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Catrina M. Johnson, Peter J. Fawcett, and Abdul-Mehdi S. Ali
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GEOCHEMICAL INDICATORS OF REDOX CONDITIONS AS A PROXY FOR MID-PLEISTOCENE CLIMATE CHANGE FROM A LACUSTRINE SEDIMENT CORE, VALLES CALDERA, NEW MEXICO

CATRINA M. JOHNSON, PETER J. FAWCETT, AND ABDUL-MEHDI S. ALI

Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, catj1952@unm.edu

ABSTRACT — This study examines several characteristics of sediments as proxies for lake level and climate, from an 81-m core of mid-Pleistocene lacustrine sediments recovered from the Valle Grande, located within the Valles caldera, New Mexico. Due to the limited sources for the lake, this core is a valuable indicator of regional climatic variations during the mid-Pleistocene. The caldera's limited watershed is dominated by rocks of rhyolitic composition with well-constrained geochemistry. Because of limited sediment sources, this record is significant, as any geochemical variations through the core will be due to aquatic chemistry and climate rather than a change in source terrain. The core spans ~180 kyr with a basal age of 552 ± 3 ka and contains a record of two glacial-interglacial cycles spanning marine isotope stages 14 through 10. Samples taken at 20 cm intervals for geochemical analysis show significant systematic variation for 8 major and 13 trace elements coinciding with glacial-interglacial cycles. We see a significant decrease in Fe and Mn concentration at glacial terminations, followed by low values maintained throughout the interglacial interval, suggesting anoxic bottom waters. Al, Ba, Co, Mg, Ni, Pb, Ti, and Zn concentrations also exhibit similar trends with higher values during glacial intervals and lower values during interglacial intervals inversely correlating with total organic carbon (TOC). Higher TOC levels during interglacial intervals indicate increased biological productivity, the decomposition of which depletes oxygen concentrations in the lake.

INTRODUCTION

Lacustrine sediments, which serve as geochemical and mineralogical archives, can answer a variety of important scientific questions concerning regional and global climate change. They have the potential to broaden current understanding of earth history by resolving continental records of long-term climatic changes, such as those associated with cyclic variation in the earth's orbit (Milankovich cycles, 23-100 kyr) and suborbital timescales. In addition, lake basins have the potential for providing high resolution paleoclimatic records on time scales comparable to polar ice cores. The Valles caldera drilling project (VC-3) is part of the Global Lake Drilling program (GLAD, <http://lrc.geo.umn.edu>) aimed at reconstructing and understanding patterns of past global climate change as archived in a worldwide network of lacustrine settings.

Core VC-3 was drilled in May 2004 in the Valle Grande, in the Jemez Mountains of New Mexico as part of the GLAD5 project. An 81 m sediment core was recovered and a variety of analyses are underway to interpret the environmental and climatic history of the core. Preliminary results of this work show two glacial-interglacial cycles present in the core spanning five Marine Isotope Stages (MIS) from MIS 14 through MIS 10 (552 ka to ~360 ka) (Fawcett et al., 2007). Other work on core VC-3 includes preliminary paleomagnetic and rock magnetic analyses (Donohoo-Hurley et al., 2007) and geochemical analyses of tephra glass (WoldeGabriel et al., 2007). In this paper, we describe the preliminary results of geochemical analyses of core VC-3.

The chronology and detailed description of sediments in core VC-3 are given by Fawcett et al. (2007). The base of the core is constrained to the mid-Pleistocene by an Ar-Ar date of 552 ± 3 ka. Glacial-interglacial intervals above this date were defined based on total organic carbon (TOC) content and other parameters in the core, including sedimentology, $\delta^{13}\text{C}$ values and C/N ratios of organic matter, pollen content, and sediment density. Addi-

tional age control was provided by correlation with the marine SPECMAP curve (Lisiecki and Raymo, 2005) and by correlation of geomagnetic field events in the sediment core with globally recognized events (Donohoo-Hurley et al., 2007; Fawcett et al., 2007). From the base of the core at 76 m to ~53 m depth, TOC values are low, indicating low productivity and a glacial climatic state (MIS 14; Fig. 1). From 53 to 39 m depth TOC values are variable but higher overall, indicating higher productivity and an interglacial state (MIS 13; Fig. 1). From 39 m to 27 m depth, TOC

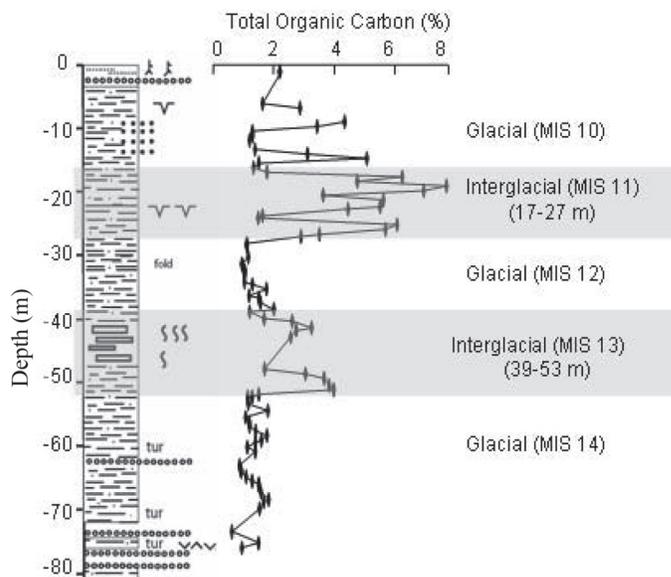


FIGURE 1. Stratigraphic column of sediment variability, total organic carbon (%), interpreted depth intervals for glacial and interglacial stages. See Fawcett et al. (2007) for stratigraphic descriptions.

values are again low, indicative of a glacial state (MIS 12; Fig. 1). A prominent interglacial period occurs between 27 m and 17 m depth, where TOC values are the highest in the core (MIS 11; Fig. 1), with a final glacial stage present from 17 to 5 m depth (MIS 10; Fig. 1).

This sediment core is important because it is one of only a few terrestrial records that span the middle Pleistocene. Other long Pleistocene records from the Southwest include a vein calcite record from Devils Hole, NV (Winograd et al., 1992) and a coarsely sampled lake core from Owens Lake, CA (Smith and Bischoff, 1997). Multiple paleoclimate records (pluvial lake and glacial records; pollen and vegetation reconstructions) for southwestern North America clearly document the climatic response of this region from wet, cold climates during the glacial late Pleistocene to warmer, drier climates of the Holocene (Elias, 1990; Anderson, 1993; Harsbargen, 1994; Allen and Anderson, 2000; Armour et al., 2002). Climate model simulations of the last glacial maximum (LGM) (COHMAP, 1988) show a southward displacement of the jet stream in response to large ice sheets in northern North America, bringing increased winter rain and cloud cover to the Southwest. Evidence for large glacial paleolakes in semiarid basins of the Southwest (Smith and Street-Perrot, 1983; Allen, 2005) and vegetation reconstructions in the northern Chihuahuan Desert (Van Devender et al., 1994) support this model of wetter glacials and drier interglacials in the southwest.

Previous studies of lacustrine geochemistry have shown that most sedimentary deposits can be divided into biogenic, detrital, and diagenetic major components (Dean and Arthur, 1998). By examining variations in these components in conjunction with other paleoclimatic proxies, details of lake chemistry, water mass characteristics, processes in the lake catchment, and ultimately climate can be resolved. The Valles caldera is unique in that it has a small catchment that is dominated by rhyolitic rocks with well-constrained mineralogy and geochemistry (Stix et al., 1995). As a result, any significant changes in elemental composition of the VC-3 sediment geochemistry are likely due to changes in the lake water mass (redox conditions, productivity) rather than changes in the source terrain.

METHODS

Whole sediment samples taken at 20 cm intervals were digested with a HF-HNO₃-HCl solution to extract acid soluble minerals. Eight major elements (Al, Ca, Fe, K, Mg, Mn, Na, Ti) and 13 trace elements (Ba, Co, Cr, Cu, Ni, P, Pb, S, Sr, V, Y, Zn, Zr) were analyzed. Digested samples were analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES), using a Perkin Elmer Optima 3000DV. Because detection limits for many elements are quite low, some in the ppb range, the dual view ICP was used in the axial mode.

Approximately 1 gram of sample was acquired at 20 cm intervals along the core to a depth of 53 m. Sample resolution was increased to 60 cm intervals for the remaining 28 m of the core. Each gram of sample was put in a beaker dried in a desiccator. Dried samples were then crushed with a mortar and pestle and hand-sieved through 200 μ m mesh. Special care was taken to

ensure against cross-contamination by washing and drying all tools between sample preparations.

A 0.1000 g of sample was then weighed into a Teflon tube to begin the digestion process. The method of Lichte et al. (1987) was adjusted by increasing the volume, ratio, and concentration of acids and heating the aliquot at a higher temperature for longer time periods, in order to achieve complete dissolution while minimizing complexation issues associated with the combined use of hydrofluoric, nitric, and hydrochloric acids.

The first step of digestion includes the addition of 3 mL HF, used to dissolve any silicates, and 6 mL HNO₃ to aid in the dissolution of the remaining material. The tubes were then capped and the 9 mL of solution heated at 130°C for 3 hrs. The caps were then removed and the acid solution heated at decreasing temperatures proportional to remaining aliquot volume, to avoid burning, until completely evaporated, leaving a dried gelatinous material behind. Four mL of concentrated Aqua-regia and 3 mL of 18 Ω ohm water was then added to the dried material and placed on a vortex to aid in the disintegration of any fragments left behind during evaporation. This 7 mL solution was heated to 130°C with partial cap for 3 hours and then reduced to 1-2 mL. This remaining liquid was then added to a 10 mL volumetric flask and brought to a final volume with 18 Ω ohm water.

The final volume of 10 mL was used to obtain values for most trace and some major elements providing a 10x dilution. A 1 mL aliquot of this 10 mL solution was pipetted into a 25 mL volumetric flask and brought to volume for a dilution factor of 250x for most major and some trace values. Data obtained from the ICP (reported in mg/L, were then converted into mg/kg based upon the initial weight of sample digested and the final volume from which the sample for analysis was taken. Oxide values were calculated based upon mg/kg values and formula weight.

We used quality assurance and quality control measures to assure accurate and precise results. Blank and calibration standards were used to calibrate the instrument and establish an analytical curve. The calibration curve was verified using an Initial Calibration Blank Verification (ICBV) solution, and initial instrument performance during an analysis was verified using an Initial Calibration Verification (ICV) solution. We used a Continuing Calibration Verification (CCV) solution after every 10 samples for periodic and final verification of calibration standards. Stock standard solutions were used to check instrument stability and calibration. A maximum of 13 samples were digested each round. One blank and two replicates were used during each phase to determine precision during sample preparation and analysis, with a resulting standard deviation of 0.05 mg/kg.

RESULTS

The geochemical data from VC-3 exhibit variations in concentration during interpreted glacial and interglacial intervals, with most elements having higher concentrations during glacial intervals. Geochemical data have been collected for MIS 10 to MIS 12, extending from the surface to 39 m. Data collection for MIS 13 and MIS 14 is incomplete; currently in progress are data extending from 45 to 60 m.

Marine isotope stages 14 and 13

The data for glacial MIS 14 show variability in Fe_2O_3 and MnO from 80 to 60 m with a spike in concentration at 68.6 m depth (Fig. 2). This spike at 68.6 m can also be seen in MgO but is not as prominent as in Fe_2O_3 and MnO. Approximately one third of the data from interglacial MIS 13 (52-39 m) has been collected. Fe_2O_3 concentration data from MIS 13 show two prominent spikes occurring at 40.6 and 43.5 m with concentrations of 6.67 and 5.75 wt %, respectively. Future data collection will resolve concentration variations at the transition from glacial MIS 14 to interglacial MIS 13 and any variations during interglacial MIS 13 from 60 to 45 m depth. MnO data collected from MIS 13 show a relative decrease in concentration when compared to average concentration in MIS 14 (Fig. 2). MgO data does not show a clear decrease in concentration during MIS 13 as expected for an interglacial interval.

Marine isotope stage 12

Fe_2O_3 data collected for glacial MIS 12 (39 to 27 m) show variation occurring throughout the glacial interval with an average concentration of 4.25 wt %. A sharp increase followed by a sharp decrease in Fe_2O_3 concentration occurs at 27 m, which is the transition from MIS 12 to MIS 11 (Fig. 2). The Fe_2O_3 data lack any distinctive peaks or troughs during this interval. MgO data show a generally decreasing trend moving upcore, with an average concentration of 1.2 wt %, and also has a sharp decrease to 0.59 wt % at 27 m, at glacial termination V (Fig. 2). MnO concentrations during MIS 12 are variable, with an average of 0.0323 wt %. Concentrations appear to increase slightly, with three peaks at 36.3, 31.6, and 27.7 m with concentrations of 0.0785, 0.0818, and 0.1408, respectively. MnO also exhibits a sharp decrease at 27 m, from 0.1408 to 0.0184 wt %, at the transition from MIS 12 to MIS 11 (Fig. 2).

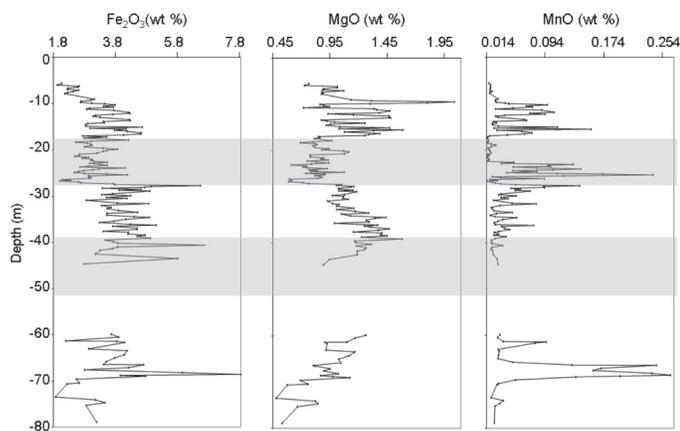


FIGURE 2. Fe, Mg, and Mn oxide wt (%) concentrations. Shaded areas are interpreted interglacial intervals with MIS 11 from 17-27 m and MIS 13 from 39-53 m.

Marine isotope stage 11

Fe_2O_3 and MgO data are variable throughout interglacial MIS 11 (27 to 17 m), with average values of 3.05 and 0.833 wt %. Data collected for MIS 11 show a lower overall concentration than that seen in MIS 12 (Fig. 2). The two highest peaks in Fe_2O_3 at 25.4 and 23.9 m have an average of 4.10 wt %, which is slightly lower than the average value of 4.25 wt % during MIS 12. MnO and MgO show a sharp increase in concentration at 17 m, the transition from MIS 11 to MIS 10, but Fe_2O_3 shows only a modest increase (Fig. 2). MnO concentration during interglacial MIS 11 does not follow the predicted pattern of lower values. After the sharp decrease in concentration at 27 m, MnO concentration increases dramatically from 0.0184 wt % at 26.4 m to 0.2414 wt % at 25.4 m and doesn't decrease until 22.5 m with a value of 0.0146 (Fig. 3). This area of high values is unexpected as it occurs during an interglacial when concentrations are expected to be lower relative to concentrations during glacial intervals. MnO values remain low throughout the remainder of MIS 11. Pb concentration follows a similar pattern to that of MnO throughout the length of the core (Fig. 3). Of particular interest is an increase in Pb concentration at a similar depth interval, with a gradual rise beginning at 26.2 m to attain a final peak at 22.2 m. Concentration increases from 5.6 to 22.3 mg/kg within this 4 m rise (Fig. 3). After attaining the peak concentration at 22.2 m, Pb values decline, reaching a minimum of 0.5 mg/kg at 20.3 m. Pb appears to lag behind MnO, displaying a more gradual rise and decline, unlike the sharp definition seen in MnO (Fig. 3).

Marine isotope stage 10

MIS 10 is represented by the remaining portion of the core, spanning 17 to 5 m depth. For the most part, Fe_2O_3 , MgO, MnO, and Pb concentrations show an average increase during glacial

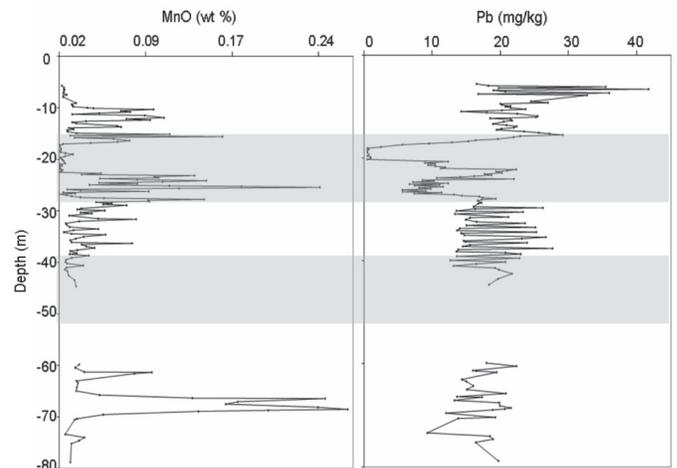


FIGURE 3. MnO wt (%) and Pb (mg/kg) concentrations. Shaded areas are interpreted interglacial intervals with MIS 11 from 17-27 m and MIS 13 from 39-53 m.

interval MIS 10, following the predicted pattern of higher values during glacial intervals and lower values during interglacials. Fe_2O_3 concentration is 2.97 wt % on average with the highest concentration of 4.61 wt % occurring at 15.1 m. MgO average values are 1.15 wt % with a maximum concentration of 2.04 wt % at 9.5 m. MnO averages 0.05 wt % with a peak of 0.157 wt % at 15.5 m. Pb concentration during MIS 10 peaks at 41.8 mg/kg at 6.7 m with an average concentration of 21.5 mg/kg.

Additional trends

Similar trends are seen in Al, K, Na, Ti, Ba, Co, Cr, Cu, Ni, P, S, Y, and Zn, with clear correlation existing between Al and Ti (Fig. 4). Because Al and Ti are considered conservative elements, their concentrations were used to determine if TOC produces a dilution effect. Using loss-on-ignition values obtained with standard procedures, the initial values for Al and Ti were mathematically corrected to account for contribution by TOC. The largest variation observed in Al_2O_3 was 0.47% and 0.54% in TiO_2 . This correction demonstrated that TOC concentrations do not produce a significant dilution effect on Al_2O_3 and TiO_2 concentrations. Concentrations of K, Na, Ba, Co, Cr, Cu, Ni, P, S, Y, and Zn show less variation within cycles, but maintain identifiable decreases at glacial terminations. All elements analyzed exhibit an inverse relationship with TOC (Fig. 1) except for Ca and Sr (Fig. 5), which show a positive correlation with TOC.

DISCUSSION

Iron has two oxidation states that are important to aquatic chemistry, Fe (II) and Fe (III). Ferrous iron, Fe (II), is stable in anoxic water, whereas ferric iron, Fe (III), is the stable oxidation state in oxygenated waters. For this study, manganese has two oxidation states that are important to aquatic chemistry, Mn (II) and Mn (IV). Manganous, Mn (II), ions are stable in anoxic water

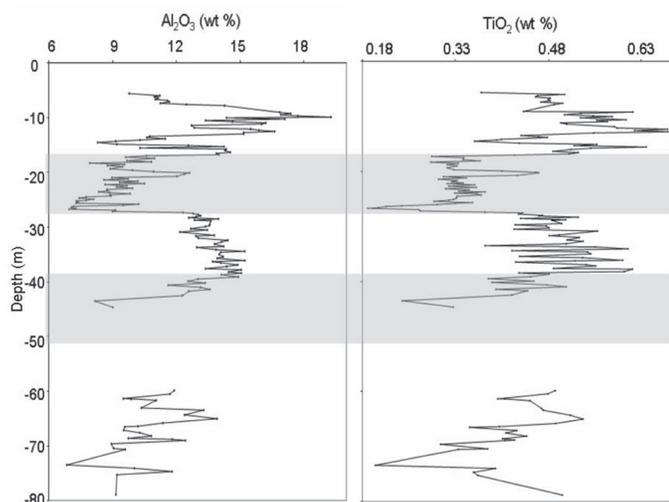


FIGURE 4. Al and Ti oxide wt (%) concentrations. Shaded areas are interpreted interglacial intervals with MIS 11 from 17-27 m and MIS 13 from 39-53 m.

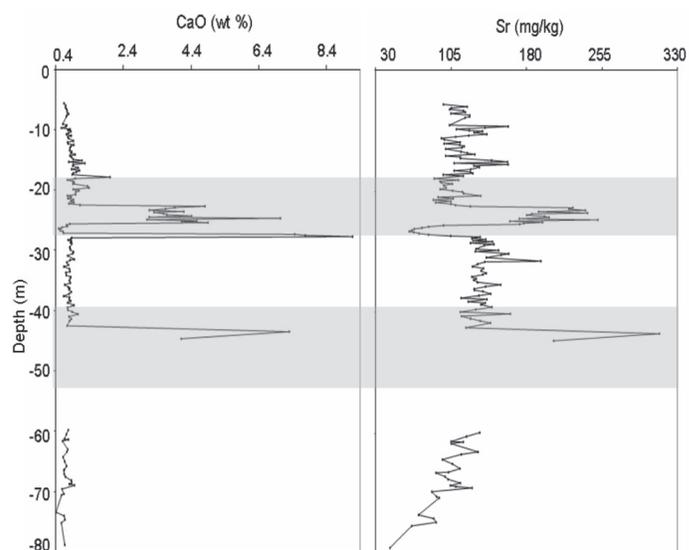


FIGURE 5. CaO wt (%) and Sr (mg/kg) concentrations. Shaded areas are interpreted interglacial intervals with MIS 11 from 17-27 m and MIS 13 from 39-53 m.

whereas Mn (IV), as MnO_2 , is the stable form in oxygenated waters. Manganese oxidation reactions occur more slowly than iron and require somewhat higher oxidizing conditions. Most of the iron and manganese supplied to lakes is in particulate form, sinking directly to the lake floor, and is associated with or bound within the crystal structure of clay minerals. Because these clay minerals accumulate as sediment, the Fe and Mn bound within the crystal structure becomes unavailable for reaction processes. If the sediments are sufficiently reducing, the free, poorly crystalline, hydrated iron hydroxides are available for reduction to ferrous iron (Hamilton-Taylor and Davison, 1995; Davison, 1993). Oxidation states of iron and manganese are influenced by six factors: the degree to which they cycle back and forth across the sediment-water interface, the release of iron and manganese from sediment, external inputs, post-burial diagenetic alteration, seasonal mixing, and metal oxidizing and reducing bacteria (Davison, 1993; Hamilton-Taylor and Davison, 1995; Wetzel, 2001).

Redox reactions are important in the natural environment, and sediment that accumulates at the lake bottom helps reveal the many processes that occur within a lake system. Cohen (2003) proposed that variations occurring in sediment, the sediment-water interface, oxic/anoxic water, and oxidation-reduction states play essential roles in the processes occurring at a redox boundary. For example, the presence and location of the redox boundary in the lacustrine environment determine the oxidation state of important elements like Fe and Mn and therefore determine their solubility and consequent mobility (Drever, 1997). Iron and manganese values provide the most information about the possible lake environment because both have soluble reduced forms and insoluble oxyhydroxides that are readily converted at a redox boundary.

As the presence or absence of Fe and Mn can be used to indicate the degree of oxygenation of bottom waters, Davison (1993)

suggested that a correlation exists between iron and manganese concentrations and the ratio of Fe:Mn. During MIS 11, from ~22 to 17 m depth, the ratio of Fe:Mn is high compared to the total iron concentration (Fig. 6), which indicates reducing conditions were present in the water mass (Davison, 1993). Davison (1993) also observed that when high iron concentration coincides with peaks in the ratio of Fe:Mn the catchment supply has likely changed. It is still unclear what role the Fe:Mn ratio plays in the Valle Grande lake because the catchment supply to the lake may have remained unchanged.

An important but as yet unresolved component of the geochemical mass balance is the large concentration variation observed in some elements. Based on observation of concentrated layers of diatoms in the interglacial periods of the core, we tentatively infer that these large variations are the result of a dilution factor produced by the presence of biogenic silica. The sediment analyzed in this study shows that during interglacial intervals the lake is more productive (Fig. 1), with increased TOC and perhaps biogenic silica as diatoms. If the clastic input to the lake is held relatively constant throughout the 180 kyr span of the core, the biogenic silica percent of total will be greater during interglacial intervals, thereby diluting the remaining elemental concentration. Graphically, a correction for this dilution would be represented by slightly increasing the interglacial concentrations. The amount by which the concentrations would need to be changed is currently unknown, owing to the lack of any tangible biogenic silica values (Fawcett et al., 2007).

Aluminum and titanium data show markedly higher concentrations during glacial intervals and exhibit sharp decreases in concentration at glacial terminations (Fig. 4). Al and Ti, which are primarily allogenic and viewed as conservative, are unreac-

tive and insoluble under most sediment conditions (Engstrom and Wright, 1984). An increase in the concentration of these elements suggests an increase in terrigenous clastic input (Cohen, 2003). X-ray diffraction shows no peaks for high or low cristobalite during interglacial intervals, but does show strong peaks for alpha-quartz. This is almost certainly derived from detrital clastic material. However, if biogenic silica has matured from opaline silica, some of the alpha-quartz may be from biogenic silica (D. Moore, personal commun., 2007). Without being able to resolve the biogenic silica component as a dilutant to element concentration it is unknown at this time whether the substantial variations in concentration are due to changes in environmental factors or primary production. An increase in primary production is most likely, because diatoms are present in greater mass and with more frequency during the interglacial intervals (Fawcett et al., 2007).

We hypothesize that during glacial intervals MIS 10, MIS 12, and MIS 14, reducing sediment is overlain by oxic bottom water, allowing reduced Fe (II) ions that diffuse from the sediment into the water column to immediately oxidize, settle to the lake bottom, and become part of the sediment (Hamilton-Taylor and Davison, 1995; Davison, 1993). Manganese that enters the lake as a component of clastic material is deposited as sediment and reduced after reaching a depth where sediment is effectively reducing (Hamilton-Taylor and Davison, 1995; Davison, 1993). Overall weight percent values for Fe_2O_3 and MnO are higher during glacial intervals (Fig. 2), supporting the hypothesis for an oxic water column during cooler periods. As Fe and Mn combine with organic matter and oxidize they become important carriers for labile elements such as Ba, Co, Mg, Ni, Pb, and Zn, which also increase in concentration during glacial intervals (Hamilton-Taylor and Davison, 1995).

We hypothesize that during interglacial intervals MIS 11 and MIS 13 anoxic bottom water produced a reducing environment, allowing newly produced Fe (II) and Mn (II) ions to diffuse from the sediment into the water column. These upwardly diffusing ions, upon reaching the redox boundary, sink to the lake floor and are deposited or enter a cycle where they may once again be reduced (Hamilton-Taylor and Davison, 1995; Davison, 1993). The slower rates of oxidation and more readily reduced behavior of Mn implies that particles reaching the lake floor are prone to rapid reduction and re-release into the water column, some to again be oxidized and some to exit the lake in solution. In a reducing lake environment it is unlikely that much manganese will remain in the sediment, except the small fraction of allochthonous manganese that may be contained within mineral structures as components of clastic particles (Hamilton-Taylor and Davison, 1995; Davison, 1993). Lower Fe_2O_3 values during interglacial intervals (Fig. 2) supports the hypothesis for an anoxic water column. The establishment of anoxic bottom water likely occurred because of increased organic matter input and subsequent decomposition in the lake.

CONCLUSIONS

Elemental variation preserved in the VC-3 core of lacustrine sediment from the Valle Grande has proven to be an effective

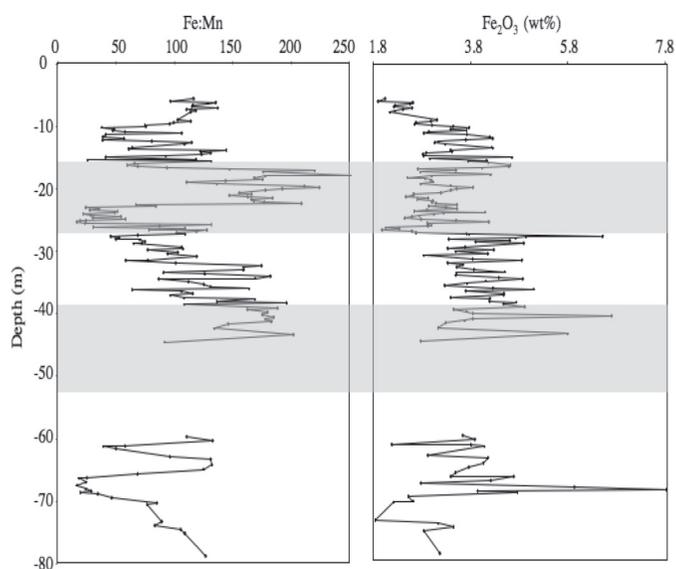


FIGURE 6. Fe:Mn ratio and Fe_2O_3 wt (%) concentration. Davison (1993) suggested that when total iron concentration is low compared to the Fe:Mn ratio, reducing conditions are present in the water mass. Note high Fe:Mn coinciding with low Fe_2O_3 concentration at 17-23 m. Shaded areas are interpreted interglacial intervals with MIS 11 from 17-27 m and MIS 13 from 39-53 m.

proxy for analyzing climate change over glacial-interglacial time scales during the mid-Pleistocene. Particularly helpful were the redox sensitive elements, Fe and Mn, showing increased concentration during glacial intervals (Fig. 2). The results of our geochemical analyses allow us to infer that lake chemistry was more oxidizing during glacial periods. Correspondingly, the lower portion of the water column was primarily reducing during interglacial intervals. The distinct correlation between Al and Ti concentrations show the overall composition of clastic material did not vary throughout the length of the core. However, the amount of Al and Ti entering the lake basin as clastic material may have been lower during interglacials.

Future work includes 1) selecting representative samples from both glacial and interglacial intervals; 2) performing X-ray fluorescence to obtain silica values; 3) using X-ray diffraction to discern changes in clay ratios; and 4) separating biogenic from clastic silica. Geochemistry and sediment mineralogy, sedimentology, TOC, organic carbon stable isotopes, C/N ratios, pollen assemblages (Fawcett et al., 2007), and magnetostratigraphic properties (Donohoo-Hurley et al., 2007), when combined and coordinated, will generate a model of regional climate for the mid-Pleistocene over the 180 kyr time interval sampled by the core.

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