to the time stationarity or nature of periodicities in each data set. It is also superior to simple peak matching, such as used by Turner and Thompson (1979) and Creer (1981), because characteristics of the entire data set are objectively compared rather than the positions of individual extrema.

In Figure V-7, the LSC and OR inclinations are compared. The maximum correlations ($r = 0.63 & 0.66$) occur with the OR inclinations lagging the LSC records by 100-200 years. Thus, secular variation
seems to have recorded the same pattern in these two sites that are at the same latitude (45°N) and 32° apart in longitude. A 100-200 year lag implies a westward drift of about 0.16-0.32° /yr which has remained constant for at least the last 3100 yrs. Interestingly, a secondary correlation maximum of r = 0.52 occurs between the OR 300-3100 yr and LSC 4100-6900 yr intervals. This association could be explained by a constant westward drift of .3° /yr (i.e., a 1200 yr periodicity).

Another high quality data set partially overlapping our time window are the archaeomagnetic measurements of Dubois and co-workers from ancient fireplaces and kilns in the American Southwest and Mesoamerica (Weaver, 1967). Although an error analysis has not been published, the smoothed curve of VGP paths at 50 year increments from 0 - 2000 yrs BP from Weaver (1967) was inverted to obtain directions at 45° N latitude and at a similar longitude as Mesoamerica and Arizona (250° E). The use of the inverse VGP transform (see Appendices) introduces a maximum error of ~4° to D and I due to geographic distortion (Shuey et al., 1970), which is comparable to the observed scatter due to the sedimentary recording process in the Oregon sediments. The time profiles of declination and inclination are compared in Figures V-8 and 9. Agreement among the two data sets is fairly good for inclination, but rather poor for declination. No obvious time delay is evident.

Considered together, the various studies seem to indicate that geomagnetic secular variation has a regional coherence. In particular, inclination fluctuations, including relative lows at 1300
Figure V-7. Oregon inclinations compared to inclination records for the last 4000 yrs from Lake Ste Croix, Minnesota (Lund, 1981). Dashed lines in the left figure are the LSC inclinations shifted forward 100 years for best fit with Oregon data.
Figure V-8. Oregon inclination profile compared to archaeomagnetic data of Dubois (in Weaver, 1967) from the SW USA and Mesoamerica. The SW US data are transformed to 45° N, using an inverse VGP transformation.

Figure V-9. Oregon declination profile compared to archaeomagnetic data of Dubois from the SW USA and Mesoamerica. The SW US data are transformed to 45° N, using an inverse VGP transformation.
and 2600 yrs BP and highs at 700-900 and 1900-2300 yrs BP are recorded at more than one North American site. This supports the idea of using paleomagnetic measurements as dating tools in regional archaeological and sedimentological investigations.

Comparison with SV Studies in Other Regions

If westward drift were a prevalent aspect of SV, then directional fluctuations in different regions would not be synchronous. Suppose that a non-dipole feature were to drift westward at 0.3°/yr, giving a period of 1200 yrs. A feature starting in Japan (longitude 140° E) at time zero would arrive in SE Europe (25° E) at ~380 yrs BP, in France and Britain (0° E) at ~470 BP and in North America (120° W) at ~870 BP.

Several detailed SV studies of Holocene SV have been made on British and European lakes by Creer, Thompson, Turner and others. The most detailed of this work concerns declination variations in Lake Windermere, Loch Lomond and Loch Neagh (Thompson, 1975, Turner and Thompson, 1979, 1981, Thompson and Turner, 1979). Unfortunately, in reporting D and I trends with time, these workers rotate their directional results so that the core mean inclinations as well as the declinations average to zero. While allowing local comparisons, this method of presentation makes comparison of their SV results with data from other regions very difficult. Efforts to obtain the original directions are underway.

Archaeomagnetic measurements spanning the last 2000 yrs are
available for France (Thellier, 1981) and Britain (Aitken et al., 1970). The British records are very similar to the French observations, but continuously cover only the last 1000 yrs and are not considered here. The French records were transformed to VGPs centered at Paris (49° N, 2° E), then inverted to obtain directions at the same latitude as the Oregon data (45° N).

Profiles of the French and Oregon directions are compared in Figures V-10 and V-11. The maximum vector correlation of 0.66 and inclination correlation of 0.74 occur with the French measurements lagging the Oregon directions by 400 years, corresponding to a westward drift of ~0.3° /yr.

Recently, Kovacheva (1980) published archaeomagnetic results for SE Europe (mostly Bulgaria), summarized by century for the last 8000 yrs. For the past 4000 yrs, she presented reasonably continuous inclination measurements. Cross correlation of the SE European and Oregon inclinations yielded a maximum correlation of 0.5 with a lag of 400-500 yrs, suggesting a westward drift of 0.3 - 0.4° /yr. As seen in Figure V-12, if the SE European data are shifted by 400 years, agreement between the two records is very good, except for an inclination high in SE Europe from 2600 - 2900 yrs BP. If this interval is excluded, the maximum correlation retains the same lag, but improves to r = 0.73. Reliable archaeomagnetic declination determinations for SE Europe are apparently limited. However, if the available declinations are lagged by 400 yrs, as seen in Figure V-13, the Oregon and Bulgarian declinations match closely, again except for the same interval. (Note that the Oregon and LSC inclinations agree.
Figure V-10. Oregon inclinations compared to archaeomagnetic data of Thellier (1981) from France (~49° N). Thellier's values are transformed to a 45°N latitude. Dashed lines are best fit with a 400 year lag.

Figure V-11. Oregon declinations compared to archaeomagnetic data of Thellier (1981) from France (~49° N). Thellier's values are transformed to a 45°N latitude. Dashed lines are best fit with a 400 year lag.
Figure V-12. Oregon inclinations compared to archaeomagnetic data of Kovacheva (1980) from SE Europe, especially Bulgaria (~42° N). Dashed lines are best fit with a 400 year lag.

Figure V-13. Oregon declinations compared to archaeomagnetic data of Kovacheva (1980) from SE Europe (~42° N).
Thus it appears that a constant westward drift of about $0.3^\circ$/yr (1200 year period) can be detected in comparing North American and European records. However, simple rigid rotation of the geomagnetic field cannot account for all of the observed secular variation.

Since the early 1960s, archaeomagnetic measurements have been made on kilns and fireplaces in Japan (Hirooka, 1971). The early results were not cleaned either thermally or by AFD, so their reliability is uncertain. Recently, Hirooka (1983) presented VGP paths for the past 2000 years from SW Japan ($35^\circ$ N), interpolated at 50 year intervals. Cleaning methods were not specified nor were error estimates presented, but Hirooka maintained that these VGP paths have been reliably used to date archaeologic sites within ±20 years.

The Japanese VGPs of Hirooka (1983) were inverted to obtain directions at $45^\circ$ N, $135^\circ$E. The resulting profiles of D and I with time compared to the Oregon data are shown in Figures V-14 and V-15. There is an inclination correlation of $r = 0.73$ between 1000 - 1900 years BP in Japan to 300 - 1200 years BP in Oregon which might be attributed to a Japanese feature drifting westward. However, in general, the two data sets differ substantially at all other lags.

This lack of agreement is problematic if westward drift is purely zonal and non-dipole features have coherence in the $10^\circ$ latitude band between $35^\circ$N and $45^\circ$N. Alternative possibilities include non-dipole drift about a rotation pole different than the spin axis or the growth and decay of local anomalies which obscure
Figure V-14. Oregon inclinations compared to Japanese archaeomagnetic data of Hirooka (1983) from SW Japan (35° N). Japanese data has been transformed to 45° N.

Figure V-15. Oregon declinations compared to Japanese archaeomagnetic data of Hirooka (1983) from SW Japan (35° N). Japanese data has been transformed to 45° N.
Table V - 4.
Cross Correlation Analysis

Best fits of Oregon directions with data from other regions. Directions have been VGP/inverse-VGP transformed to 45° N. Vector correlations greater than 0.4 are significantly different than a null correlation at a $\alpha = .05$ level.

<table>
<thead>
<tr>
<th>Locality</th>
<th>East Interval</th>
<th>Vector</th>
<th>Incl</th>
<th>Decl</th>
<th>Lag (yrs)</th>
<th>Vector</th>
<th>Incl</th>
<th>Decl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Long. (Ky)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA</td>
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<td></td>
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<tr>
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<td>.59</td>
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<td>(Dubois, in Weaver, 1967)</td>
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</table>

*) Correlation values with SE European inclinations from 2.6-2.9 Ky removed.
the westward drift. The reasons for the differences between the Japanese SV curves and the curves from other regions is presently unclear, but merits further study.

Comparison with the Present Field

By comparing isoporic foci for several epochs from 1829-1945 AD, Bullard et al. (1950) showed that the geomagnetic field has drifted westward at a rate of .32 ° /yr, while non-dipolar features drifted at .18° /yr. Yukatake and Tachinaka (1968) divided the non-dipole field into drifting and standing components and showed that the difference in drift rates was due to stationary features which lowered the apparent non-dipole westward drift rate. In another paper, Yukatake (1968) showed that the geomagnetic secular variation between 1743-1965 AD could be modelled as a rigid body rotation of the field about the Earth's spin axis. By rotating the field back in time for different drift rates and correlating the rotated field with the fields at earlier epochs, he found that the maximum correlation occurred at 0.3° /yr. Furthermore, the maximum correlations were independent of latitude, suggesting that zonal westward drift of a rigid core relative to the mantle was a reasonable first approximation for historical secular variation.

In modelling the sediment data from the Oregon continental slope, we have adopted Yukutake's maximum correlation approach. For this zonal drift model, directions of the 1975 International Geomagnetic Reference Field (IGRF) were rotated along a latitudinal
band at 44.8°N at various drift rates and using different longitudes
to start the rotation. The resulting field directions were then
correlated to the observed data. Since correlating D and I indepen-
dently neglects the different scaling factors and interdependence of
D and I, a vector correlation was used. Since the direction in Core
26 at 100 cm (811 years) disagreed with all of the data from other
regions for this interval, this point was discarded and a vector
interpolation was made from adjacent directions.

The field was rotated both westward and eastward from 0.02-0.5 ° /yr
in 0.02 ° /yr steps and starting longitudes (i.e., time zero) were
varied in 10° increments. The starting longitude parameter is an
independent check on the model, since the best fit should start
near the sediment/water interface at t = 0 with the site longitude of
235° E.

A plot of best correlations for each drift rate is shown in
Figure V-16 along with associated starting longitudes. The maximum
vector correlation (r = 0.55) occurred at a drift rate of 0.30° /yr
with a starting longitude of 200° . Individually, D and I had corre-
sponding correlations of 0.59 and 0.55, respectively.

The significance of the 0.55 vector correlation was tested by
Monte Carlo experiments, using random data sets (N= 30) generated
from Fisher distributions of different k's. Using this technique,
the observed correlation was found to be significantly different at
a <0.01 level from random data sets with Fisher distributions of
directions.

A starting longitude of 200° means that about ~115 yrs is not
Figure V-16. Oregon directions compared to zonal drift model of present field. a) Best correlations of Oregon and IGRF directions at different drift rates. The shaded area show correlations different from zero at a 95% confidence level. b) Correlations at different starting longitudes for the best fit drift rate of 0.30'/yr. The optimum fit should ideally show a maximum at the site longitude (235° E).
accounted for in the top of the core. If the observed directions are indeed causally related to the westward drift of the present field, then either the chronology is off by 115 years, a hiatus of 115 years occurred in the top meter, or 14 cm have been lost from the core, perhaps due to surface washout. If remanence was set at 10-15 cm depth, rather than at the surface, then an additional 100 years must have been lost from the core.

Downcore profiles of the best fit IGRF and observed declinations and inclinations are plotted against time in Figure V-17. For declination, the timing of the swings match fairly closely, but amplitudes in the core data are attenuated. The observed inclination trends are somewhat noisy, but it is apparent that compared to the IGRF, fluctuations in the core data are reduced in amplitude and are systematically shallow.

Assuming that the correlation between the observed data and the IGRF is real, the attenuation in amplitudes could be due to the averaging process of the sedimentary recorder or the persistence of standing non-dipole features, especially over North America and Mongolia. The amplitudes of fluctuations in the Lake Ste Croix data and Southwest US archaeomagnetic measurements are of comparable magnitude to the those of the Oregon muds, thus simple sediment mixing may not be a plausible explanation.

The above reasoning, however, does not suffice to explain the systematic shallowing of the observed data relative to the IGRF. Non-vertical coring seems unlikely, since it would be fortuitous that both cores penetrated the sediment at the same angle. Tectonic rotation
Figure V-17. Best fit of Oregon directions with 1975 IGRF data drifting zonally at .30°/yr.
also seems rather unlikely, since the block rotation would have to occur after deposition of the topmost sample (i.e., within the last century). Inclination error is a convenient, albeit ad hoc explanation, but resettling and drying experiments show no evidence of such a mechanism. Moreover, inclination error is a depositional feature and the observed remanences are certainly fixed below the bioturbation zone. Other explanations which could account for the apparent inclination shoaling are a far-sided dipole effect, the presence of a persistent equatorial multipole or a relatively stronger equatorial dipolar field in the past.

To further test the hypothesis of persistent zonal drift, the directions from France of Thellier (1981) were compared to the 1975 IGRF at 49° N using the same correlation procedure as described above. The maximum vector correlation of .54 occurred with a drift rate of .32°/yr. The significance test of the correlation described earlier suggests that the observed correlation is different from correlations of random Fisherian data sets at a 95% confidence level. The starting longitude for drifting the IGRF was the same as the site longitude, giving independent confirmation of the validity of the correlation. Inclination and declination correlations were .69 and .42, respectively. Interestingly, the French inclinations were also shallower than predicted by the IGRF model.

To this point we have assumed that the SV drift is zonal with a pole of rotation coincident with the spin axis. We can relax this constraint and allow the drift to rotate about a pole different
than the spin axis at different rates and with various starting points. Using the same correlation scheme as before, the IGRF was successively rotated with poles in a grid from 70-90° N latitude and in 15-30° longitude increments. For rotation poles with a maximum correlation greater than 0.5, each gave a best fit drift rate of 0.29-0.30°/yr. The overall best fit (r = 0.67) with the Oregon data was for a rotation pole at 85° N, 150° E. This pole gave a best fit drift rate of 0.30°/yr and a starting longitude of 200°, which is the same as for the zonal drift model.

The 85° N, 150° E pole gives the best fit for the Oregon data. However, this pole would require the Japanese inclinations to be steeper than the expected dipole value. In fact, the opposite (i.e., a far sided effect) is observed. For the Oregon sediments, we have assumed that the core mean declinations average to zero over time. If we have not sampled over complete cycles of secular variation, then the resulting corrected declinations will be biased by a small amount. This could introduce an error in azimuth to the rotation pole, causing a large error in the apparent pole longitude. Before the hypothesis of non-zonal drift is accepted, optimum drift rotation poles must be computed for several regions to determine whether a common pole can be isolated. This will be the subject of continuing research in the near future.

CONCLUSIONS

1) Based on statistical comparisons of variability between samples, horizons, and cores, the Oregon sediments appear
to give a reliable record of secular variation for the past 3.1 Ky.

2) Comparisons of the Oregon results with data from Lake Ste Croix, MN suggest that SV trends have a regional coherence. Cross correlation analyses with archaeomagnetic data from France and SE Europe yield phase lags consistent with a westward drift of the main geomagnetic field at a rate of 0.3°/yr. This rate is similar to historical observatory measurements of SV for past 300 years.

3) Correlation of the Oregon directions with a zonal drift model of the present field also yields a maximum correlation at a drift rate of 0.3°/yr, suggesting that a significant portion of the main field has rigidly drifted westward for at least the past 3 Ky.
CHAPTER VI

PALEOMAGNETIC RESULTS FROM LAMINATED SEDIMENTS IN THE GUAYMAS BASIN IN THE GULF OF CALIFORNIA -- DSDP SITE 480

INTRODUCTION

The sediments of DSDP Site 480, located in the Guaymas Basin in the Gulf of California (27° 54.10'N, 111° 39.34'W, 665 m water depth), consist of 152 m of finely laminated diatomaceous oozes interstratified with mottled and homogeneous muds. At Site 480, the Serocki-Storms-Cameron Hydraulic Piston Corer was used for the first time and obtained a virtually undisturbed sedimentary section with 80% recovery (Curray and Moore et al., 1979). Because of a high sedimentation rate and an anaerobic, low energy depositional environment underlying a seasonal upwelling regime (Schrader et al., 1980), the sediments of Site 480 offer an excellent opportunity to study the behavior of the geomagnetic field over the past few hundred thousand years. Some specific questions that we would like to address in this study include:

- Does the nature of secular variation (SV) remain constant or vary through time?
- Does the magnetic field average through time to the expected geocentric axial dipole (EGAD)?
- Are there significant periods when the field displays anomalous behavior?
- How long is required to average out SV?
- Does the amount of SV agree with models of geomagnetic
behavior?

In this paper we present preliminary results of natural remanent magnetization (NRM) measurements of samples of varied lithology taken throughout the recovered sedimentary section. In this initial phase of our work, our intent was to examine the reliability of the magnetic recording process in the different types of sediments and to make a preliminary assessment of whether any significant paleomagnetic excursions were recorded at Site 480. Later work will include intensive sampling of the entire section to deliniate secular variation trends and geomagnetic field behavior during brief excursions.

METHODS

Two hundred and eighty-six samples were taken at approximately 40 cm intervals from undisturbed sections of Cores 1-31. A thin-walled square stainless steel tube, mounted in a frame oriented perpendicularly to the core liner, was used to obtain undisturbed samples (v = 6.5 cm³). In cases where laminated sediments were slightly tilted (<5°) relative to the core liner, samples were oriented parallel to the laminations.

Reconnaissance measurements of NRM were made on 20 samples using a Schoenstedt DSM-1 spinner magnetometer. Because NRM intensities were extremely weak, all subsequent measurements were made on SCT cryogenic magnetometers at the US Geological Survey in Menlo Park, California, and the University of Washington. For each remanence determination, three-axis measurements were made on the cryogenic magnetometer in six different orientations. Regarding each orientation as an independent
observation, mean directions, intensities and measures of angular
dispersion values were calculated. The angular dispersion values were
used as estimates of the internal consistency and homogeneity of the
magnetization for each sample.

All samples were partially demagnetized stepwise in peak alter-
nating fields (AF) demagnetization to at least 150 oe, or to the
limit of reliable measurement. Based of relative changes in direction
at the 50, 75, 100, and 150 Oe levels, a cleaning field of 75-100 Oe
was considered optimum for obtaining stable directions.

Of the 286 samples taken, 22 were excluded from further consider-
ation because of probable coring or sampling disturbance. The
directions of an additional 9 samples were considered unreliable
because of weak magnetization and lack of internal consistency. Due
demand for the core, we were allowed only quarter sized samples
in the top 4 cores. Because of possible warpage during and after
sampling, our results must be regarded as somewhat tentative with
regard to the uppermost sections of Site 480 until better samples
become available.

For the top 3 cores, varve counts of 29 samples provided by A.
Soutar and R. Byrne (pers. comm., 1980) were used to estimate temporal
sampling resolution in the laminated sections of the upper part of the
sedimentary column. Considering each laminae pair as a single annual
varve, the varve counts yielded an average sedimentation rate of 103
± 13 cm/Ky and a time span of 20 ± 3 years per paleomagnetic sample.
Ten laminated samples from cores 22-31 yielded a mean sedimentation
rate of 58.5 ± 8.8 cm/Ky (34 ± 6 years/sample) for the lower part of
the hole.

RESULTS

Directions

The behavior of the samples upon AF demagnetization is shown in Figure VI-1 and VI-2 for several typical specimens. In general, upon demagnetization to the limit of sensitivity of the magnetometer, the samples had median destructive fields of 75-150 Oe and showed vector changes in direction of less than 5 deg. between successive steps. Thus the samples appear relatively uncontaminated by secondary magnetization, despite relatively low stabilities.

Core mean inclinations and the respective 95% confidence intervals, cleaned at 100 Oe AF, are summarized for the hole in Figures VI-3. Since the cores were unoriented azimuthally due to the HPC coring method, core mean inclinations were corrected using a modification of the technique of McFadden and Reid (1982) (see Appendix). This technique yields essentially identical results as the methods of Kono (1980) with both assuming a random Fisher distribution of directions, that is, an $\exp(K \times \cos(\Theta))$ distribution in angular deviation from the mean and a uniform density in azimuth.

For the entire sampled section, the raw vector mean inclination for 255 samples (100 Oe Af) was 43.9 degrees. If a uniform distribution in azimuth is assumed for each core, the orientation correction yields a corrected site mean inclination of 45.8 degrees with an $\alpha(95) = 2.7$ deg. and $K = 18.3$. These values are remarkably close
Figure VI-1. AF demagnetization characteristics of several samples from Core 26.
Figure VI-2. AF demagnetization characteristics of several samples from Core 29.
to the expected geocentric axial dipole (EGAD) inclination of 46.6° at this site. Thus, when averaged over the greater than the \(10^5\) years represented by the sedimentary section at Site 480, no inclination error, such as found in some dry and wet lake sediments (e.g., Denham and Cox, 1971; Verosub, 1977), was observed. In addition, no shallowing of the inclination with depth, caused presumably by compaction (Creer, 1974), was apparent in the sediments.

We can test whether the core mean in any particular interval differs significantly from the EGAD by examining whether the confidence bounds on the corrected mean inclinations include the expected inclination. As seen in Figure VI-3, for all cores, the EGAD direction is included within the \(I_0 \pm \alpha_{95}\) bounds. Therefore, given the present sampling density, we can tentatively conclude that for the entire upper Brunhes epoch, the field behaves as a geocentric axial dipole. Moreover, secular variation 'averages' to the EGAD over a period less than the time span covered by each 4.75 m core (5-10 Ky). Note that the calculation of the mean, error bounds and the precision parameter \(k\) depend on the assumption of a Fisherian distribution of directions, i.e., random deviations from a true value. As discussed later, if the field exhibits any characteristic periodicities or a significant degree of serial correlation, directions will not display a Fisher distribution. In such a case estimates of the mean may be correct, however the amount of scatter may be severely underestimated and confidence bounds on the mean may be too small.

The conclusions regarding the minimum averaging time and dipolar
SITE 480 - GUAYMAS BASIN
(100 Oe AF)

Corrected
Core mean inclination
(degrees)

ALPHA 95
(degrees)

Samples
per core

Lithology

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<tr>
<td>2</td>
<td>L</td>
</tr>
<tr>
<td>3</td>
<td>M-H</td>
</tr>
<tr>
<td>4</td>
<td>L</td>
</tr>
<tr>
<td>5</td>
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<tr>
<td>8</td>
<td>M-M</td>
</tr>
<tr>
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</tr>
<tr>
<td>10</td>
<td>L</td>
</tr>
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<td>11</td>
<td>M-M</td>
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<tr>
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</tr>
<tr>
<td>16</td>
<td>L</td>
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<tr>
<td>17</td>
<td>S-m</td>
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<tr>
<td>18</td>
<td>L</td>
</tr>
<tr>
<td>19</td>
<td>M-M</td>
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<tr>
<td>20</td>
<td>L</td>
</tr>
<tr>
<td>21</td>
<td>M-M</td>
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<td>L</td>
</tr>
<tr>
<td>31</td>
<td>L</td>
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Figure VI-3. Summary of Cores 1-31, Site 480 a) core mean inclinations, partially demagnetized at 100 Oe AF, b) alpha-95s per core c) number of samples per core. The dashed line at 46.6° is the expected geocentric axial dipole value expected at the site. Open circles are core means with all data considered. Open squares are core means with inclination outliers excluded.
nature of the field for a particular interval are somewhat weakened by the rather large confidence bounds on the core means (+/- 10 deg). However, since the alpha(95) is proportional to 1/sqrt(N), we cannot expect to make more definitive statements on fine scale structure until the sampling density is increased. If we go the other way and average over large intervals (e.g., 9.75, 13, 19 m), the core means tend to cluster about the EGAD inclination and the confidence bounds decrease. Thus, over longer intervals, the conclusion that the field averages to the EGAD throughout the upper Brunhes remains intact.

To gain some insight into the reliability of the magnetic recording process among the various lithologies, the 255 samples were grouped into laminated, homogeneous, mottled and other (layered, mottled layered, etc.) sediment classes. Homogeneous and mottled sediments were distinguished on the basis of presence or absence of color changes or sedimentary structures such as burrows on the X-radiographs.

As seen in the statistics of Table VI-1 and in the frequency histogram of inclination for the different classes in Figure VI-4, the laminated, homogeneous, and mottled sediments have mean inclinations which are very close to the expected geocentric axial dipole value. The larger standard deviation in the inclinations of the laminated sediments probably reflects the greater number of samples in this class, since the standard error (σ / sqrt (N)) of the various sediment classes is comparable.

The homogeneous and mottled sediments have virtually identical mean inclinations and similar standard deviations of less than 10°.
### Table VI-1

Summary of corrected mean inclinations (at 100 Oe AF) and NRM wet weight normalized intensities for the different lithologies of Hole 480.

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Inclination (100 Oe)</th>
<th>NRM Intensity (x 1.E-7 emu/gm)</th>
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<td></td>
<td>Mean</td>
<td>α 95</td>
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<tr>
<td>Laminated</td>
<td>44.6</td>
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<td>Mottled</td>
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<td>Other</td>
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<td>45.8</td>
<td>1.9</td>
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### Table VI-2

Summary of mean inclinations and wet weight normalized intensities at 100 Oe AF above and below 75 m for the different lithologies of Hole 480.

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<th>Mean</th>
<th>α95</th>
<th>Mean</th>
<th>s</th>
<th>Samples</th>
<th>J(&lt;75 m)/J(&gt;75 m)</th>
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<td>3.3</td>
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<td>&lt;75</td>
<td>45.3</td>
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<td>20</td>
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<tr>
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<td></td>
<td>&gt;75</td>
<td>46.9</td>
<td>2.3</td>
<td>1.64</td>
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<tr>
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<td>&lt;75</td>
<td>49.4</td>
<td>4.1</td>
<td>1.79</td>
<td>.67</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;75</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Other</td>
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<td>&lt;75</td>
<td>56.0</td>
<td>26.3</td>
<td>1.77</td>
<td>.38</td>
<td>3</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>&gt;75</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>3.1</td>
<td>1.71</td>
<td>.64</td>
<td>116</td>
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<td>139</td>
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SITE 480 -
INCLINATION AND
INTENSITY BY LITHOLOGY
(100 Oe AF)

Figure VI-4. Relative frequency histograms of inclinations and intensities for laminated, homogeneous, and mottled sediment lithologies.
(Table VI-1). The similarity of the mean inclinations of the homogeneous and mottled sediments to the dipole value and the relatively small scatter amongst the samples suggest that the remanence was locked in at a depth below the level of active benthic activity. Thus, post-depositional bioturbation probably has not affected the remanence. No significant intervals of reversed polarity were observed in the sediments, although several samples in Cores 10, 18, 20, and 22 showed inclinations of less than 30° (Figure VI-5). In each case, the anomalous zones were less than 2 m thick, corresponding to a time span of less than 2000 years. The sediments in these anomalous zones were well laminated and showed no evidence of deformation.

A sample in core 18 (18-1-127, 86.77m) showed a stable reversed direction antipodal to adjacent samples (Figure VI-6) with demagnetization characteristics (Figure VI-7) typical of a reversed primary remanence with superimposed normal secondary components.

Given the best available estimates of sedimentation rates, anomalous zones in cores 10, 18, 20, and 22 correspond roughly to ~40Ky, 120 Ky, and 140 Ky. Excursions reported elsewhere include the Mono Lake excursion at 25-36 Ky (Denham, 1974) the Laschamps/Lake Mungo event at 30-50 Ky (Bonhommet and Zahringer, 1969, Barbetti and McElhinny, 1972, 1976), the Blake event at 110-120 Ky (Smith and Foster, 1969, Denham, 1976) and the Lake Biwa events at 49 Ky, 110 Ky, and 176 Ky, respectively (Yaskawa et al., 1973). Thus, although it is tempting to ascribe significance to these anomalous directions, given the present sparse sampling density, it would be premature to place any confidence in the reliability of these measurements.
Figure VI-5. Anomalous inclination intervals of Site 480.
Figure VI-6. Stereonet of anomalous inclinations in Core 18, Site 480.
Figure VI-7. AF demagnetization characteristics of several samples from Core 18.
Intensities

For the entire section, the intensities at 100 OE AF for all samples averaged $10^7$ emu/gm wet weight. As seen in Figure VI-8 and in Table VI-2, NRM mean intensities are higher above 75 m by a factor of 1.7 than mean intensities below this depth. In Figure VI-9, the frequency distribution of intensity for the different lithologies show that the laminated sediments have substantially lower intensities than the other lithologies, probably due to a higher percentage of diluent biogenic material in the laminae. Since most of the homogeneous and mottled sequences occur above 75 m, some of the observed intensity difference may be attributable to differences in lithology. However, when the lithologies are considered separately, as in Table VI-2, in the upper 75 m the individual lithologies show intensities which are higher by factors of 1.4-1.5 than their counterparts in the lower half of the section. Nevertheless, within each lithology, NRM mean inclinations above and below 75 m are virtually identical. Although only limited bulk density and GRAPE data are available, increased compaction below 75 m may have caused randomization of a portion of the magnetic carriers and a reduction in NRM intensity with no accompanying change in inclination with depth. This effect has been observed in drying experiments of wet lake sediments (Stober and Thompson, 1979; Levi and Banerjee, man. in prep.). Alternatively, the reduction in intensities may be related to continued reduction of the magnetic oxides due to organic matter decomposition, sulfide formation and methanation (see Chapter I). Planned studies of downcore geochemis-
SITE 480 - GUAYMAS BASIN
(100 Oe AF)

Figure VI-8. Summary of a) core mean intensities (x 10^-7 emu/gm wet weight), partially demagnetized at 100 Oe AF b) standard deviations per core and c) number of samples per core for Cores 1-31. The dashed line is the site mean intensity.
SITE 480 - INTENSITY COMPARISON

LAMINATED

Above 75M (N=56)
Below 75M (N=117)

HOMOGENEOUS AND MOTTLED

Above 75M (N=57)
Below 75M (N=22)

Figure VI-9. Relative frequency histograms of inclinations and intensities above and below 75 m for laminated, homogeneous, and mottled sediment lithologies.
try should help in distinguishing between these two hypotheses.

CONCLUSIONS

1) The NRM inclinations of the 152 m of sediments at Site 480 are normally magnetized. This result is consistent with micropaleontological and varve count chronologies, suggesting that the cored section was deposited entirely within the Brunhes epoch. No geomagnetic reversals could be confirmed for the sampled section, but several zones of anomalously shallow inclinations were seen and one section contained a single reversed sample.

2) The mean NRM inclination for the entire section is about 46° which is identical to the expected geocentric axial dipole inclination. No inclination error or shallowing of the inclination with depth was observed.

3) There was no significant difference in the mean inclinations of the laminated, homogeneous, and mottled sediments, suggesting that remanence was acquired below the zone of bioturbation.

4) Intensity differences between mottled/homogeneous and laminated sediments are probably due to biogenic dilution of the magnetic fraction in the laminated sediments.

5) The mean NRM intensities of sediments above 75 m is significantly greater than the intensities below this depth, independent of lithology. The decrease in intensity with depth may be related to increased compaction which may have caused randomization of the remanence-carrying grains without affecting the remanence directions.
CHAPTER VII
A TEST FOR PAIRWISE CORRELATION OF UNIT VECTORS

In the historical development of paleomagnetism, primary emphasis was placed on interpretation of directions recorded in piles of lava flows. Vector statistics were developed (Fisher, 1953, Watson, 1956, Watson and Irving, 1957) for analyzing mean directions and variability, based on the assumptions of a Fisher distribution. Since the precise times of eruptive events is usually unknown, there was little need for statistics which examine relations between time series of unit vectors.

As measurement techniques have become more sensitive, there have been a growing body of paleomagnetic studies from sedimentary deposits where detailed vector time series can be constructed, given adequate age control. To examine the synchronicity of fluctuations between cores within a site, among sites in a region or between observed and modelled geomagnetic behavior, a statistic for pairwise vector correlations is necessary.

For measurements in which \( x \) and \( y \) are independent, the classical Pearson correlation coefficient is defined: (Snedecor and Cochran, 1980)

\[
 r = \frac{\sum (x(i) - \bar{x})(y(i) - \bar{y})}{\sqrt{\sum (x(i) - \bar{x})^2 \sum (y(i) - \bar{y})^2}} = \frac{\text{cov}(x,y)}{s(x) \cdot s(y)}
\]

where \( [x(i), y(i)] \) are the \( i \)th measurements from two data sets of length \( N \) and \( \bar{x}, \bar{y} \) are the means of the individual data sets. The numerator is a measure of how the individual data pairs covary,
while the denominator is a scaling factor proportional to the standard deviations of the data sets. A common use of this statistic is to test whether the observed $r$ is different from a correlation between two sets composed of randomly distributed (i.e., Gaussian) data. The appropriate test is done using a $t$ statistic:

$$t = \frac{r \times \sqrt{N - 2}}{\sqrt{1 - r^2}}$$

which is compared to a table value of a Student $t$ distribution at some level of significance (Snedecor and Cochran, 1980).

For unit vectors, direct use of the $t$ test is inappropriate because the components of $x(i)$ or $y(i)$ are correlated. Epp et al. (1971) proposed a pairwise vector correlation statistic based on

$$L = \frac{\sum (X^t Y)}{N}$$

where $X^t$ is a $3\times N$ vector matrix transpose of $X$ and $Y$ is a $N \times 3$ vector matrix. Using permutation methods, they derived the expectation values of $L$ and $L^2$ and suggested that confidence limits on $L$ could be placed using a normal approximation.

It can be easily shown that $\sum (X^t Y)$ is equal to the sum of the cosines of the angular distances between the pairs $x(i)$ and $y(i)$. If we let $[I_1, D_1]$ and $[I_2, D_2]$ represent the inclinations and declinations of vectors $x(i)$ and $y(i)$, then from spherical trigonometry, the cosine of the angular distance $\theta$ between the vectors is given by

$$\cos \theta = \sin I_1 \sin I_2 + \cos I_1 \cos I_2 \cos (D_1 - D_2)$$

$$\cos (D_1 - D_2) = \cos D_1 \cos D_2 + \sin D_1 \sin D_2$$

Converting to cartesian coordinates $[l, m, n]$: $l = \cos D \cos I,$
m = \sin D \cos I, n = \sin I \text{ and combining with 4) and 5):}

6) \cos \theta = n_1 n_2 + l_1 l_2 + m_1 m_2

If we then sum over the entire data set,

7) \sum \cos \theta = \sum (n_1 n_2 + l_1 l_2 + m_1 m_2) = \sum (X^t Y)

The L statistic is then proportional to the mean angular distance between paired vectors in the time series. As given by Epp, et al., this statistic is scale dependent; that is, L depends on the magnitude of the fluctuations in each data set. Also, the L statistic differs from the accepted correlation definition because the mean values are not removed and the covariance term in the numerator is not normalized by the standard deviations of each vector set.

I propose the use of an alternate pairwise vector correlation statistic based on the conventional correlation definition:

8) \[ R = \frac{\sum (x(i) - \bar{x})^t (y(i) - \bar{y})}{\sqrt{\sum (x(i) - \bar{x})^2 \sum (y(i) - \bar{y})^2}} \]

If we define \( \theta^2 = (|x(i) - \bar{x}|)^2 \) as the angular deviation of an individual direction from the mean, for angular distances \(<30^\circ\)

\[ \theta^2 = 2(1 - \cos \theta), \text{ and } \sum \theta^2 = 2\sum (1 - \cos \theta) = 2(N - \sum \cos \theta) = 2(N - R') \text{ where } R' \text{ is the resultant length of the data.} \]

Thus, for small angular dispersions, the vector correlation coefficient R then becomes

9) \[ R = \frac{\sum |x| |y| \cos p}{2 \sqrt{N} \sum (N - R_1^2) (N - R_2^2)} \]

where \( R_1 \) and \( R_2 \) are the resultant lengths of each vector time
series and p is the azimuthal angle between the vector means and the
individual dpairs. |X| and |Y| are the angular distances between
the data points and their respective means.

The R statistic has a range of [-1,1]. For a perfect
correlation of R = 1, p = 0° and the data pairs are colinear. For
R = 0, no correlation occurs since the demeaned data trend at right
angles to each other.

A relevant use of the R statistic would be to examine the
probability that an observed correlation differs, at, say, the 95% confidence level, from correlations based on random data sets drawn from a Fisher distribution of specified N and k (k is the Fisher precision parameter). More simply, the hypothesis to be tested is "what is the probability that the observed R differs significantly from a random correlation distribution?".

In order to establish such a test, Monte Carlo techniques were used to generate cumulative probability distributions of correlations between realizations of two time series of random vectors drawn from populations of given N and k. W. Menke kindly provided his expertise in this task. Table VII-1 shows the critical R values for a two-tailed test at a α = 0.05 significance level for several values of N and k. The case where k = 0 corresponds to the limit of a Fisher distribution where the series are taken from points with a uniform probability distribution on a sphere. As k increases, random points in each series cluster more closely to the mean and lower values of observed R become significant. The random correlation distributions are approximately symmetric about R = 0 for all N. Note that the random
correlation distributions are relatively insensitive to the size of the data set for \( N > 5 \). To use this table the observed value of \( R \) is compared against the table value with the same \( N \). If the observed value is positive and greater than the critical \( R \) for some \( k \), then the null hypothesis is rejected at 95% confidence. In other words, there is less than a 5% chance that \( R(\text{obs}) \) is derived from correlations of random vectors from a Fisher distribution of some \( k \).
Table VII - 1.

Pairwise Vector Correlation Statistic Test Table of Critical Values at a 0.05 Significance Level.

This table gives critical values for a two tailed test of significance (α = .05) for the hypothesis that a correlation can be derived from the correlation of two sets of Fisher distributed vectors. \( l \) = lower bound, \( u \) = upper bound.

<table>
<thead>
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<th>Number of Samples</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k )</td>
<td>( l )</td>
<td>( u )</td>
<td>( l )</td>
<td>( u )</td>
<td>( l )</td>
<td>( u )</td>
</tr>
<tr>
<td>0</td>
<td>-.50</td>
<td>.50</td>
<td>-.44</td>
<td>.44</td>
<td>-.43</td>
<td>.43</td>
</tr>
<tr>
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<td>-.50</td>
<td>.63</td>
<td>-.29</td>
<td>.47</td>
<td>-.16</td>
<td>.35</td>
</tr>
<tr>
<td>10</td>
<td>-.58</td>
<td>.64</td>
<td>-.36</td>
<td>.47</td>
<td>-.24</td>
<td>.33</td>
</tr>
<tr>
<td>20</td>
<td>-.62</td>
<td>.65</td>
<td>-.40</td>
<td>.47</td>
<td>-.27</td>
<td>.32</td>
</tr>
<tr>
<td>50</td>
<td>-.65</td>
<td>.66</td>
<td>-.43</td>
<td>.47</td>
<td>-.29</td>
<td>.31</td>
</tr>
<tr>
<td>100</td>
<td>-.65</td>
<td>.66</td>
<td>-.44</td>
<td>.47</td>
<td>-.30</td>
<td>.31</td>
</tr>
</tbody>
</table>
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APPENDICES
APPENDIX

SPHERICAL ANALYSIS AND FISHER STATISTICS

In paleomagnetism, the remanence directions that we measure are distributed as three dimensional vector quantities on a unit sphere. Since spherical descriptive measures and inference methods based on Fisher statistics may be somewhat unfamiliar to the reader, a review of some of the quantities used in characterizations and comparisons of spherical data may be helpful. This appendix is divided into three sections. Section I reviews some basic spherical descriptive measures and properties of the Fisher distribution. Section II discusses the use of inference statistics in examining secular variation. Section III examines two different techniques proposed to correct inclination data when declinations are not available. The essential equivalence of the two techniques is demonstrated when certain errors are rectified. In the last section, assumptions inherent in the use (or misuse) of VGP paths in secular variation studies is discussed.

Section I

Basic spherical descriptors

A unit vector on a sphere can be described in terms of its direction cosines \( l, m, n \): 
\[
\hat{v} = l\hat{i} + m\hat{j} + n\hat{k},
\]
where 
\[
R^2 = l^2 + m^2 + n^2 = 1 ; \quad R = \text{resultant vector length}.
\]

Alternately, we can describe a vector in terms of its angular deviation from north (i.e., declination (D)) and the angle between the horizontal projection and vertical axis (inclination (I)).
\[ h^2 = l^2 + m^2 \]

\[ \tan(D) = m/l \]
\[ \tan(I) = n/h = n/\sqrt{l^2 + m^2} \]

The transformation between cartesian and spherical coordinates is given by:

\[ l = \cos D \cos I \]
\[ m = \sin D \sin I \]
\[ n = \sin I \]

For a series of \( N \) observations the vector sum along each of the cartesian axes is given by

\[ x = \sum l_i \bar{R}; \quad y = \sum m_i \bar{R}; \quad z = \sum n_i \bar{R}; \quad h = \sqrt{\sum (l_i \bar{R})^2 + (m_i \bar{R})^2 + (n_i \bar{R})^2} \]

and the resultant vector length \( R \) is given by

\[ R = \sqrt{\sum (l_i \bar{R})^2 + (m_i \bar{R})^2 + (n_i \bar{R})^2} \]

The mean inclination and declination are found from

\[ \tan(\bar{D}) = \sum m_i / \sum l_i \bar{R}; \quad \sin(\bar{I}) = \sum n_i / R \]

Fisher Statistics

A commonly used statistical distribution appropriate to directional data was derived by R.A. Fisher in 1953. It is based on the distribution function:

1) \[ f(\theta, \phi) = N \exp( \kappa \cos \theta ) \]

where \( \theta \) is the polar angle \((\pi/2 - I)\) separating an observed direction from the vector mean direction and \( \phi \) is the azimuthal angle.
\( \kappa \) is a precision parameter (analogous to the inverse of the variance) and \( N \) is a normalization factor making the probability density equal to one.

Upon integrating (1) over all possible values of \( \cos \theta \rightarrow [-1,1] \) and \( \phi \rightarrow [0,2\pi] \) we obtain the normalization factor \( N = \kappa / (4\pi \sinh \kappa) \). This gives us the Fisher probability density:

\[
2) P(\theta, \phi) = [\kappa / (4\pi \sinh \kappa)] \exp(\kappa \cos \theta)
\]

This function gives the distribution of a population of random errors on a unit sphere. It is unimodal with a maximum probability at the mode \((\theta = 0^\circ)\) and a uniform probability in azimuth \((\phi)\) about the mode for a given \( \theta \). In many ways, it resembles the Gaussian normal distribution and many inference tests arise from this similarity as will be discussed later.

To find the probability \( dP \) of observing a point in an infinitesimally small area \( dA \), the probability density is multiplied by the area \( dA \)

\[
3) dP = P(\theta, \phi) dA = [\kappa / (4\pi \sinh \kappa)] \exp(\kappa \cos \theta) \sin \theta d\phi
\]

The marginal distribution for (3) is found by integrating \( P d\phi \) from \( \phi \rightarrow 0,2\pi \):

\[
4) dP(\phi) = [\kappa / (2 \sinh \kappa)] \exp(\kappa \cos \theta) \sin \theta d\theta
\]

Fisher (1953) showed that the best estimate of \( \kappa \) (for \( \kappa > 3 \)) is given by

\[
5) \kappa = N - 1
\]

\[
\frac{N - R}{N - R}
\]

where \( N \) is the number of observations and \( R \) is the resultant vector length discussed earlier.
Watson (1956) showed that for $K > 3$, the statistic $2K (N-R)$ has a $\chi^2$ distribution with $2(N - 1)$ degrees of freedom

6) $\chi^2_{2(N-1)} = 2K (N-R)$

Since $k$ is the best estimate of $K$, Cox (1969) derived equations for upper and lower confidence bounds for $k$ and presented tables for easy computation:

7a) $k_u = \frac{P_\alpha}{\chi^2_{\alpha/2,2(N-1)}}$

7b) $k_l = \frac{P_{1-\alpha}}{\chi^2_{1-\alpha/2,2(N-1)}}$

$k_u$ and $k_l$ are the upper and lower confidence limits for $k$ and $P(\chi^2_{a,b})$ is the cumulative $\chi^2$ distribution from $\chi^2 = a$ to $\chi^2 = \infty$ for $b$ degrees of freedom.

Fisher further showed that the uncertainty angle of the cone of confidence of an observed mean direction from the true direction is given by:

8) $\cos \alpha = 1 - (N-R) \left[ \frac{1}{R} \frac{1}{P} - 1 \right]$

For $P = .05$, substituting (5) into (8) gives the 95% cone of confidence

9) $\cos \alpha = 1 - \frac{(N-R)}{R} \left[ 20 \frac{1}{P} - 1 \right]$

If we wish to know the probability that $\theta_1 < \theta < \theta_2$, we can
integrate 4) from \( \theta_1 \) to \( \theta_2 \). Substituting \( c = \cos \theta \),
\[
dc = -\sin \theta \ d\theta
\]

\[
P(\theta_1 < \theta < \theta_2) = -\int_{\cos \theta_1}^{\cos \theta_2} \frac{\cos^2 \theta}{2} \exp\left(\frac{-K c}{\sinh(K)}\right) \ d\cos \theta
\]

10) \( P(\theta_1 < \theta < \theta_2) = \frac{1}{(e^K - e^{-K})} \left[ \exp[-K(1-\cos \theta_1)] - \exp[-K(1-\cos \theta_2)] \right] \) from \( \theta_1 \) to \( \theta_2 \)

If \( K > 3 \), \( e^{-K} \approx 0 \), therefore

11) \( P(\theta_1 < \theta < \theta_2) \approx \exp[-K(1-\cos \theta_1)] - \exp[-K(1-\cos \theta_2)] \)

For the probability that \( \theta \) is greater than some angle \( \delta \) we get

12) \( P(\theta > \delta) = \exp\{ -K (1-\cos \delta) \} \)

An interesting case occurs when \( P = 1 - e^{-1} = .6321 \). If we integrate (11) from \( \theta_1 = 0 \), \( \cos \theta_1 = 1 \) to \( \theta_2 \), we get

13) \( 1 - 1/e = 1 - \exp(-K(1-\cos \theta_2)) \)

Taking the log of (13) and rearranging

14) \( 1/e = 1 - \cos \theta_2 \)

Again using the small angle approximation,

15) \( 1 - \cos \theta \sim \theta^2/2 \), inserting into (14) yields

16) \( \theta_2 = \sqrt{2I/k} \) for \( P = .6321 \)

In many paleomagnetic problems we wish to test whether the scatter in a data set is comparable to a theoretical scatter (e.g. secular variation) or scatter from another data set. In analogy to Gaussian statistics, one measure of scatter, the population variance,
can be defined as the sum of the squared deviation of observed data, \( \theta_i \), from the true mean, \( \mu \), normalized by the number of observations:

\[
\sigma^2 = \frac{\sum (\theta_i - \mu)^2}{N}
\]

Again using the small angle approximation (15):

\[
\sigma^2 \approx \frac{\sum (2-2\cos \theta)}{N} = 2(1 - \frac{\sum \cos \theta}{N}) = 2(1 - \bar{R})
\]

Fisher (1953) has shown that the mean resultant length, \( \bar{R} \), can be estimated by the Langevin function \( L(\kappa) = \coth \kappa - 1/\kappa \). For \( \kappa > 3 \), \( \coth \kappa \approx 1 \), thus \( \bar{R} = L(\kappa) \approx 1 - 1/\kappa \) (for \( \kappa > 3 \)).

Inserting into (18) yields an estimate of \( \sigma^2 \) which is approximately valid for deviations <30° from the true mean, and for \( \kappa > 3 \):

\[
\sigma^2 \approx \frac{2}{\kappa}
\]

Comparing (16) to (19) we note that in the Fisher distribution 63.21% of the samples lay within one angular standard deviation of the true mean. It turns out, in general, that for \( \kappa > 3 \),

\[
\sigma = \sqrt{2/\kappa} \quad (\text{Roberts and Ursell, 1960}).
\]

In most instances in paleomagnetism, the true mean is unknown and we require statistics to evaluate and compare mean directions and scatter. A useful descriptive measure often used in secular variation models is the standard deviation, \( s \). As defined by Cox (1970):

\[
s^2 = \frac{1}{(N-1)} \sum \delta^2
\]

where \( \delta \) is the angular deviation between an individual observation and the mean direction. Using the small angle approximation as before, we find that

\[
s^2 = \frac{2}{(N-1)} \sum (1 - \cos \delta_i) = \frac{2(N - \bar{R})}{(N - 1)}
\]
since the resultant R is given by \( \Sigma \cos \delta \). Recalling that 
\[ k = (N - 1) \]
we find that

22) \( s^2 = 2/k \)

If \( s \) is converted from radians to degrees

23) \( s = 81/\sqrt{k} \)

We note that for a Fisher distribution, 63% percent of the samples will lie within one angular standard deviation from the mean, whereas for a Gaussian, about 68% of the samples lie ± 1 standard deviation from the mean.

Cox (1969) further showed that the confidence limits for \( s \) are given by

24) \[ s_u = s \left[ \frac{2(N - 1)}{P(x^2_{1-\alpha/2,2(N-1)})} \right]^{1/2} \]

25) \[ s_l = s \left[ \frac{2(N - 1)}{P(x^2_{\alpha/2,2(N-1)})} \right]^{1/2} \]

where \( P(x^2) \) is defined as in equation 7. Using similar techniques, it can be shown that the 95% confidence level for large \( N \) and \( k \) can be approximated by

26) \( \alpha_{95} \sim 140 / \sqrt{Nk} \)

Section II Statistical Tests

A variety of statistical tests are available to the paleomagnetist for comparing estimates of mean directions and precision to other data sets and theoretical predictions. These tests can be divided into three classes: 1) goodness of fit criteria for examining similarities between observed and theoretical frequency distributions;
2) tests for comparisons of mean directions, 3) and tests for comparisons of precisions.

Goodness of Fit (Watson and Irving, 1957; Irving, 1964)

The test for goodness of fit measures the divergence between frequency distributions of observed data and theoretical expectations. The test is based on the $\chi^2$ statistic,

$$\chi^2 = \sum \frac{(f_o - f_t)^2}{f_t}$$

where $f_o$ is the frequency of observations within an observed class interval and $f_t$ is the theoretical frequency expected for that interval. The number of degrees of freedom is equal to the number of classes minus the number of fitted constants minus one.

To use this statistic, the data is divided into $N$ classes and a frequency histogram is generated. For each class, the observed-theoretical frequency difference is squared and normalized by the theoretical value. The class values are then summed over the $N$ classes and compared to a theoretical $\chi^2$ value at some level of confidence for the given number of degrees of freedom. If the observed value exceeds the table $\chi^2$ value then at that the confidence level, the hypothesis that the observed distribution matches the theoretical distribution is rejected.

Irving (1964) describes an example of fitting observed directions to a Fisher distribution. The theoretical distribution is given by equation 11) in the last section times $N$
2) \[ f(\theta_1, \theta_2) \sim N \left[ \exp\left\{-\kappa (1-\cos \theta_1)\right\}, \exp\left\{-\kappa (1-\cos \theta_2)\right\} \right] \]

with \( \kappa \) estimated by \( \kappa = (N-1)/(N-R) \). The angle \( \theta \) is the angular distance from the estimated mean. A uniform distribution in azimuth is expected about the mean.

Comparison of Mean Directions

The simplest test of whether an observed mean direction (\( \theta \)) is the same as some expected direction (e.g., geocentric axial dipole) is to use the \( \alpha_{95} \) defined in the first section. If the known direction falls within the interval \( \theta \pm \alpha_{95} \), then at the .05 significance level, the expected and observed mean directions are the same (McElhinny, 1973).

If the true direction is not known, Watson (1956), and Watson and Irving (1957), using an analysis of variance approach, presented an F test to determine if the mean directions are identical. Essentially the test is whether there is a significant difference in between-site scatter and total within-site scatter.

For \( x \) populations with \( N_1 \) directions and a resultant vector length \( R_1 \) in each population the mean square within-site dispersion is given by

3) \[ MS_w = \frac{\sum (N_1 - R_1)}{2(\sum N_1 - x)} \]

If \( R \) is the vector sum of the resultants of all of the individual directions, the mean square between site scatter is:

4) \[ MS_b = \frac{\sum R_1 - R}{2(x - 1)} \]
The statistic

\[ F = \frac{1}{k_w} = \frac{1}{k_b} = \frac{2(\sum N_1 - x)}{2(x - 1)} \frac{\Sigma R_1 - R}{\Sigma (N_1 - R_1)} \]

can be compared to the expected value of \( F_{\infty} \) at some confidence level \( \alpha \) with \( df_1 = 2(x-1) \) and \( df_2 = 2(\Sigma N_1 - x) \). If \( F_{obs} \) exceeds \( F_{\infty} \) then the null hypothesis that no difference exists between the population means must be rejected.

If there exists a significance between-site scatter as deduced from the F test, \( MS_b \) and \( MS_w \) can be equated to their expectation values to obtain estimates of \( k_b \) and \( k_w \):

\[ MS_w = \frac{1}{2 k_w} = \frac{(\sum N_1 - R_1)}{2(\Sigma N_1 - x)} \]

6) \( k_w = \frac{(\sum N_1 - x)}{\sum N_1 - R_1} \)

7) \( MS_b = \frac{\Sigma R_1 - R}{2(x - 1)} = \frac{1}{2} \left[ \frac{1}{k_w} + \frac{\bar{N}_1}{k_b} \right] \)

where \( \bar{N}_1 = \frac{1}{x - 1} \left| N - \frac{\Sigma N_1^2}{N} \right| \)

is the weighted average number of observations per site.

If the direction of the resultant of all \( N \) observations is used as the mean direction, it will be distributed in a Fisher distribution (McElhinny, 1967) with

8) \( \frac{1}{k_0} = \frac{1}{k_w N} + \frac{1}{k_b x} \)
It should be noted that the above analysis holds only if $k_w$ is approximately constant for each site.

**Comparison of Precisions**

In studying secular variation, we may want to test whether an observed value of $k$ is the same as a predicted value of $k$. There are two methods whereby an observed and theoretical $k$ can be compared. The simplest is to use the confidence bounds for the observed $k$, as defined by Cox (1969) in equations (7a) and (7b). If the theoretical value falls within the confidence limits of observed $k$, then we can conclude that the observed and theoretical values are equal. Another technique suggested by McFadden (1980) is to formulate the problem as an F test.

Since Watson (1956) showed that

$$2k (N - R) = X^2_{2(N - 1)}$$

and

$$k = \frac{(N - 1)}{(N - R)}$$

(9) $k = \frac{X^2_{2(N-1)}}{2(N-1)} = F [2(N-1), \infty]$ 

If we hypothesize that the theoretical value is given by $k$, at some confidence level $\alpha$, if the F value exceeds the table value at $(1-\alpha/2)$ then we must conclude that the theoretical and observed values of $k$ are different.

An analogous procedure is used if we want to compare two sample variances. In this case we are testing whether the expected $k$ for the two data sets is the same. The appropriate F statistic is
If the calculated $F$ exceeds the table $F$, at some confidence level we conclude that the two sample variances are different. If we are dealing only with inclination data, the appropriate statistic is given by (Mcfadden, 1982)

$$10) \frac{k_1}{k_2} = F \frac{2(N_2-1),Z(N_1-1)}{Z}$$

A similar method can be used to test the equality of angular variances. However, since $s^2 = 2/k$, the appropriate $F$ (or $\chi^2$) statistic(s) are inverted. As noted by McFadden (1980), sample variances ($s^2$) rather than standard deviations ($s$) should be compared because of the square root dependence of $s$ on $k$.

Section III

Comparison of Directions When Declinations Are Not Available

When sampling from cores or drill holes, absolute declinations are often not available because of the lack of absolute azimuthal orientation. The use of inclination data alone to estimate mean directions gives an apparent mean inclination which is shallower than the true inclination. The easiest way of visualizing this problem is to imagine a set of vectors oriented randomly about the vertical axis. Any arithmetic or vector average of these inclinations will be less than the true mean vertical inclination.

Brjden and Ward (1966) were the first to attempt to calculate the true mean inclination and associated precision parameter, $k$, when the
data consists of only inclinations. They started by assuming a
Fisherian distribution of directions and calculated expected values of
\( \cos \theta \) and \( \sin \theta \) where \( \theta = 90^\circ - I \). Unfortunately, they were unable
to reduce the expectation equation to elementary functions. They were
forced to calculate \( E(\cos \theta) \) and \( E(\sin \theta) \) for various combinations
of \( \theta \) and \( k \) and provide tables for reference.

By calculating the moment generating function of \( \cos \theta \) about a
vertical axis, Kono (1980) showed that any moment of \( E(\cos^n \theta) \) could
be computed. He equated the first and second moments of \( E(\cos^n \theta) \)
with mean values of the observed data, and suggested that \( \theta_o = 90^\circ - I \) and \( k \) could be calculated from the simultaneous solution of
two equations:

1) \( \cos \theta_o [\coth(k) - 1/k] = 1/N \sum \cos \theta \)

2) \( \cos^2 \theta_o + 1/k \times [1-3\cos^2 \theta_o] \times [\coth(k) - 1/k] = 1/N \sum \cos^2 \theta \)

He suggested that \( \alpha_{95} \) and confidence limits for \( k \) could be computed
as discussed in section 1.

McFadden and Reid (1982) disputed Kono's methods and suggested
another procedure for calculating \( \theta_o \) and \( k \). Starting with the Fisher
probability density function transformed to coordinates about a ver-
tical axis, they integrated the distribution with respect to the azimuth
to obtain the marginal distribution of \( \theta \) for an individual direction.

3) \( P(\theta)d\theta = \sqrt{k} \exp(k \cos(\theta_o - \theta_i))(\frac{\sin \theta}{\sin \theta_o})^{1/2} d\theta \)

where \( \theta_o = \text{true mean inclination} = \pi/2 - I \) (radians)
\[ \theta_i = \text{individual } i\text{'th direction} = \pi / 2 - I_i \]

Since they used the small angle approximation for the azimuth, equation 3) holds only when \( k > 5 \). From 3), McFadden and Reid derived the log likelihood of this distribution. By taking the partial derivatives with respect to \( k \) and \( \theta \) and setting them equal to zero, they suggested that the maximum likelihood estimators \( \hat{k} \) and \( \hat{\theta} \) could be obtained by iterative solution of the equation:

\[
4) \quad N \cos \theta + (\sin^2 \theta - \cos^2 \theta) \sum \cos \theta_i - 2 \sin \theta \cos \theta \sum \sin \theta_i = 0
\]

The equation has three solutions, but the correct solution occurs when the second derivative of the log likelihood function \( U \) is negative.

\[
5) \quad U = \frac{1}{2} N \left( \csc^2 \theta - \left[ C / (N - C) \right] \right)
\]

where \( C = \sum \cos(\theta - \theta_i) \).

McFadden and Reid found that \( \hat{k} \), the maximum likelihood estimator of \( k \), is biased. By Monte Carlo experiments they asserted that if \( k \) is defined as

\[
6) \quad k = \frac{N - 1}{2(N - C)}
\]

then \( 1/k \) is an unbiased estimator for \( 1/k \).

Further, they maintained that the statistic \( (N - 1) \kappa /k \) is distributed as a \( \chi^2 \) distribution with \( N - 1 \) degrees of freedom. McFadden and Reid noted that, regardless of the technique, when the dispersion is large and the true direction is near the vertical, the joint distribution of \( \kappa \) and \( \theta \) is folded back about the vertical and
the problem of independently estimating $\theta_0$, and $k$ is intractable.

Using the relation between $k$ and $\chi^2$, they went on to show

that the angular error $\alpha$ in $\Theta$ could be obtained from the solution to the quadratic equation

$$
(N - 1)(\alpha^2 C - 2\alpha S)
= \frac{F(1,N-1)}{2(N - C)}
$$

where $S = \Sigma \sin(\Theta - \Theta_1)$; $C = \Sigma \cos(\Theta - \Theta_1)$

$S$ and $C$ are the sums of the sines and cosines of the angular
differences between the maximum likelihood mean direction $\Theta$ and the
individual directions.

For the error $\alpha_1$ in $\Theta$ on the high inclination side of $\theta_0$,

$$
\theta_0 = \Theta - \alpha_1
$$

8) $\alpha_1 = S/C \pm \alpha$

9) $\alpha = 1/(2C) \pm \sqrt{(4S^2 + 8 f C (N - C)/(N-1))}$

where $f$ is the F table value at some level of confidence. Similarly, for the error $\alpha_2$ in $\Theta$ on the low inclination side of $\theta_0$,

10) $\alpha_2 = -S/C \pm \alpha$

For some reason, McFadden and Reid chose only to consider the
positive root of 9) yielding an error estimate of

11) $\theta_0 = \Theta (-S/C \pm \alpha)$

They suggested that the "corrected" estimate of $\Theta$ should be

12) $\theta_0 = \Theta - S/C$ with an error angle $\pm \alpha$.

While McFadden and Reid's use of maximum likelihood is a reasonable
approach to estimating the true mean direction, their error analysis is
problematic. Equation (12), as used as an estimate of $\theta_0$, is clearly
in error as can be easily shown.

If we again use the small angle approximation, $\sin \delta = \delta$,
\[ \cos \delta = 1 - \frac{1}{2} \delta^2 \] where \( \delta = (\Theta - \Theta_1) \), then \( S/C \) becomes

\[
\frac{S}{C} = \frac{\Sigma \sin \delta}{\Sigma \cos \delta} = \frac{\Sigma \delta}{\Sigma (1 - 1/2 \delta^2)} = \frac{\Sigma (\Theta - \Theta_1)}{N - 1/2 \Sigma (\Theta - \Theta_1)}
\]

In the instance applicable to these equations, \((\Theta - \Theta_1)\) is small, therefore, the squared term in the denominator is approximately zero.

\[
\frac{S}{C} = \frac{\Sigma (\Theta - \Theta_1)}{N} \approx \frac{N \Theta - \Sigma \Theta_1}{N} = \Theta - \frac{\Sigma \Theta_1}{N} = \Theta - \bar{\Theta}
\]

where \( \bar{\Theta} \) is simply the complement of the mean inclination.

Substituting back into (12), we get

\[ \theta_o = \Theta - \frac{S}{C} \approx \Theta - (\Theta - \bar{\Theta}) \approx \bar{\Theta} \]

Thus McFadden and Reid's "corrected" true inclination is simply approximated by the arithmetic mean of the complement of the observed inclinations !!! Their mistake was in calculating the error angle in terms of its \( \chi^2 \) relation. What they actually calculated is the confidence limits on the error angle \( \alpha \) rather than \( \alpha \) itself. As noted by Kono (1980), the error angle could be computed from Fisher's relation. At the 95% confidence level,

\[ \cos \alpha = 1 - \frac{(N - R)}{R} \left( 20 \frac{1}{(N-1)} - 1 \right) \]

with \( K \) defined as in equation 6). Confidence levels for \( K \) could be compared (as discussed in the last section) by using the techniques of Cox (1969).

The correct estimate of the true inclination is given by

\[ I_o = (90 - 180/\pi \Theta) \]

The Kono and modified McFadden techniques of obtaining true mean
inclinations and associated statistical parameters were compared on a variety of data sets. For the McFadden method, the maximum likelihood estimator of $\theta$ was obtained from iterative solution to equation (4) using a secant convergence algorithm. Estimates of $I_0$, $k$, and $\alpha_{95}$ were derived using the equations discussed earlier.

Data sets tested included the original data of Briden and Ward (1966), McFadden and Reid's (1982) data, 1965 IGRF inclinations about latitude 27° N at 1° intervals and inclination data from Site 480. While these tests are no means exhaustive, they give a good indication that the two techniques yield essentially similar results over commonly encountered inclination ranges. For all cases tested, mean inclinations differed by a degree or less and $\alpha_{95}$'s were comparable. Estimated values of $k$ showed some differences especially for tight clustering (high $k$). Since the angular standard deviations ($s = 81/\sqrt{k}$) and confidence bounds for the mean ($\alpha_{95} \approx 140/\sqrt{k}$) are inversely related to $k$, the differences in the estimated precision at high values of $k$ is of little consequence since $s$ and $\alpha_{95}$'s are small.

Virtual Geomagnetic Poles

In order to compare magnetization directions between different sites, it is helpful to transform the directions into quantities that take into account the geographic position of the various sites. The virtual geomagnetic pole (VGP) is defined as the pole of the dipolar field that gives the observed magnetization direction at the site (Cox and Doell, 1960). The pole, with coordinates ($\lambda_p$, $\phi_p$), can be considered the point at which the dipolar field intersects the earth's
surface with $D = 0^\circ$, $I = 90^\circ$. The use of a VGP is a convenience. It refers only to the mapping of a spot reading of a field direction onto a hypothetical dipole, and no inference is made that the field is dipolar.

If the geographic site coordinates are $(\lambda_g, \phi_g)$, the geographic coordinates $(\lambda_p, \phi_p)$ of the VGP can be derived from solution to the following equations (McElhinny, 1973):

1) $\lambda_p = \arcsin (\sin \lambda \cos \phi + \cos \lambda \sin \phi \cos D)$
2) $\phi_p = \phi_g + \beta$ for $\cos \phi > \sin \lambda_g \sin \lambda_p$
   $\phi_p = \phi_g + 180 - \beta$ for $\cos \phi < \sin \lambda_g \sin \lambda_p$
3) $\tan I = 2 \cot \phi$
4) $\sin \beta = \sin \phi \sin D / \cos \lambda_p$

Latitudes are positive in the northern hemisphere and longitudes are measured eastward from Greenwich from $0^\circ$ to $360^\circ$. The angle $\beta$ is the longitude difference between the site and VGP. The angle $\phi$ is the geomagnetic colatitude or angular distance of the site from the VGP.

Another way of expressing 3) is in terms of the geomagnetic latitude $\lambda_m$:

5) $\tan I = 2 \tan \lambda_m$

This important expression relates the observed inclination at a site to the paleomagnetic latitude. If the axial dipole hypothesis is assumed, then the observed mean inclination maps directly into $\lambda_m$ and the VGP can be interpreted as the geographic pole.

Because of the trigonometric relation between the inclination and geomagnetic latitude, error estimates of the mean and scatter in field directions do not map in a one to one correspondence to similar measures for the poles. As discussed by Harrison (1980), the simplest
way of understanding this problem is to consider a site located on the geomagnetic equator, where the field is essentially horizontal. At this site, a $1^\circ$ change in declination maps into a $1^\circ$ change in pole position. However, because of (5), a $1^\circ$ change in inclination corresponds to only one half that change in pole position. Thus symmetric scatter in field directions about a mean translates into a non-symmetric distribution about the VGP, and vice versa.

As a consequence of the nonlinearity of the mapping function, in any paleomagnetic investigation, we must decide whether to assume a symmetric distribution in scatter about either the field directions or the poles. Paradoxically, the present Earth's magnetic field shows a symmetric distribution in scatter about the poles, although this may be an artifact of the geographic dependence of the VGP mapping function, as discussed later. Consequently, most models of secular variation assume a Fisherian distribution about the VGPs for present and ancient fields.

Cox (1970) derived analytical expressions relating the variance in field direction ($S_f$) to the variance in the poles ($S_p$) for either case. Since $S^2 = 2/\kappa$, the equations also apply to variations in the Fisher precision parameters $k_f$ and $k_p$.

Assuming a symmetric Fisherian distribution in scatter about the field directions

\[
k_p = \frac{k_f}{S_f^2} \times \left( \frac{\kappa}{S_p^2} \right) \left( 5 + 18\sin^2 \lambda + 9\sin^4 \lambda \right)
\]

where $\lambda$ = geomagnetic latitude from equation (5).

For the case where the scatter has an azimuthally symmetric
Fisher distribution about the poles.

\[ \frac{k'_p}{k'_f} = \frac{s^2_f}{s^2_p} + \frac{2(1 + 3\sin^2 \lambda_m)^2}{(5 + 3\sin^2 \lambda_m)} \]

Cox (1970) noted that these expressions are strictly valid only if the angular standard deviation \( S_p \) is less than about 10 deg. Harrison (1980) showed that for values of \( S_p \) more typical of secular variation (\( S_p \approx 15 \) deg.), these transformations are only approximate in the range of \( \lambda_m = 20-90^\circ \) (\( I = 36-90^\circ \)), and are not accurate for low \( \lambda_m \) (or \( I \)) values.

For the purposes of this study the utility of these equations is in permitting us to examine observed scatter in directions in relation to values predicted by secular variation models.

Section IV

On the use of VGP paths to study secular variation

Archaeomagnetic and sedimentary paleomagnetic investigations give important information on trends in geomagnetic secular variation (SV). A standing difficulty has been how to compare SV records from different localities, since the main dipole field has a latitude dependence given by:

\[ F = F_e \cdot (1. + \sin L)^{1/2} \]

where \( F \) is the field at some latitude \( L \) and \( F_e \) is the equatorial field at the Earth's surface. Two methods of presenting directional data based on a VGP transform are commonly used. I shall presently
show that these techniques give misleading results when the assumptions upon which the methods are based are violated.

Kawai, et al. (1965) and Aitken and Weaver (1965) originally suggested that directional data should be converted to Virtual Geomagnetic Poles (VGPs) and a polar curve constructed to study SV wandering paths. A VGP is the hypothetical dipole that would give rise to the observed declination (D) and inclination (I) at the geographic site. Equations for the transformation are given in the Section II pf this appendix. The VGP wandering curves are probably the most commonly used method of presenting SV data (Champion, 1980, Lund, 1981, Kovacheva, 1980, Wolfman, 1983, Dubois, 1975, Hirooka, 1971).

An alternative approach is to convert the directions at various sites to D and I at some central location. Shuey, et al., (1970) suggested that the most satisfactory way of handling this problem is to calculate the VGP for each point and to apply an inverse VGP transform to derive directions at the common site. Their work was originally intended to allow mean statistics to be calculated for local sites. However, this method has also been suggested for comparison of data from diverse areas (Barton and Merrill, 1983).

Both of these techniques rely on the VGP transform which assumes a DIPOLAR configuration of the field. However, if the fluctuations are NON-DIPOLAR (as is generally the case), then severe distortions arise. Two simple examples can illustrate this point.

Assume that we have three sites (A,B,C) at the same latitude,
but located 90° apart in longitude. A non-dipole feature causes a shallow inclination at site A. For simplicity, we will assume that no change in declination is seen. Observers at sites B and C note no corresponding change in direction, since the field is localized. A transform places the Site A VGP on the far side of the spin axis at a longitude opposite the site at an angular distance of \( p = \arccot(0.5 \tan(I)). \) If site B is chosen as the common site for comparison of the SV records of A, B, and C, then the low inclination at site A transforms into a declination change at site B.

Suppose that the non-dipole trough were to drift unchanged in character under Site C. At the maximum deviation, the corresponding VGP at Site C would now occur on the far side of C, towards Site A. The common site transform would give a negative declination at B. Finally, when the feature drifted over site B, a shallow inclination anomaly would be noted. Thus the transformed VGP records for the same drifting shallow inclination feature at the three sites would be recorded at common site B as a positive D anomaly for A, a negative I anomaly for B, and a negative D anomaly for C.

If VGP polar wandering curves were used instead of the common site inverse transform, the feature would be recorded as a far-sided VGP loop for each site, so the common nature of the drifting feature would be obscured. If VGPs from different areas are averaged to obtain mean SV wandering paths for various periods as was done by Dawson and Newitt (1982), complicated and apparently random paths emerge. These results are meaningless, because of the geographic
dependence of the VGP transform. The situation is further aggravated if systematic errors are propagated, for example, by assuming a zero mean direction for an azimuthally unoriented core which records only portions of SV cycles.

Wilson and Ade-Hall (1970), in studying dispersions of Upper Tertiary and Quaternary lavas, first noted that there was a tendency for poles to cluster on the far side of the collection sites. Wilson (1971) recognized the VGP geometric problem and suggested the use of a 'common site longitude' (CSL) projection. The CSL method simply rotates each collection site around a band of latitude to a common longitude, taken as zero. This has the effect of rotating the VGP paths so that the poles are seen as they would be by each observer. For the zonal drift example cited above, the CSL projection would give overlapping loops with a time delay as should be expected. Thus for comparing SV records from sites at the same latitude, the CSL technique is preferable to simple VGP wandering curves.

There remains the problem of how to compare results from sites at different latitudes. Distortion will be introduced for non-dipolar features whose latitudinal dependence differs from that of a dipole. Since the VGP transform assumes a dipolar field, any non-dipolar fluctuations must change in the same manner as a dipole in order for the technique to be valid. If a 6100 gamma (.0614 Oe) negative Z anomaly (20% of the equatorial dipole field) drifted unchanged from 30° N to 60° N, the difference in inclination observed and predicted values is only 1.3° for 60° N (70.6° vs 71.9°), and
2.7° (42.7° vs 45.4°) if the 60° N anomaly is inverted to 30° N. The declination of 0° is unaffected by the transform.

If the same amplitude anomaly were in the Y direction, however, the resulting VGP locations would be 74.4N, 87.7E for the 30°N anomaly and 78.6° N, 89.8° E for the 60° N anomaly. This 4° difference in VGP latitude, upon inversion, results in a 8° error in D and 1° error in I in predicting the 60° N feature from the 30° N VGP and errors of 5° in D and 0° in I for the converse case. In general, use of the VGP transform causes latitudinal errors if poleward drifting Y (or X) anomalies are present. This results in minor errors in I, and small, but significant errors in D when the VGP poles are inverted. Thus the CSL method is adequate for comparing gross changes in the secular variation, but care should be taken in interpreting fine scale fluctuations.