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Climate of the Past Discussions

Rock magnetic properties, magnetic susceptibility, and organic geochemistry comparison in core LZ1029-7 Lake El'gygytgyn, Far Eastern Russia

K. J. Murdock, K. M. Wilkie, and L. L. Brown

University of Massachusetts, Amherst, MA 01003, USA

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Correspondence to: K. Murdock (kmurdock@geo.umass.edu)

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Abstract

Susceptibility measurements performed on initial short (3–16 m) cores taken from Lake El'gygytgyn exhibited a large range in values. This observation led to the suggestion of widespread magnetite dissolution within the sediments due to anoxic conditions within the lake. Rock magnetic properties and their comparison with magnetic susceptibility, Total Organic Carbon (TOC), and bulk $\delta^{13}C_{org}$ proxies in core LZ1029-7 provide an insight into the character of the magnetic minerals present within the lake and can further the understanding of processes that may be present in the newer long core sediments Susceptibility measurements (χ) of discrete samples corroborate the two order of magnitude difference seen in previous continuous susceptibility measurements (κ), correlating high values with interglacial periods and low values with glacial intervals. Hysteresis parameters defined the majority of the magnetic material to be magnetite of PSD size. TOC values increase while $\delta^{13}C_{org}$ values decrease in one section of LZ1029-7, which is defined as the Last Glacial Maximum (LGM), and help confine the age of the core to approximately 62 kyr. Increases in TOC during the most recent glacial interval suggest increased preservation of organic carbon during these times High TOC and low magnetic susceptibility during the LGM support the theory of perennial ice cover during glacial periods, which would lead to lake stratification and therefore anoxic bottom water conditions. Low temperature magnetic measurements also confirmed the presence of magnetite, but also indicated titanomagnetite, siderite and/or rhodochrosite, and vivianite were present. The latter three minerals are found only in anoxic environments, and further support the notion of magnetite dissolution.

1 Introduction

Magnetic susceptibility is a widely used property that, in its most basic of magnetic inferences, gives some indication of the amount of magnetic minerals, mainly the mineral magnetite. Magnetic susceptibility is a common measurement employed in

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paleoclimate reconstruction of terrestrial, marine, and lacustrine environments (Anderson et al., 2002; Chlachula et al., 1998; Demory et al., 2005; Evans, 2001 and the references therein; Geiss and Banerjee, 1997; Langereis et al., 1997; Maher, 1992; 2011; Nawrocki et al., 1996). Often, high values correlate to warm and/or wet periods whereas low values denote cold and/or dry periods (Vlag, 1999; Evans, 2003). However, in some cases, high susceptibilities signify cold, glacial periods while low values indicate interglacials (i.e., Alaska – Begét, 1996; Evans, 1998, 2003). This correlation between climate and relative values of magnetic susceptibility can be made due to the nature of magnetic susceptibility: essentially it is a measure of the amount of magnetic minerals within a sample, which can be related to erosional output from terrestrial sources. There are, however, caveats to what the source of the magnetic particles may have been, such as if it was a terrestrial source, secondary formation of minerals, or possibly biogenic in origin. This leads to the necessity of identifying the types, sizes, and distribution of magnetic minerals present within a location. Several other rock magnetic measurements can be made in order to clarify the identity and origin of magnetic particles, and therefore provide a more comprehensive understanding of lake conditions and from that climate conditions.

Lake El'gygytgyn, located in the Far East Russian Arctic, has provided and continues to provide a wealth of information for paleoclimate reconstruction over the past 3.6 Myr (Melles et al., 2012). Magnetic susceptibility was one of the first properties to be measured on the initial short cores from 1998, later short cores from 2002, and the new long cores (315 m lake sediment) drilled in 2009. Susceptibility measurements showed an extreme range of values – in some cases two orders of magnitude (Nowacyzk et al., 2002); high and low values correspond to interglacial and glacial periods, respectively. Such high susceptibilities in the sediment – on the order of 10^{-4} SI – can be attributed to the large amount of magnetite-bearing volcanic rocks surrounding Lake El'gygytgyn. Low values, however, are more difficult to explain. Nowacyzk et al. (2002, 2007) suggest the low susceptibility values indicate the dissolution of magnetite during glacial periods owing to a stratification of the lake with severely anoxic bottom water. This is a valid and probable theory for the range in susceptibility and has been suggested for other lake systems (Snowball, 1993). Nowaczyk et al. (2007) also suggest that dissolution occurs through most of the short cores, even during some interglacial periods, and that it is not a reliable indicator of terrestrial input.

Although the dissolution of magnetite would cause such fluctuations as seen in the susceptibility measurements of Lake El'gygytgyn, there are some questions left with this theory: if such a large amount of magnetite is being dissolved prolifically throughout the cores, where is the free iron in the lake? Also, the relationship with other climate proxies is not well defined, such as Total Organic Carbon (TOC), which should have a near perfect anti-correlation with magnetic susceptibility. The 2009 drilling of Lake El'gygytgyn long cores presented a need for a more in depth study of magnetic properties of the short core LZ1029 drilled in 2003 in order to better understand the processes affecting the lake and also refine a series of measurements that will later be performed on the new cores. The magnetic data from LZ1029-7 was interpreted and compared to such proxies as TOC and bulk $\delta^{13}C_{org}$ to gain a better understanding of lake conditions.

2 Background

Lake El'gygytgyn was formed as the result of a meteorite impact (Belyi and Chereshnev, 1993; Belyi and Raikevich, 1994; Belyi et al., 1994). The lake itself is approximately 12 km in diameter and 175 m deep. It is located in Central Chukotka, Northeastern Siberia, Far East Russian Arctic (Fig. 1a). Because of the location of Lake El'gygytgyn within this unglaciated region, it is theorized to be an ideal candidate for paleoclimate reconstruction due to the lack of ice sheet cover since its formation, thus providing a continuous terrestrial sedimentary record (Brigham-Grette et al., 2007). In 1998 the first international scientific expedition to the lake occurred as a result of collaboration between Russian, German, and US scientists (Melles et al., 2005). Two cores, PG1351 (12.7 m) and PG1352 (4.1 m) were recovered. A second expedition in 2003, retrieved a multitude of samples including two cores, LZ1024 (16.37 m) and LZ1029 (2.85 m)

– the core under study here – as well as other sediment, rock, and water samples (Fig. 1b). In early 2009, an international team of scientists, drillers, and ice engineers returned to Lake El'gygytgyn for an ICDP supported drilling project. Successful drilling operations recovered a composite core consisting of 315 m of lake sediment as well as ~200 m of bedrock breccia from the meteor impact that created the lake (Melles et al., 2011, 2012).

2.1 General geology

Lake El'gygytgyn is located in a meteorite crater formed 3.58 (±0.04) Myr (Layer, 2000), and has a diameter of 18 km. Various igneous rocks – both extrusive and intrusive – surround the lake and provide the bulk of sediment input. Rock types including rhyolite, andesite, granite, gabbro, basalt (mantles and dikes), dacite, tuff, and combinations of those types can be found, most of which date to the Cretaceous period. The stratigraphy was later explained in detail by Belyi and Raikevich (1994). Geochemical analyses of the sediments provide evidence of significant amounts of aluminum, potassium, sodium, calcium, iron, magnesium, and titanium (Minyuk et al., 2007).

There are roughly 57 ephemeral streams draining into the lake basin from the surrounding catchment (Nolan and Brigham-Grette, 2007). These streams provide the vast majority of the water into Lake El'gygytgyn. There is one outlet, Enmyvaam River, located to the southeast. Due to the climate of the area, deep permafrost surrounding the lake prevents significant flow of groundwater. Therefore, the majority of water going into and coming out of Lake El'gygytgyn flows through the ephemeral streams and single out flowing river (Schwamborn et al., 2006; Federov et al., 2009, 2012; Wilkie et al., 2012).

Presently, lake freeze-up occurs in mid-October at Lake El'gygytgyn and remains ice covered through early to mid-summer (Nolan et al., 2003; Melles et al., 2005). Climate conditions during previous glacial periods have been theorized to produce perennial ice cover (Nowaczyk et al., 2002; Melles et al., 2005) with virtually no significant time of ice-free water at the lake. This ice-covered state would considerably limit the influx

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of terrestrial sediment and aeolian particles into the lake, even during summer months, though continuous deposition throughout the record precludes complete isolation.

2.2 Previous magnetic analyses

Previous magnetic investigations on short cores were performed by Nowaczyk et al. (2002, 2007), with paleomagnetic data from the forthcoming ICDP 5011 core (Nowaczyk et al., 2012). Magnetic susceptibility, Natural Remanent Magnetization (NRM), Characteristic Remanent Magnetization (ChRM), and hysteresis properties were measured on PG1351. One of the intriguing early observations on core PG1351 is the several order of magnitude range of the magnetic susceptibility. High susceptibilities can be explained with the occurrence of volcanic rocks surrounding the lake, with magnetite being the major magnetic contributor. Low susceptibilities, however, could not be explained by the dilution effect of large amounts of organic material and/or biogenic silica in comparison to magnetic materials (Nowaczyk et al., 2002).

Nowaczyk et al. (2007) provided a more accurate time scale for core PG1351 using magnetic susceptibility, TOC, TiO_2, and biogenic silica. The earlier paper (Nowaczyk et al., 2002) based the age model on mostly infrared-stimulated luminescence (IRSL) and pollen, and only partially on magnetic susceptibility and its correlation to the GRIP ice record. It was clear from the first age model that more work was needed to better constrain the older parts of the core. Only magnetic susceptibility was useful for the age model and not paleomagnetic directions, since the first core only represented approximately 250 kyr. The opportunity to revisit the magnetic susceptibility to better pinpoint ages in the core allowed for its reexamination in relation to other proxies. Magnetic susceptibility was compared to several proxies (TOC, TiO_2, biogenic silica) in an effort to explain the large range seen in susceptibility. The working theory developed by Nowaczyk et al. (2002) for the particularly low susceptibilities is that during glacial times with perennial ice cover, Lake El'gygytgyn would have stratified, causing severe anoxia in the bottom waters. With so little oxygen, magnetite could then be dissolved, and thus the magnetic susceptibility values would become extremely low. TiO_2 is typically used

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as a proxy for terrigenous input and should positively correlate to the magnetic susceptibility. However in Lake El'gygytgyn it is not correlated and this has been interpreted as supporting evidence of magnetite dissolution during glacial periods due to severe anoxia.

2.3 Microscopy

In 2005, Dr. Richard Reynolds of the US Geological Survey in Denver, Colorado, prepared several samples of magnetic separates from 1029-7 for reflected microscopy work (unpub.). Preliminary observations of several of the samples indicated the abundance of very small angular magnetite particles in areas of high or relatively high magnetic susceptibility. There were also volcanic fragments – consistent with the parent rocks surrounding Lake El'gygytgyn – that contained tiny magnetite grains. A small amount of titanomagnetite and magnetite grains larger in size to the very small magnetite grains were observed. Three photomicrographs of samples taken from 1029-7 are shown in Fig. 2. Figure 2a shows a volcanic rock fragment approximately 80 µm in length containing small magnetite (bright spots). Figure 2b is of particular note as it shows a partially dissolved titanomagnetite grain with titanium oxide. The last photomicrograph (Fig. 2c) is an example of the very small angular magnetite grains (~ 14 µm) found in various sections of high susceptibility.

2.4 Lake sediment core LZ1029-7

The short core LZ1029 that is used in this study was drilled in 2003 at the same site as PG1351 – drilled five years earlier – so as to repeat the upper 80 cm of core which had been subsampled in the field instead of keeping it in the core liner. Nine separate sections were drilled from the LZ1029 site using either a gravity corer or a piston corer. Five sections were sent to the University of Massachusetts Amherst for study biology of the fluff layer, organic and inorganic geochemistry, and pore water chemistry. The other four cores were sent to Leipzig University for physical properties, paleolimnology, and

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surface sediment composition. LZ1029-7 was one of the untouched percussion piston cores (2.91 m in length) sent to the University of Massachusetts Amherst for organic and inorganic geochemistry, and later provided subsamples for the magnetic data in this study.

2.5 Chronology

Chronology for this core (Fig. 3) was established by correlation to sister cores LZ1029-5/8/9 and to core PG1351 based on sedimentology and stratigraphic markers (e.g., turbidites, one of which is quite apparent in the anomalous peak shown in Fig. 4). Although laminations observed in other short sister cores (e.g., Melles et al., 2007; Juchus et al., unpub.) were only weakly visible and/or absent in core LZ1029-7, similar trends in TOC % and bulk $^{13}C_{org}$ are present and were used to provide additional tie points and further constrain the age-depth model. Ages were calculated by linear interpolation between correlation tie points. The chronology for core PG1351 was derived by tuning the magnetic susceptibility record to Northern Hemisphere insolation, supported by the biogenic silica, TOC and TiO_2 records as well as OSL dates yielding a basal age of 275 kyr (Nowaczyk et al., 2002, 2007; Forman et al., 2007; Frank et al., 2012). Development of an age model for LZ1029-7 sediments allows for direct comparison of multiple proxies both regionally and throughout the El’gygytgyn basin.

3 Methods

3.1 Rock magnetic measurements

Samples were taken from freeze-dried, crushed sediment from core LZ1029-7 housed at the University of Massachusetts Amherst. Each vial represents a 2 cm section of the core. Sample depths can be found in Table 1. Six samples were taken from the earlier PG1351 core at greater depths than LZ1029-7 to extend the longer record as well as comparison to trends within LZ1029-7. Automated logging of magnetic susceptibility

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was measured at the University of Massachusetts Amherst on the whole core. A selection of 33 samples from LZ1029 was taken to the Institute of Rock Magnetism (IRM) at the University of Minnesota in Minneapolis for detailed magnetic measurements. Magnetic susceptibility, Anhysteretic Remanent Magnetization (ARM), and hysteresis properties were measured on all samples brought to the IRM, and nine samples were tested using the Magnetic Properties Measurement System (MPMS) for various low temperature magnetic properties.

3.1.1 Magnetic susceptibility

Magnetic susceptibility was measured over the entire split core of LZ1029-7 at the University of Massachusetts Amherst using an automated logging system equipped with a Barrington Magnetic Susceptibility 2E/1 spot reading sensor at 1-mm increments. This measurement provided a continuous magnetic susceptibility measurement by volume (κ). Magnetic susceptibility measurements on the 31 discrete samples were made with a Geofyzika KLY-2 KappaBridge AC Susceptibility Bridge at the Institute of Rock Magnetism (IRM) at the University of Minnesota. Initial, or low frequency, susceptibility is herein referred to as χ or χ_{lf}, and is mass normalized. Additionally, high frequency susceptibility (χ_{hf}) – also mass normalized – was measured at a frequency ten times that of the low frequency susceptibility (χ_{lf}).

3.1.2 Hysteresis

Hysteresis loops were collected from the twenty-five LZ1029-7 and six PG1351 samples using a Princeton Measurements Vibrating Sample Magnetometer at the Institute of Rock Magnetism at the University of Minnesota. Peak magnetizing fields of 1 T were used, with continuous measurements of magnetization and coercivity.

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3.1.3 Low temperature magnetic properties

Low temperature remanence measurements were made on nine samples – five from LZ1029-7 and four from PG1351 – using a Quantum Designs MPMS2 Cryogenic Susceptometer at the Institute of Rock Magnetism. All samples underwent room temperature saturating isothermal remanent magnetization (RT-SIRM). The remanence was measured as temperature was reduced in 5 K increments to 10 K and then back to room temperature. In addition to RT-SIRM, two other measurements were made on three of the samples. Frequency-dependent magnetic susceptibility versus temperature was measured, again, in 5 K increments down to 10 K from room temperature. Samples were also cooled in either a 2.5 mT field (FC) or no field (ZFC). Remanence was then measured in increments of 5 K upon warming to room temperature after a 5 T field was applied at 10 K.

3.2 Organic geochemistry

Preliminary analysis of this core was undertaken to guide further sampling for organic geochemical analyses. Representative samples were also collected to identify target compounds for use in compound specific isotopic analysis of Lake El'gygytgyn sediments (both $\delta^{13}C$ and δD). These samples were also used to streamline the analytical method to be used on smaller samples collected from a longer sediment core, LZ1024.

Sediment samples from core 1029-7 were freeze-dried, crushed and stored in combusted glassware (2 cm sampling resolution; 139 samples total). Each sample was sub-sampled for both total organic carbon content (%TOC) and bulk $\delta^{13}C_{org}$ analysis.

3.2.1 TOC analysis

After freeze-drying and homogenization in an agate mortar, sediment samples were packed in tin capsules and acidified (1 NH_2SO_3, evaporated to dryness at 55 °C for 12 h) prior to analysis to remove carbonates. Total organic carbon concentrations were determined using a Costech ECS140 Elemental Analyzer (Costech, Valencia, CA). Total organic carbon content was calculated from the integrated response of the sample compared to a calibration curve derived from standard samples of known C and N content (acetanilide: 71.09 % C, 10.38 % N). The precision, calculated by replicate analysis of the internal standard was 0.4 % for TOC.

3.2.2 Bulk $\delta^{13}C_{org}$ analysis

Samples for bulk $\delta^{13}C_{org}$ analysis were also acidified (1 NH_2SO_3, evaporated to dryness at 55 °C for 12 h) prior to analysis to remove carbonates. Bulk $\delta^{13}C_{org}$ values were determined by continuous flow isotope ratio mass spectrometry using a Costech elemental combustion system (ECS140 EA) interfaced to a Thermo Delta V isotope-ratio mass spectrometer (EA-irms). Analyses were run in triplicate and are reported relative to the Vienna PDB (VPDB) standard in ‰ notation. More detailed description of $\delta^{13}C$ methods and results can be found in Holland et al. (2012).

4 Results

The automated magnetic susceptibility logging of core LZ1029 provided an initial look at the range of the susceptibility to compare to the earlier core PG1351 (Fig. 4). The range in volume susceptibility (κ) is 2.0×10^{-6} to 111×10^{-3} SI. Magnetic susceptibility shows a wide variability in range, at least 2 orders of magnitude, as was shown in the previously measured cores, proving reliability between cores and providing further evidence that PG1351 and LZ1029-7 can plausibly be compared.

Thirty three discrete samples from various points in the core LZ1029-7 were measured for magnetic susceptibility (χ) at the IRM (Table 1, Fig. 5). Overall the susceptibility shows a large amount of smoothing as compared to the down core logging of susceptibility which is to be expected due to the large difference in measurement intervals. Continuous susceptibility was measured at every 1 mm, whereas the discrete samples

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were taken from mixed 2 cm intervals. Also, the continuous susceptibility was volume normalized (κ) whereas the discrete samples were mass normalized (χ). The range in susceptibility (χ) for the discrete samples is 1.29×10^{-7} to 2.49×10^{-6} $m^3 kg^{-1}$.

Hysteresis properties are shown in a Day plot (Day et al., 1977) (Fig. 6) using the parameters explained in Dunlop (2002a,b). The shapes of most of the hysteresis loops indicate the major magnetic mineral is magnetite (Fig. 7). For samples from LZ1029-7, magnetic remanence (Mr) versus saturation magnetization (Ms) range from 0.10 to 0.19. PG1351 samples have a similar range, with the exception of a few samples in the multi-domain (MD) range (Nowaczyk et al., 2002). Corresponding coercivity of remanence to coercive force measurements (Bcr/Bc) in LZ1029-7 vary from 2.46 to 3.31. These data reveal the samples fall entirely within the pseudo-single domain (PSD) field, indicating magnetite grains 0.1–20 nm in size. Samples studied here from PG1351 also plot within the PSD field, but show a wider range of values. The PSD grain size is consistent with detrital input of magnetite grains from the crater surrounding Lake El'gygytgyn.

Low temperature magnetic properties data indicate the presence of magnetite, as seen from the strong Verwey transition present at 120 K (Fig. 8). There is some indication of titanomagnetite in several samples where the Verwey transition occurs over the range between 110 K and 120 K. This is consistent with the minerals found in the surrounding lithologies at the lake that would be the main sources of magnetic minerals.

Anomalous changes in the magnetic properties are observed at temperatures between 10 K and 40 K during MPMS runs. Small changes are observed in several samples at 12 K (Fig. 8f), indicative of vivianite (Frederichs et al., 2003). Vivianite can be visibly observed within the cores taken from Lake El'gygytgyn (Minyuk et al., 2007), and for that reason it is plausible to find small amounts of vivianite in various areas of the core. Changes in the magnetic properties at slightly higher temperatures ($\sim$ 25 K) as seen in Fig. 8b,c,e point to the presence of pyrrhotite, siderite and/or rhodochrosite – $Fe_{(1-x)}S$, $FeCO_3$ and $MnCO_3$ respectively. These minerals are paramagnetic at room temperature but become magnetic at low temperatures.

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Total Organic Carbon (TOC) concentrations are very low, ranging from 0.2 % to 1.9 % (Fig. 5). The range of TOC values is slightly smaller in core LZ1029-7 than observed in core PG1351 (ranges from 0.1 % to 2.5 %; Melles et al., 2007) however, the trends are very similar. Repeated movement of the redox boundary within the sediments and extending into the water column has been linked with decomposition of organic matter (Lehmann et al., 2002; Melles et al., 2007). Fluctuations in TOC are anti-correlated with transitions in bulk $\delta^{13}C_{org}$ (Fig. 3). The lower correlation between TOC and bulk $\delta^{13}C_{org}$ in the bottom ~50 cm of core LZ1029-7 may be due to coring disturbance weakly visible in the bottommost section of this core.

5 Discussion

Cores PG1351 and LZ1024 provide information over several glacial/interglacial cycles. Although LZ1029-7 is significantly shorter, this core provides an opportunity for investigation of the most recent glacial/interglacial cycle at high resolution The highest values of TOC lowest values of bulk $\delta^{13}C_{org}$ and magnetic susceptibility highlight the Last Glacial Maximum (LGM), occurring about 20 kyr, at about 1.45 m sediment depth. Both the Holocene (most recent interglacial) and Marine Isotope Stage 3 (MIS3) are well represented above and below the LGM in the core respectively, marking transitions into and out of the glacial period from interglacials.

Comparison of several hysteresis parameters and magnetic susceptibility measurements provides further evidence supporting the presences of one major glacial period in LZ1029-7. Figure 9 shows the relationship between Mr/Ms and Bcr/Bc. Bcr/Bc values (Fig. 9) stay between 2.4 and 3.4, indicative of PSD grain sizes and consistent with the Day Plot (Fig. 6) throughout the core. Mr/Ms show similar consistencies, however are on the low side for PSD grains, tending towards larger grain size (MD) aspects. Where Bcr/Bc and Mr/Ms cross in the middle, around 140 cm, can easily be interpreted as the LGM. χ_{lf} and χ_{ferri} (or $\Delta\chi$, $\chi_{lf} - \chi_{hf}$) (Fig. 10) are extremely close in value, and hardly deter from similar shapes indicating a very minor contribution of susceptibility from paramagnetic sources. χ_{ferri} values were determined by subtracting high-field susceptibility (χ_{hf}, measured from hysteresis loops) from low-field or initial susceptibility (χ_{lf}, measured on the same discrete samples before hysteresis). As in Fig. 9, a low at the same position can be seen in χ_{lf} and χ_{ferri}, indicative of the LGM.

Low-field susceptibility versus the susceptibility of the ferrimagnetic contribution (Fig. 12) can be used to determine the frequency-independent fraction within the samples (Fig. 10) (Forster et al., 1994; Yamazaki and Ioka, 1997). By solving the regression line for the x-intercept (χ_b, or background susceptibility from frequency-independent sources) obtained by plotting these two parameters, the frequency-independent fraction equals approximately 7.07×10^{-8} – an extremely small amount. This indicates that the frequency-independent susceptibility, usually caused by either ferromagnetic material but in this case more likely paramagnetic silicates typically found in volcanic rocks similar to those that surround Lake El'gygytgyn (Forster et al., 1994), does not play a major role in the bulk susceptibility of Lake El'gygytgyn.

Differences can be seen between κ and χ susceptibility measurements (Fig. 5), nevertheless major trends are still present. This is to be expected since the measurement intervals are so drastically different, and because most of the discrete samples taken were preferentially taken from areas of lower susceptibility to better understand lake processes during glacial periods (Table 1). The consistency in the ranges of magnetic susceptibility between PG1351 and LZ1029-7 provides the important insight that the wide range of susceptibilities is consistent between the two cores, and possibly pervasive throughout the lake, at least in the upper part of the sediment record. The areas of high susceptibility can be interpreted as a result of the high magnetic mineral content of the surrounding rocks being transported into the lake during warmer interglacials, consistent with previous investigations of grain size and sediment transport (Asikainen et al., 2007). Areas of low susceptibility indicate a lessening effect in the erosion of the sediment into the lake and correlate to the glacial periods of the region. Yet, the orders of magnitude difference in susceptibility between glacial and interglacial periods does not seem to be resolved solely by fluctuations in sediment transport.

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Perennial ice cover and lake stratification that would have resulted in bottom water anoxia reducing degradation and increasing preservation of organic material also show the highest values of TOC during glacial periods (Melles et al., 2007). During these cold, dry climate modes (Melles et al., 2007), persistent ice cover excluded wind generated mixing as well as seasonal density-driven overturning by warming surface waters. Although extremely limited terrestrial input at these times would be expected, aquatic productivity likely remained relatively high, which may also contribute to higher TOC values. Investigation of the molecular composition of this TOC confirms a higher ratio of aquatic to terrestrial input during glacial periods (Wilkie, 2012; Holland et al., 2012). TOC values are low during warmer, interglacial periods possibly due to greater organic matter degradation within a fully mixed, oxic water column, likely extending to the sediment water interface. Reactive organic matter degrades at similar rates under oxic and anoxic conditions (Kristensen and Holmer, 2001); however, the proportion of organic matter resistant to degradation is much lower under anoxic conditions (Borrel et al., 2011). Notably, only minor fluctuations in TOC values are observed from ~ 60 kyr to 75 kyr, in contrast with a distinctly higher trend in core PG1351. This may be due to lower preservation of LZ1029-7 as laminations noted within this interval in sister cores 1029-5/8/9/ and PG1351 were absent. Large excursions in bulk $^{13}C_{org}$ during glacial intervals along with higher TOC values suggest migration of the redox boundary into the water column and enhanced preservation of organic matter coupled with possibly greater bacterial methanogenesis. Bacterial methane oxidation would produce isotopically light carbon within the lake, eventually resulting in overall reduction of bulk $^{13}C_{org}$ values. Investigation of compound-specific $\delta^{13}C$ signatures will help to better identify and deconvolute the source(s) of the $^{13}C_{org}$ depletion (Holland et al., 2012; Wilkie et al., 2012).

Total organic carbon (TOC) measurements were performed in LZ1029-7, although total carbon (TC) was not measured. At the time, it was believed that carbonate was not present in Lake El'gygytgyn sediments and therefore the major contribution to carbon within the lake was due to aquatic flora and fauna and the influx of terrestrial organic

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matter. During glacial periods, it is theorized the lack of oxygen in the bottom waters of the lake supply an environment where the organic material would be preserved rather than oxidized as it would be during interglacials. Magnetic susceptibility is typically used as an indicator of terrestrial input into the lake, and therefore in this area should be higher during warm and wet climates (i.e., interglacials), and lower during periods of ice cover and cold, dry climates (i.e., glacial) and therefore be anticorrelated with TOC. When the continuous magnetic susceptibility is compared to the TOC (Fig. 5), there is agreement in many parts of the core. Most notably, what is considered to be the Last Glacial Maximum in the TOC record (high peak at about 1.5 m in Fig. 5) does correlate well with the low susceptibility at about the same depth. Discrepancies between TOC and MS may be explained by the presence of large amounts of inorganic carbon, but given that TC was not measured, it cannot be proven explicitly. It would be assumed that such a large amount of inorganic carbon would be in the form of carbonate, yet this was not found in the early geochemical analyses of the lake sediments (Melles et al., 2007; Minyuk et al., 2007).

MPMS data consistently shows the presence of magnetite with a strong Verwey transition at about 120 K (Fig. 8), and there is no indication of the presence of hematite with a Morin transition at 260 K. Hematite would not be expected, given the theory that severely anoxic bottom waters associated with glacial periods would dissolve magnetite and therefore an oxidizing environment in which to create hematite would be lacking. There may be mixing of magnetic minerals that influence the Verwey transition to a slightly lower temperature (such as magnetite and titanomagnetite) (Fig. 8a,d,e). Hematite does not appear to be a major influence if it is even present at all.

As observed in several samples there is anomalous behavior between 20 K and 30 K (Fig. 8b,c,e). Pyrrhotite, rhodochrosite, and siderite all have Néel temperatures within this range: both siderite and rhodochrosite are paramagnetic above their Néel temperatures, where siderite becomes antiferromagnetic and rhodochrosite becomes canted antiferromagnetic (Frederichs et al., 2003). At this temperature the structure of pyrrhotite changes from monoclinic to triclinic (Wolfers et al., 2011). It is unlikely that pyrrhotite should be found in Lake El'gygytgyn in measurable amounts since it is a sulfur-limited system. Lake chemistry measurements suggest a deficiency in sulfur (Melles et al., 2007), and therefore it is unlikely pyrrhotite would be present. Siderite and rhodochrosite are better candidates for minerals present in the lake sediments and coincide with the observed Néel temperatures and may explain the apparent "missing source" of inorganic carbon. In addition, iron and manganese have been measured in lake water geochemistry (Melles et al., 2007), yet iron is most certainly more abundant than manganese. However, using just low-temperature magnetic properties, it is not possible in this study to determine if the Néel temperature observed is related to the presence of siderite or rhodochrosite, or both. The presence of one or both of these minerals, which were originally not thought to be present in the lake since they are carbonates, can provide useful information as to climatic change and lake biogeochemical cycling, since both require anoxic waters for their genesis. Their presence also indicates that carbonate is present in Lake El'gygytgyn and therefore TIC is a necessary measurement to make in order to attain a clear picture of the carbon within the lake.

Some samples also exhibited a change in slope at approximately 15 K (Fig. 8d,f), which most likely indicates the presences of vivianite. Vivianite has been observed in significant proportions (Minyuk et al., 2007) and therefore its presence in low temperature magnetic measurements is more than feasible. However, unlike the widespread vivianite Minyuk et al. (2012) observes, low temperature measurements indicating vivianite are not consistent through all samples measured (Fig. 8a). This may be due to the greater proportions of other magnetic minerals present in the samples tested, including magnetite, titanomagnetite, and possibly even siderite or rhodochrosite.

The presence of the low-temperature magnetic minerals siderite, rhodochrosite and vivianite are indicative of anoxic bottom waters (Frederichs et al., 2003), and therefore support the hypothesis that magnetite is dissolved in Lake El'gygytgyn during glacial intervals. Rhodochrosite forms in anoxic waters that may or may not contain significant sulfur. Siderite, alternatively, cannot form in a sulfidic environment, yet still forms in an anoxic environment. Since Lake El'gygytgyn is a fresh water lake, and water chemistry

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does not indicate a substantial amount of sulfur (Melles et al., 2007), it would be possible for siderite to form, as well as rhodochrosite. Vivianite forms in severely anoxic waters, which may provide evidence for differing depositional environments within the lake.

However, it is still not clear what quantity of magnetite is dissolved, if all of it forms siderite or vivianite or other minerals as of yet unidentified, at what point these minerals are precipitated, and why the magnetic susceptibility is several orders of magnitude different between glacials and interglacials. It should be noted, however, that pollen (Lozhkin et al., 2007) and biomarker investigations (Wilkie et al., 2012b) have documented continued input of pollen and terrestrial leaf wax lipids during glacial intervals and throughout glacial/interglacial cycles. Nowaczyk et al. (2002) and Melles et al. (2005) have postulated that glacial intervals would provide cold enough temperatures year round for perennial ice cover over Lake El'gygytgyn. However, the presence of these terrestrial sources have led to the theory that during full glacial summer months, moat formation around the perimeter of perennial ice cover could provide a mechanism to allow terrestrial signals into the lake (Wilkie et al., 2012). If this theory is valid, then there should be some small but significant input of sediment into the lake that would provide magnetic particles and therefore a more significant magnetic susceptibility measurement than is seen during glacial periods. Because a more significant susceptibility measurement is not found during glacial periods and the presence of minerals that form in anoxic environments (siderite, rhodochrosite, vivianite) can be found throughout the core, magnetite dissolution due to lake stratification is a highly probable theory to explain some of the magnetic measurements.

Susceptibility may provide an effective proxy for some climatic models, but based on the work in this study and of that done previously, there may be other influences that need to be addressed in order to create a reasonable climate proxy. The most glaring issue with susceptibility is the large range measured between glacials and interglacials. Dissolution is a very plausible theory as to why there is such a wide range; however the iron freed from dissolution of magnetite must be utilized somewhere else in the lake, be

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it as free iron in the sediment, the formation of secondary minerals, or the utilization of iron by aquatic life. There is not enough evidence that the amount of siderite or vivianite observed in LZ1029-7 could utilize the amount of free iron from magnetite dissolution.

6 Conclusions

Susceptibility and TOC measurements on LZ1029-7 further validate the initial observations on PG1351of the large oscillations between glacial and interglacial periods. For glacial periods, perennial ice cover with or without moat formation during glacial summer months would prohibit complete mixing within the lake and hence it would become stratified, creating an anoxic bottom water layer. This, therefore, would provide the correct environment for magnetite to dissolve, and thus continues to prove to be a valid theory and is further corroborated by the magnetic minerals found at low temperatures.

Irregularities in MPMS measurements at about 10 K and 32 K indicate the occurrence of minor low-temperature magnetic minerals such as vivianite and siderite (respectively) – the former having been observed in the core by visual inspection and other methods – and possibly rhodochrosite. These minerals can help to identify the bottom water setting (suboxic to severely anoxic) at various times in the past which then can be utilized to reconstruct climate over time that would produce such environments The presence of these minerals further supports the theory of magnetite dissolution in Lake El'gygytgyn; however its pervasiveness over time – and extensiveness throughout the lake – is still not well determined. Additional detailed comparison between carbon measurements (both organic and inorganic) and susceptibility will need to be more thorough to fully address and understand lake biogeochemical cycling at Lake El'gygytgyn, as will the comparison between magnetic susceptibility and TiO_2. More work is required to fully understand the magnetic, geochemical, and biogenic consequences of the dissolution of magnetite, and through that understanding, hopefully better clarify the connection between terrestrial input, organic matter preservation, and magnetic properties within Lake El'gygytgyn.

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Table 1. Samples taken from LZ1029 and PG1351 for discrete susceptibility and other rock magnetic property measurements.

Sample #	Depth (cm)	Approx. Age (yr)	Susceptibility (χ) × 10^{-5}
LZ1029-5	9	2459	0.1357
LZ1029-12	23	4360	0.1418
LZ1029-14	27	4889	0.1509
LZ1029-24	47	8299	0.1529
LZ1029-25	49	8682	0.179
LZ1029-26	51	9064	0.1621
LZ1029-27	53	9617	0.1313
LZ1029-28	55	10 341	0.08729
LZ1029-32	63	11 739	0.05546
LZ1029-43	85	14 997	0.09155
LZ1029-49	97	16 769	0.06683
LZ1029-56	111	18 834	0.05695
LZ1029-60	119	19 821	0.0261
LZ1029-64	127	20 692	0.02787
LZ1029-65	129	20 910	0.02821
LZ1029-68	135	21 564	0.02001
LZ1029-69	137	21 782	0.0252
LZ1029-70	139	22 252	0.02063
LZ1029-71	141	22 973	0.02049
LZ1029-73	145	23 905	0.02178
LZ1029-81	161	28 044	0.03825
LZ1029-91	181	33 836	0.09028
LZ1029-94	187	35 573	0.07539
LZ1029-96	191	36 732	0.05825
LZ1029-98	195	37 890	0.07096
LZ1029-103	205	40 786	0.05852
LZ1029-108	215	43 722	0.09202
LZ1029-109	217	44 318	0.08688
LZ1029-111	221	45 509	0.08644
LZ1029-114	227	47 295	0.1134
LZ1029-115	229	48 742	0.1097
LZ1029-119	237	57 939	0.2489
LZ1029-122	243	63 338	0.1013
LZ1351-391	392	95 790	0.01724
LZ1351-477	478	111 349	0.03065
LZ1351-481	482	111 651	0.08879
LZ1351-585	586	137 004	
LZ1351-609	610	149 993	0.01292
LZ1351-111	1119	279 770	

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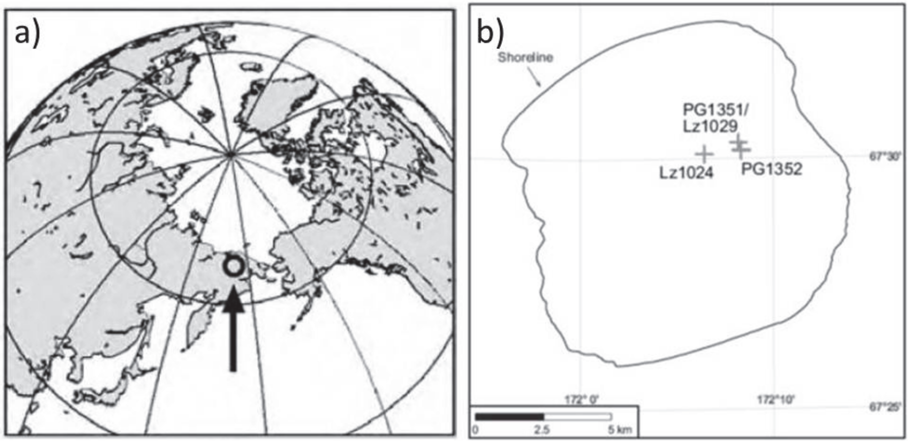

Fig. 1. (a) Location of Lake El'gygytgyn in Far East Russian Arctic, 67°30′ N, 172°5′ E. **(b)** Location of collected cores in Lake El'gygytgyn. Cores PG1351 and PG1352 were drilled in 1998, cores LZ1024 and LZ1029 were collected in 2003, and long cores were drilled in 2009.

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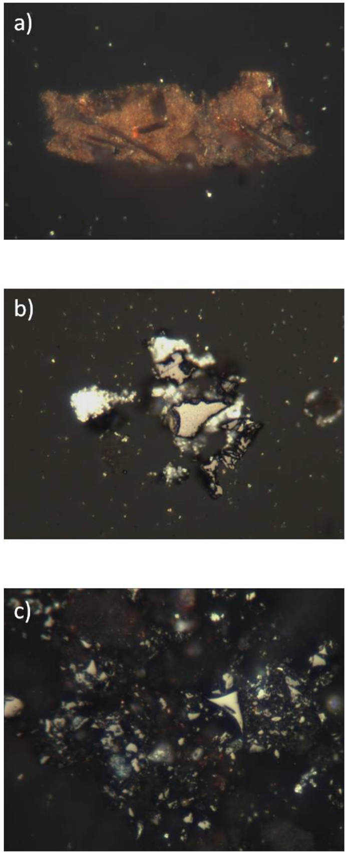

Fig. 2. Photomicrographs of LZ1029-7 of magnetic separates. **(a)** Volcanic rock fragment measuring approximately 80 µm in longest dimension. **(b)** Partially dissolved titanomagnetite with precipitated titanium dioxide (bright white versus dull white) about 74 µm along longest dimension. **(c)** Small, angular magnetite grains. Bright white triangular magnetite grain measures approximately 14 µm along long dimension.

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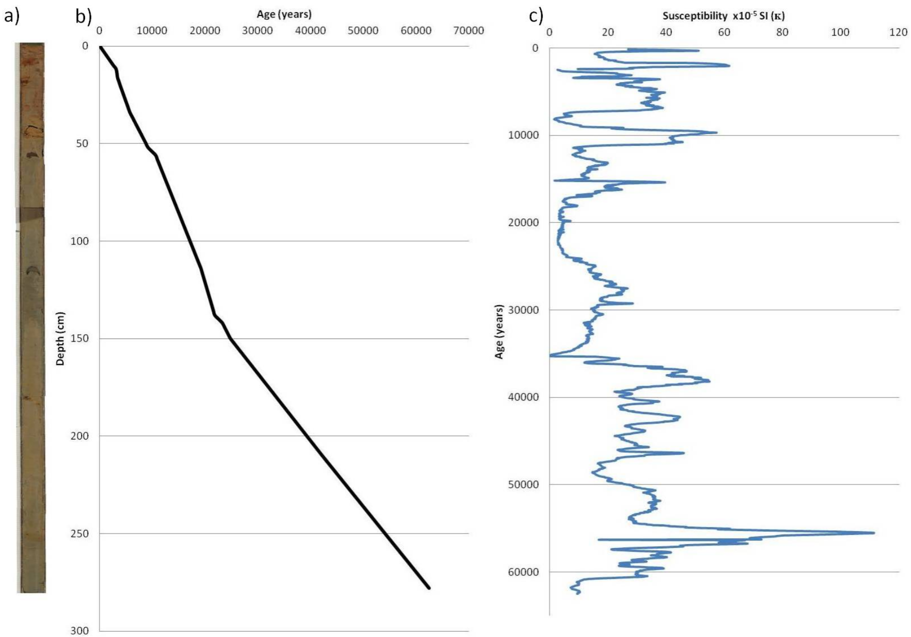

Fig. 3. Depth-age model developed for 3 m core LZ1029-7 based on linear interpolation of ages between tie points between cores LZ1029-5/8/9 and PG1351. **(a)** High resolution scanned image of core LZ1029-7 prior to sampling. **(b)** Depth-age model for core LZ1029-7. Correlation between cores was based on sedimentology and stratigraphic markers (e.g., turbidites, ash layer) and fluctuations in the TOC and bulk $\delta^{13}C_{org}$ data. **(c)** Magnetic susceptibility (κ_{lf}) of LZ1029-7.

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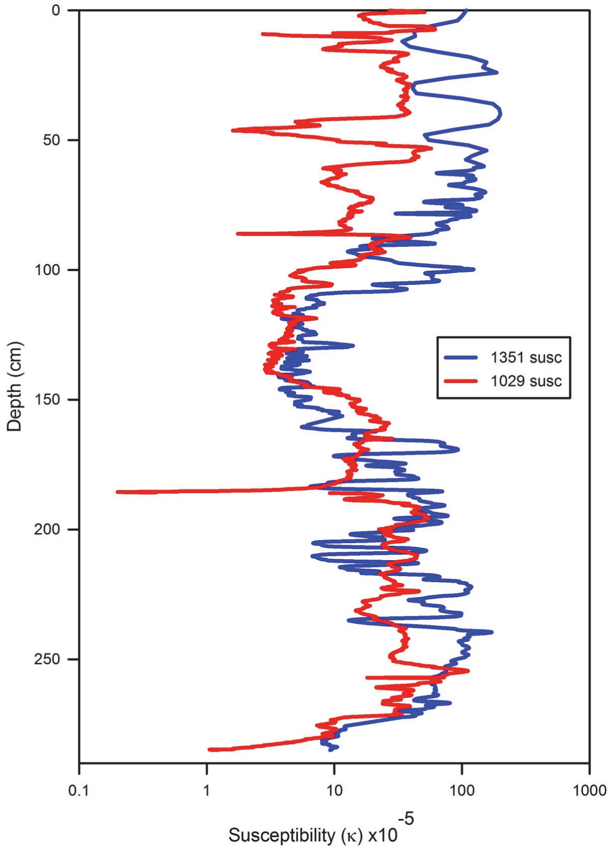

Fig. 4. Comparison of susceptibility (κ) between PG1351 (Nowaczyk et al., 2002, 2006) and LZ1029.

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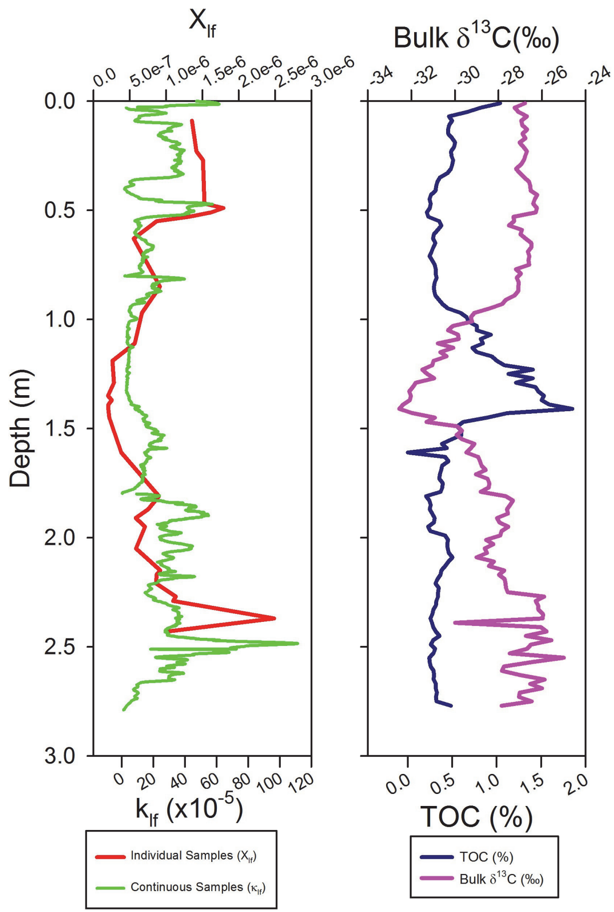

Fig. 5. Comparison of magnetic susceptibility (χ and κ, red and green curves, respectively), bulk $\delta^{13}C_{org}$ (pink), TOC (purple).

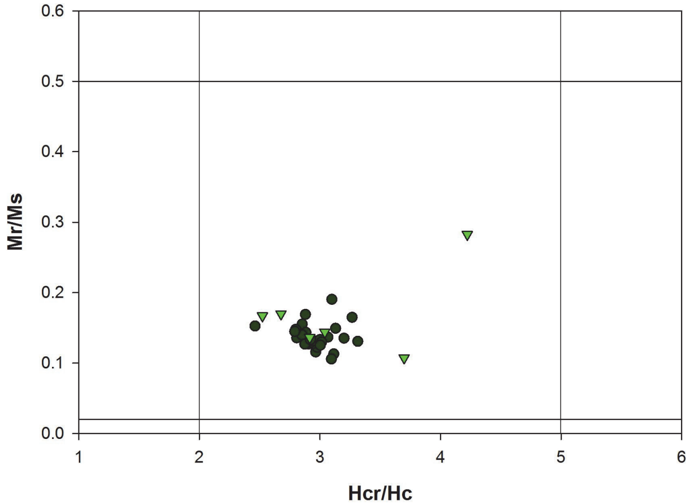

Fig. 6. Day plot of LZ1029 (dark green circles) and PG1351 (light green triangles) all plotting within the PSD range.

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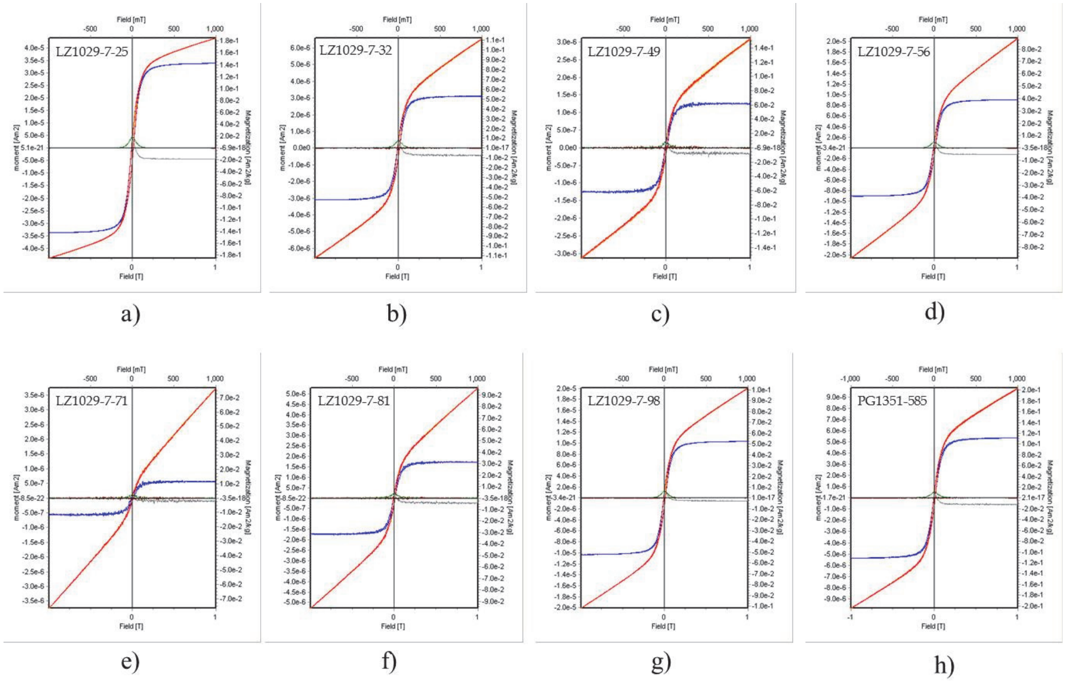

Fig. 7. Selected examples of hysteresis loops from high susceptibility areas **(a, b, g, h)**, transitional **(c, d, f)** and low susceptibility areas **(e)** in LZ1029.

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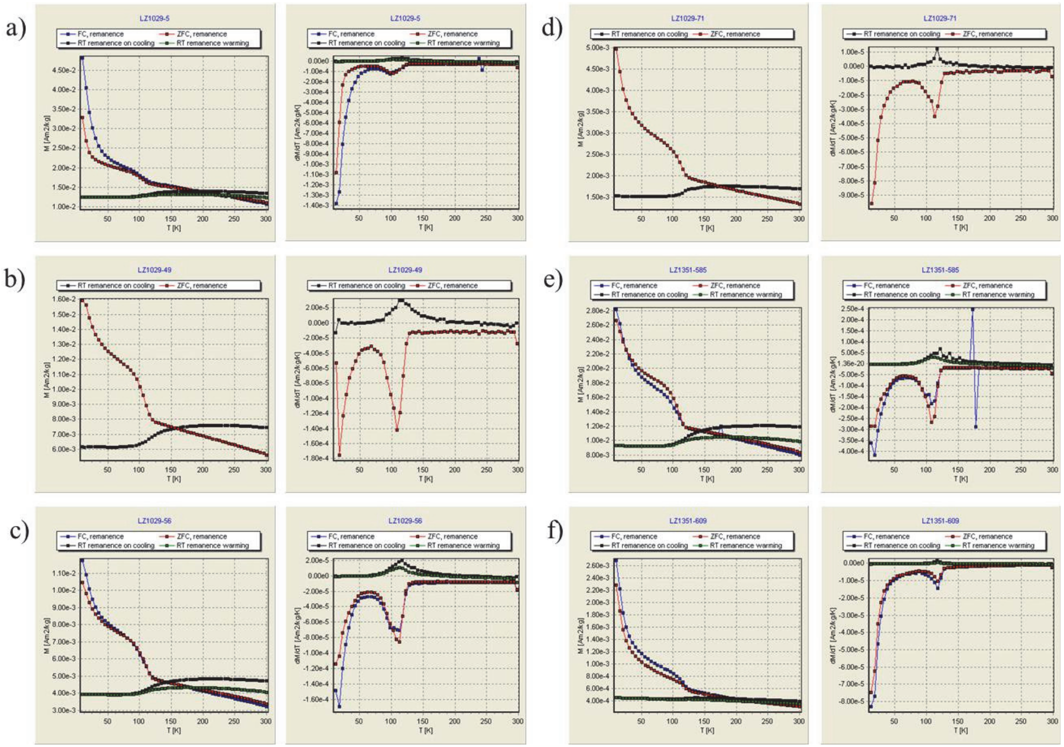

Fig. 8. A selection of MPMS graphs from LZ1029 and PG1351. Left-hand columns show original graphs from MPMS measurements. Right-hand columns show the derivatives of the left graphs to better indicate changes in slope between 10 and 35 K, indicating the presence of room-temperature paramagnetic minerals vivianite and siderite (or rhodochrosite), which become magnetic at about 12 and 32 K, respectively. Samples from LZ1029 were from depths of **(a)** 5 cm, **(b)** 49 cm, **(c)** 56 cm, and **(d)** 71 cm. Samples from PG1351 were from depths of **(e)** 585 cm and **(f)** 609 cm.

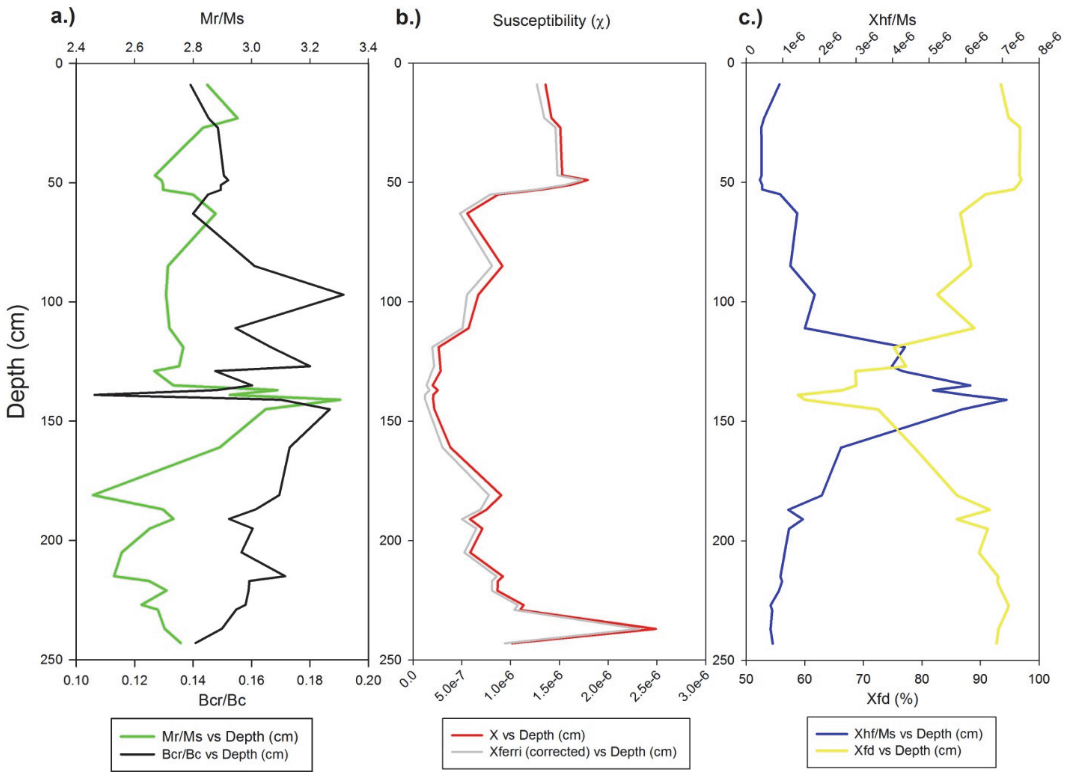

Fig. 9. Hysteresis and susceptibility measurements versus depth. **(a)** Mr/Ms and Bcr/Bc versus depth, with the most significant peak/trough at 1.4 m, coinciding with the Last Glacial Maximum (LGM). **(b)** Initial or low field susceptibility (red) as compared to susceptibility of the ferrimagnetic components (gray), showing little difference and therefore a very small contribution of paramagnetic material to the susceptibility.

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Rock magnetic properties in core LZ1029-7 Lake El'gygytgyn

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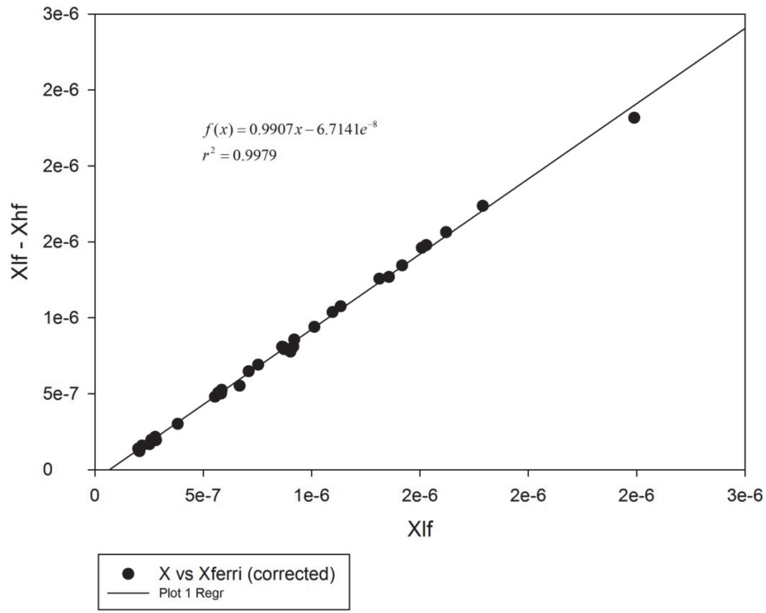

Fig. 10. $\chi_{\mathrm{lf}} - \chi_{\mathrm{hf}}$ (also known as χ_{ferri} or $\Delta\chi$) versus initial susceptibility (χ_{lf}). Solving the regression line for the x-intercept (χ_{b}, or the frequency-independent fraction of susceptibility) gives a value of 7.07×10^{-8}.

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