

## Greigite ( $\text{Fe}_3\text{S}_4$ ) as an indicator of drought – The 1912–1994 sediment magnetic record from White Rock Lake, Dallas, Texas, USA

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### Abstract

Combined magnetic and geochemical studies were conducted on sediments from White Rock Lake, a reservoir in suburban Dallas (USA), to investigate how land use has affected sediment and water quality since the reservoir was filled in 1912. The chronology of a 167-cm-long core is constrained by the recognition of the pre-reservoir surface and by <sup>137</sup>Cs results. In the reservoir sediments, magnetic susceptibility (MS) and isothermal remanent magnetization (IRM) are largely carried by detrital titanomagnetite that originally formed in igneous rocks. Titanomagnetite and associated hematite are the dominant iron oxides in a sample from the surficial deposit in the watershed but are absent in the underlying Austin Chalk. Therefore, these minerals were transported by wind into the watershed.

After about 1960, systematic decreases in Ti, Fe, and Al suggest diminished input of detrital Fe-Ti oxides from the surficial deposits. MS and IRM remain constant over this interval, however, implying compensation by an increase in strongly magnetic material derived from human activity. Anthropogenic magnetite in rust and ferrite spherules (from fly ash?) are more common in sediment deposited after about 1970 than before and may account for the constant magnetization despite the implied decrease in detrital Fe-Ti oxides.

An unexpected finding is the presence of authigenic greigite ( $\text{Fe}_3\text{S}_4$ ), the abundance of which is at least partly controlled by climate. Greigite is common in sediments that predate about 1975, with zones of concentration indicated by relatively high IRM/MS. High greigite contents in sediment deposited during the early to mid-1950s and during the mid-1930s correspond to several-year periods of below-average precipitation and drought from historical records. Relatively long water-residence times in the reservoir during these periods may have led to elevated levels of sulfate available for bacterial sulfate reduction. The sulfate was probably derived via the oxidation of pyrite that is common in the underlying Austin Chalk. These results provide a basis for the paleoenvironmental interpretation of greigite occurrence in older lake sediments. The results also indicate that greigite formed rapidly and imply that it can be preserved in the amounts produced over a short time span (in this lake, only a few years). This finding thus suggests that, in some lacustrine settings, greigite is capable of recording paleomagnetic secular variation.

### Introduction

Many methods can be used to decipher environmental-change records in lake sediments. One method, commonly referred to as environmental magnetism, involves a combination of magnetic and petrologic

analysis to determine the types, distributions, and origins of magnetic minerals. Environmental magnetic studies have been especially effective when applied to problems in climate change, in landscape disturbance related to land-use changes, and in the dispersal of

pollutants (e.g., Thompson & Oldfield, 1986; Verosub & Roberts, 1995).

Magnetic studies of lake sediments to understand climate change usually focus on variations in the detrital iron oxide minerals that may reflect changing conditions of weathering, erosion, sediment transport, and deposition (e.g., Reynolds & King, 1995). However, post-depositional alteration can modify or obscure the detrital magnetic signals (Reynolds & King, 1995; Verosub & Roberts, 1995; Rosenbaum et al., 1996). One kind of lake-sediment diagenesis results in the dissolution of detrital magnetite via iron removal in the presence of organic acids. Another kind, which involves the formation of iron sulfide minerals, may diminish or enhance the original magnetization depending on the type of iron sulfide formed. The replacement of magnetite by pyrite (FeS<sub>2</sub>), for example, suppresses the detrital magnetic signal (Reynolds et al., 1994a). In contrast, the authigenesis of two magnetic sulfide minerals, greigite (Fe<sub>3</sub>S<sub>4</sub>) and a variety of pyrrhotite (Fe<sub>7</sub>S<sub>8</sub>) (see Krs et al., 1990; Tuttle et al., 1990; Tuttle & Goldhaber, 1993), leads to increased magnetization.

Greigite was first described in western literature from Pliocene lake beds in California (Skinner et al., 1964). Other lacustrine occurrences include modern sediments (Dell, 1972; Ariztegui & Dobson, 1996), Holocene sediments (Giovanoli, 1979; Snowball & Thompson, 1990; Hilton, 1990; Snowball, 1991), as well as middle and late Pleistocene sediments (Roberts et al., 1997). Greigite is also reported in modern (Jedwab, 1967) and ancient (Krs et al., 1990) swamp deposits. Greigite is considered metastable with respect to pyrite, to which greigite converts in the presence of HS<sup>-</sup> above pyrite saturation and an oxidizing agent (Berner, 1981; 1984). Nevertheless, its occurrence in old lacustrine and marine sediments indicates that greigite can persist under favorable conditions. In fact, sulfur isotopic studies of greigite in marine mudstone in the North Slope Basin, Alaska, document its diagenetic origin during the Cretaceous (Reynolds et al., 1994b).

We know little, however, about the environmental conditions that control the formation and preservation of greigite in lacustrine settings. Possible influences include redox conditions as controlled by climate (Jelinowska et al., 1995) and human activity (Ariztegui & Dobson, 1996), or the availability of certain essential components (such as dissolved sulfate) that may depend on limnic conditions, such as whether a lake is hydrologically closed or open. Detailed study

of modern settings (e.g., Ariztegui & Dobson, 1996), from which to interpret past records, is sparse. Berner (1970, 1974, 1978, 1984) and Canfield & Raiswell (1991) discuss the general conditions of the formation of pyrite and its monosulfide precursors, such as greigite, mainly from the perspective of marine sediments.

In this paper we present results of a magnetic study of sediments in White Rock Lake, Dallas (USA), that were deposited during the past 80 years. This study was designed to test whether changes in land use and in lake-sediment geochemistry are reflected by changes in the type, amount, and grain size of detrital iron oxide minerals (e.g., Thompson & Oldfield, 1986; Kodama et al., 1997). We found a more complicated magnetic mineral assemblage than was anticipated. The magnetic record results both from detrital input of iron oxide minerals, partly related to the kind and intensity of land-use practices, and from diagenetic greigite, the concentrations of which are strongly related to climate. Although the focus of this paper is on the diagenetic signal, we also discuss the detrital part of the magnetic record, because it is important to illustrate how the two signals were recognized.

## Background and setting

White Rock Lake and surrounding parks encompass a major recreational area in suburban Dallas (Figure 1), but current recreational uses are jeopardized as the 4.4-km<sup>2</sup> lake fills with sediment. The recreational importance of the White Rock Lake watershed motivated studies to quantify water-quality trends of White Rock Creek. In the absence of historical data, van Metre & Callender (1997) and Bradbury & van Metre (1997) reconstructed the water-quality history of White Rock Creek from geochemical and paleolimnological studies of three dated lake-sediment cores. These studies provide much of the background material for this report, in terms of local climate; development, management, and land-use practices of the watershed and lake; limnology; sampling; as well as the lake-sediment chronology, lithology, and geochemistry. Some of these aspects are summarized here, because they bear directly on the magnetic-property results and interpretations.

### *Land-use and geologic setting of the catchment*

In 1912 White Rock Creek in Dallas County, Texas, was dammed by a 12-m high concrete weir, impound-

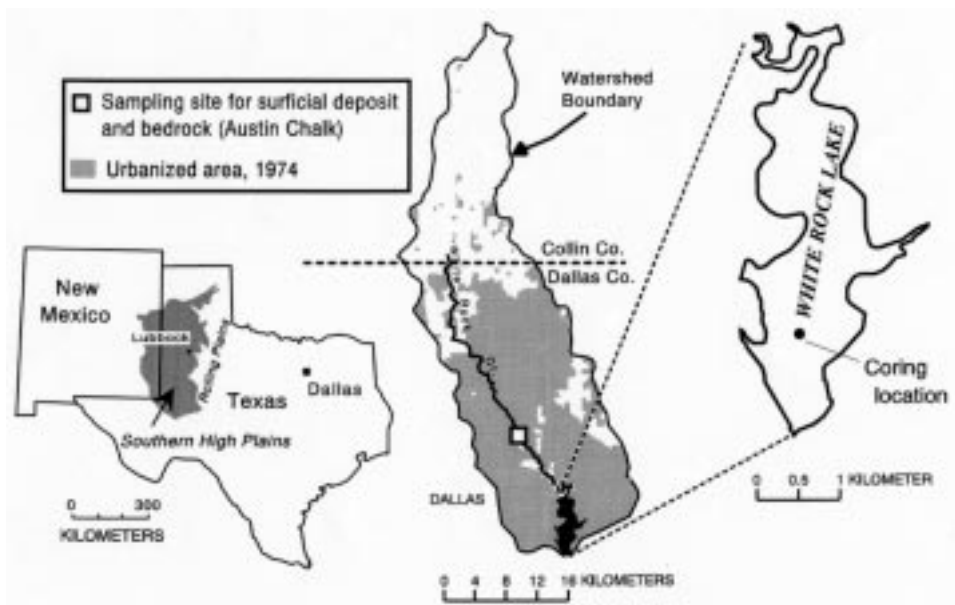


Figure 1. Location of White Rock Lake and White Rock Creek, Dallas, Texas. (Modified from van Metre & Callender, 1997). The coring site is at Lat.  $32^{\circ} 49' 33''$  N., Long.  $96^{\circ} 43' 25''$  W.

ing White Rock Lake to supply water for the development of urban Dallas. At the time, the 259-km<sup>2</sup> watershed was used predominantly for cotton farming and cattle grazing. After about 1950, the dominant land use shifted from agriculture to suburban housing, and by 1990 about 72 percent of the watershed was suburban. Since 1964 the lake has been used for public recreation.

By 1993, sediment input had reduced the original capacity ( $22.4 \times 10^6$  m<sup>3</sup>) of the lake by about half, related to lack of soil conservation from 1912 to the 1940s (Marshall & Brown, 1939) and to rapid suburban growth since then. Today, White Rock Lake has a maximum depth of 6 m, in contrast to the maximum depth of 10 m in 1939 (Patterson, 1942). Three major dredging operations have been conducted to offset the high rate of sediment input; the major operations took place in the northern part of the lake near the mouth of White Rock Creek, and each operation was remote from the coring site. Major dredging occurred during 1936–1941 ( $446\,000$  m<sup>3</sup>) and 1974 ( $1.03 \times 10^6$  m<sup>3</sup>). Dragline methods extracted about  $11\,740$  m<sup>3</sup> of sediment during 1955–1956.

The Cretaceous Austin Chalk, a marine limestone (Durham, 1957; Cloud, 1975), comprises bedrock in the catchment. The Austin Chalk is covered by surficial deposits that have been mapped as different soil units on the basis of soil properties (Marshall and

Brown, 1939). The surficial deposits are at least partly eolian, as discussed later. Both the Austin Chalk and the surficial deposit were sampled at one location in the bank of White Rock Creek, 6 km upstream from the mouth of the creek (Figure 1). The sample from the surficial deposit was taken in soil 0.5 m below the land surface (van Metre & Callender, 1997).

#### Limnology

Because of its shallow depths, White Rock Lake is probably polymictic, mixing at intervals through the year under high winds (Bradbury & van Metre, 1997). When the lake was deeper, however, a 4- to 9-m thick thermocline probably contributed to temporary stratification and to oxygen depletion in the hypolimnion during the summer (Patterson, 1942; Bradbury & van Metre, *op. cit.*). During a period of the early 1940s, Patterson (*op. cit.*) made a series of limnologic observations, including surface water temperature and pH. Surface water temperatures ranged from 8.8 °C in February to 28.5°C in July. Measurements of pH (7.2 to 8.3) from this earlier period compared to pH values (6.7 to 9.0) taken between 1973 and 1993 show little change (Bradbury & van Metre, *op. cit.*). Measurements of nutrients, suspended solids, chloride, and NO<sub>3</sub> were not made before 1973 (see Bradbury & van Metre, *op. cit.*).

*Sampling, lithology, and chronology of the core*

In 1994, three gravity cores, 6.5-cm in diameter, were taken in the southern part of White Rock Lake (Figure 1) at a water depth of 5 m. Each of the cores penetrated the pre-reservoir surface at 136 cm down core. One core was split and described on site and then was analyzed for organochlorine compounds as well as carbon, and a second core was analyzed for  $^{137}\text{Cs}$ . The third core was sub-sampled at 2-cm intervals from 0 to 136 cm and at 4-cm intervals from 136 to 156 cm and then analyzed for major and minor elements, grain size, diatoms, and pollen (van Metre & Callender, 1997; Bradbury & van Metre, 1997) as well as for magnetic properties for this study.

The core contained olive-gray and olive-black silty clay that oxidized to dark yellowish brown hues after exposure to air. In this core three zones were distinguished on the basis of color: a gray and black mottled appearance in the interval from 0 to 51 cm; a dark zone from 51 to 59 cm, and uniform olive gray to tan hues below 59 cm. The dried samples used for magnetic measurements generally followed this description, although black sediment was noted at a depth of 60 to 64 cm. Organic carbon contents range from 1.1 to 3.4 weight percent (van Metre & Callender, 1997: 242, Figure 2). Sediment color shows no correspondence to organic carbon content.

The chronology of the core was established on the basis of the following observations (van Metre & Callender, 1997): (1) the construction date of the reservoir (1912) at the depth of the pre-reservoir surface (136 cm); (2) the top of core at 1994; (3) the year 1963 in the sample from 48-51 cm (mid-range at 49.5 cm), based on the peak of atomic-bomb produced  $^{137}\text{Cs}$ ; (4) the year 1952 in the sample from 60-63 cm (mid-range at 61.5 cm), based on the first appearance of  $^{137}\text{Cs}$ ; and (5) linear interpolation between these points. Linear sedimentation rates derived from the age model are  $1.9 \text{ cm yr}^{-1}$  before 1952,  $1.0 \text{ cm yr}^{-1}$  between 1953 and 1963, and  $1.6 \text{ cm yr}^{-1}$  after 1963.

**Methods**

Elemental concentrations were determined using the techniques of inductively coupled plasma-atomic emission spectrometry, for which samples were digested using nitric, hydrofluoric, and perchloric acids (Lichte et al., 1987). Sulfur data were obtained using induction-furnace techniques coupled to an infrared-detection system (Jackson et al., 1987).

Combined petrographic and magnetic methods were used to determine the types, amounts, and grain sizes of magnetic minerals. The identification of magnetic particles was primarily done with reflected-light microscopy. Although identification of different Fe-Ti oxide minerals cannot reliably be made on grains smaller than about  $3 \mu\text{m}$ , the oxides can be easily distinguished from sulfide minerals at much smaller sizes because of strong differences in color and reflectivity. The grains were prepared in polished grain mounts after they had been isolated from the bulk sediment in a magnetic separator similar to that described by Petersen et al. (1986). X-ray diffraction analysis using Cu  $K\alpha$  radiation of both bulk sediment and magnetic-mineral separates was also applied to identify magnetic minerals.

Information on the abundance of different magnetic minerals, as well as on magnetic grain size (magnetic domain state), is provided by magnetic-property measurements (see Thompson & Oldfield, 1985; Verosub & Roberts, 1995). These measurements were made on dried bulk sediment packed into  $3.2\text{-cm}^3$  plastic cubes. MS is a measure of all magnetic material but mainly ferrimagnetic minerals such as magnetite when it is present; MS was determined in a 0.1 milliTesla induction at frequencies of 600 Hz and 6000 Hz, using a susceptometer with a sensitivity better than  $4 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$ . A measure of the quantity of magnetite sufficiently large (magnetic grain size greater than about 30 nm) to carry remanence is isothermal remanent magnetization (IRM), the magnetization acquired by a sample after exposure to a strong magnetic field. In this study, remanent magnetization was measured using a 90-Hz spinner magnetometer with a sensitivity of about  $10^{-5} \text{ A m}^{-1}$ . The parameter IRM/MS has been found to be an approximate measure of greigite when it coexists with magnetite (Snowball & Thompson, 1990; Reynolds et al., 1994b; Roberts, 1995; Roberts et al., 1996). High ratio values often indicate the presence of greigite, because it usually occurs in much smaller magnetic grain sizes than detrital Fe-Ti oxides, thus enhancing IRM, while contributing relatively little to MS. Hard IRM (HIRM) is a measure of high-coercivity ferric oxide minerals, such as hematite. Whereas magnetite and maghemite saturate magnetically below applied fields of about 0.3 Tesla (T), hematite and related minerals continue to acquire IRM above 0.3 T. In this study, HIRM is calculated:  $(\text{IRM}_{1.2T} - \text{IRM}_{0.3T})/2$ . We determined frequency-dependent MS (FDMS) to test for the presence

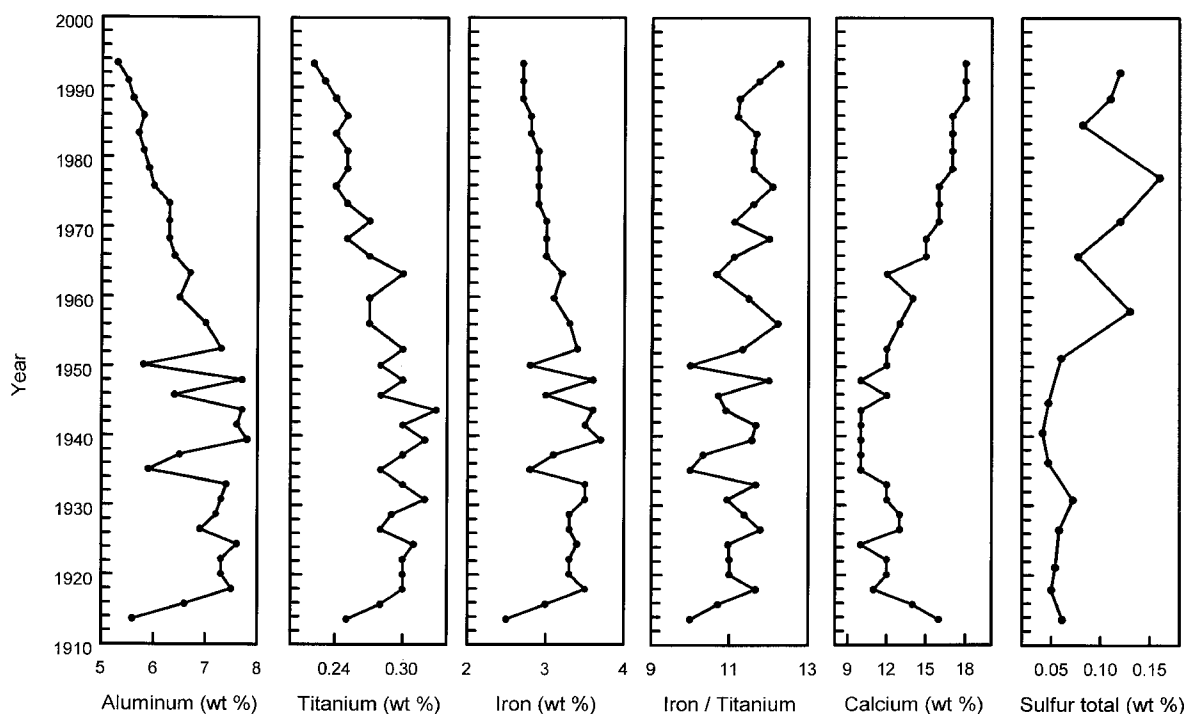


Figure 2. Depth profiles of elemental concentrations in core samples. All data are from van Metre & Callender (1997) except sulfur (this study).

of ultrafine (<30 nm) superparamagnetic magnetite or maghemite grains near the superparamagnetic-single domain (SP-SD) boundary. Higher MS at low frequency than at high frequency (typically expressed as a percentage,  $FDMS\% = ((MS_{600\text{ Hz}} - MS_{6000\text{ Hz}}) / MS_{600\text{ Hz}}) \times 100$ ) provides an estimate for concentrations of SP grains.

### Summary of major-element geochemical results

Elemental variations (Figure 2) reflect changes in land-use practices from dominant agriculture before 1950 to dominant suburban development thereafter (van Metre & Callender, 1997). The older part of the core (pre-1952) contains relatively high contents of elements (Al, Mg, Fe, and Ti) apparently derived from the surficial deposits, including soils and associated clays. Sediments in this part of the core are characterized also by abrupt variations in elemental composition, while exhibiting no long-term trends, and by nearly constant Ca content. In contrast, the younger part of the core is characterized by gradual decreases in the contents of Al, Mg, Fe, and Ti, as well

as by gradual increases in Ca and inorganic carbon, the dominant components in the underlying Austin Chalk.

Van Metre & Callender (1997) considered two possible explanations for the elemental trends after 1952. In the first explanation, accelerated erosion during agricultural land use promoted the loss of the upper soil horizons that exposed the less weathered substrate to subsequent erosion. The second explanation is that the decline in agricultural activity led to decreased soil erosion, while suburban development led to greater erosion of bedrock.

### Magnetic minerals

#### *Detrital iron and iron-titanium oxides*

Detrital iron oxide grains show many types and origins, having been derived via both natural processes and human activity. Based on reflected-light microscopy, titanium-bearing magnetite is the most common magnetic mineral in lake sediment (Figure 3). Compositionally and texturally similar Ti-magnetite in the surficial deposit indicates that the Ti-magnetite in the lake sediments was derived from the erosion of this

deposit. The textures, compositions, and mineral associations of the Ti-magnetite are evidence of its original formation in igneous rocks: (1) Many magnetite grains contain ilmenite and (or) related titanium-rich iron phases that are only produced via high-temperature oxidation in igneous source rocks; and (2) ilmenite grains are found in both the surficial deposits and the lake sediment along with Ti-magnetite. Some forms of hematite occur in association with the magnetite and ilmenite; it is found as intergrowths with ilmenite, formed initially in igneous rocks; as intergrowths with magnetite, resulting from high-temperature oxidation in igneous source rocks; and as specular hematite grains, all of which indicate origins in rocks other than the Austin Chalk. The titaniferous magnetite and associated ilmenite and hematite, derived from igneous source rocks, must have been wind blown into the surficial deposits.

Ferric oxide is also seen as replacement of framboidal pyrite in the lake sediment, in the surficial deposits, and in rock samples of Austin Chalk. Such ferric oxide in the lake sediment, in conjunction with reduced sulfur minerals discussed below, thus reflects pre-depositional oxidation of pyrite. Some ferric oxide may have formed as the result of post-coring oxidation of fine-grained iron monosulfide as suggested by the rapid color change of some sediment after exposure to air.

A high proportion of grains in the magnetic separates have textures and compositions, which can be inferred from colors, that indicate their origins from human activities. Such grains, termed anthropogenic magnetic grains (AMG in Figure 3), are found in nearly all examined samples, and include iron oxides (magnetite, maghemite, and hematite) in rust fragments and in probable fly ash, oxide grains of unknown composition and source, and steel alloys. We have not attempted to identify the compositions of obvious steel alloys or of the iron oxides doped with other metals, nor have we tried to trace their sources. Likely sources include construction materials, coal combustion wastes, as well as wear, rust, and erosion of vehicles, pipes, and steel surfaces (e.g., Puffer et al. 1980; Beckwith et al., 1986; Flanders, 1994).

#### *Authigenic sulfide, greigite ( $Fe_3S_4$ )*

A magnetic sulfide mineral is present in nearly all extracts. Many grains were sufficiently large (several tenths of a micrometer) to recognize the characteristic colors of reflection of sulfide minerals but too small

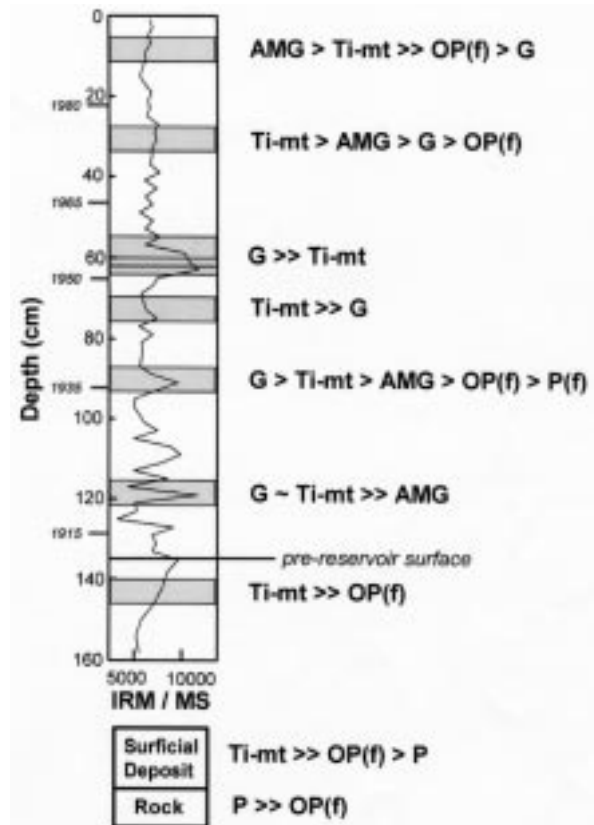


Figure 3. Summary of petrographic observations of samples from core and surface exposures, showing iron-bearing particles in order of relative abundance (based on observation of polished grain mounts) and the intervals (shaded) sampled for magnetic-mineral separation. G, greigite; Ti-mt, titanomagnetite commonly with associated hematite and ilmenite; AMG, anthropogenic magnetic grains (includes oxides in rust, fly ash, steel alloys); P, pyrite; OP, ferric oxide formed from pyrite; (f), framboidal pyrite. >, denotes greater relative abundance; >>, denotes much greater relative abundance. ~, denotes nearly equal amounts. IRM/MS in  $A m^{-1}$ . A few years (in italics) from the age model are shown along with depths.

to identify the type of mineral on the basis of optical properties alone. Their occurrence in aggregates and within cell lumens of detrital organic fragments, identical to occurrences of confirmed greigite in other studies (Reynolds et al., 1994b), along with the absence of crystal habits diagnostic for authigenic pyrrhotite, suggests greigite. This suggestion was confirmed by XRD (Figure 4) and thermomagnetic analyses (Figure 5). Greigite is found in nearly all examined samples but in variable amounts relative to detrital Ti-magnetite. Greigite is clearly the predominant magnetic mineral in samples from depths of 86–92 cm, 62–64 cm, 60–62 cm, and 54–60 cm; greigite is at least as abundant as detrital magnetite in a sample from 116–122 cm.

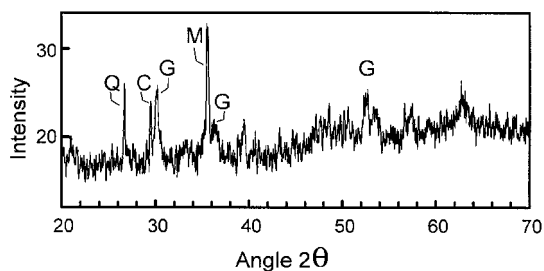


Figure 4. X-ray diffraction pattern for magnetic grains extracted from sediment from a depth interval of 62 to 64 cm, showing peaks for greigite (G), quartz (Q), calcite (C), as well as magnetite, maghemite and (or) hematite (M).

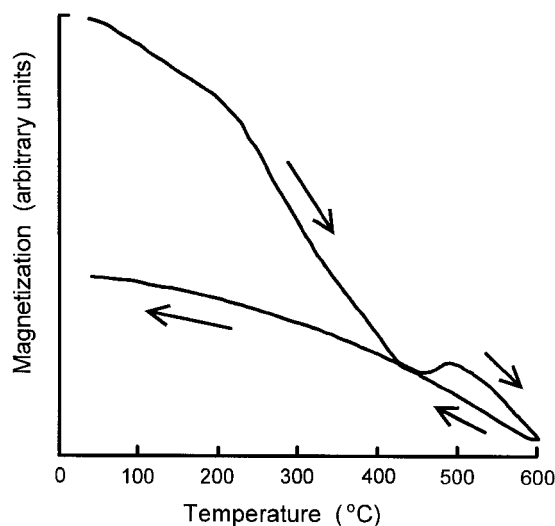


Figure 5. Magnetization vs temperature curve for magnetic grains extracted from sediment from a depth interval of 62 to 64 cm. Sample run in air in a field of 0.2 Tesla. Shape of the curve is typical of greigite (see Reynolds et al., 1994b).

These depth intervals correspond to distinctly high values of IRM and IRM/MS. Greigite is sparse in the examined sediments from depths shallower than about 50 cm.

Scanning electron microscopy (SEM) with attached energy-dispersion analyzer (EDA) was used to determine the origin of greigite, whether it formed via post-depositional bacterial sulfate reduction (Berner, 1981; 1984; Reynolds et al., 1993) or as magnetosomes within microorganisms (Mann et al., 1990; Stanjek et al., 1994). Such magnetosomes are characterized by common shapes and uniformly small size (typically  $<0.1 \mu\text{m}$ ), below the resolution of the SEM. SEM can discern the sizes and shapes of the greigite (particles of iron and sulfur in a magnetic-mineral extract) and reveals a range in particle size (mostly

between  $0.2 \mu\text{m}$  and  $2 \mu\text{m}$ ) and morphology (Figure 6). SEM analysis thus confirms the reflected-light microscopic examination indicating that the greigite in the sediments of White Rock Lake formed via sulfate reduction outside bacterial cells.

## Magnetic properties and interpretations

### *Variations related mainly to changes in detrital input*

Magnetic susceptibility increases overall, nearly doubling from 1912 to the early 1950s, after which it is variable but without long-term trends (Figure 7A). IRM varies abruptly in sediments deposited before the late 1950s but varies little in sediments deposited afterward (Figure 7B). The constant MS and IRM values (constant ferrimagnetic-mineral content) since the mid-1950s, along with the inferred decrease in the input of detrital Ti-magnetite (Ti decreases while Fe/Ti remains constant), suggest the increased input or growth of small amounts of highly magnetic Ti-free minerals since 1950. Such Ti-free grains might include (1) pedogenic iron oxides from soil imported to the watershed, (2) anthropogenic grains, such as oxides in fly ash and rust, (3) particles of steel, and (4) authigenic minerals. The paucity of greigite and absence of other observed authigenic minerals in the upper part (post-1960) of the core argues against the fourth possibility. As noted above, the peaks in IRM correspond to intervals in which greigite is concentrated.

The HIRM profile (ferric oxide content) is characterized by large variations prior to the late 1960s after which values decline systematically (Figure 7C). The diminished HIRM values since the late 1960s may reflect the diminished erosion of ferric-oxide bearing surficial deposits as development covered most of the landscape. The HIRM and IRM profiles track closely in the profile between 1912 and the mid-1940s. A close relation between hematite and magnetite contents is expected from fluvial transport of these related heavy minerals from the magnetite- and hematite-bearing surficial deposits. Another possibility for some correspondence between IRM and HIRM might be the post-coring oxidation of iron monosulfide to ferric oxide. These possibilities combined, however, do not fully explain the distribution of hematite. First, the high values of IRM are related to greigite content, not magnetite. Second, HIRM and IRM show different patterns in parts of the core. For example, spikes in HIRM and IRM are offset over the late 1940s to mid

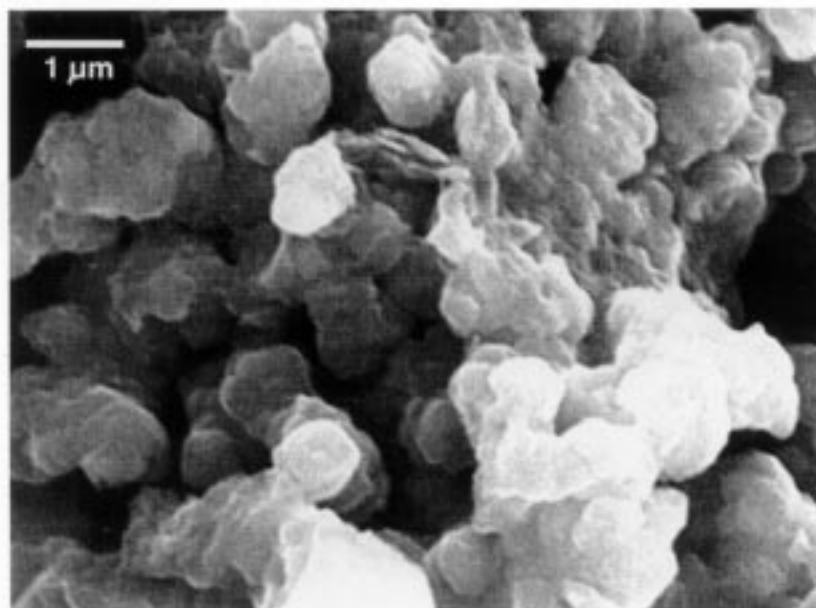


Figure 6. Scanning electron micrograph of magnetic grains extracted from sediment from depth interval of 62 to 64 cm. The sizes (many grains between 0.2 and 2  $\mu\text{m}$ ) and variable shapes indicate an origin via extracellular bacterial sulfate reduction.

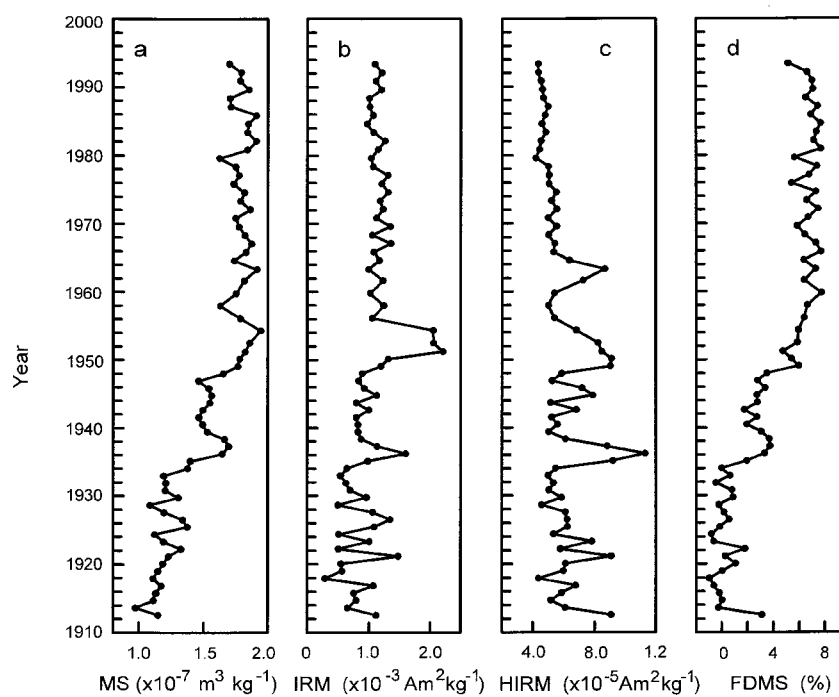


Figure 7. Depth profiles of magnetic properties in core samples. MS, magnetic susceptibility; IRM, isothermal remanent magnetization; HIRM, 'hard' IRM; FDMS, frequency-dependent magnetic susceptibility.



1950s record, and the HIRM spike over the interval of the early and mid 1960s lacks a corresponding feature in IRM.

Another possible source for hematite in the lake beds is eolian sediment transported during dust storms from the red surficial deposits (Quaternary loess and sand) of the southern High Plains of western Texas and eastern New Mexico (Figure 1; see Finnell, 1954; Wigner & Peterson, 1987; Holliday, 1990; 1991; Lee et al., 1993; Lee & Tchakerian, 1995). This region probably has the greatest amount of blowing dust in the United States (Lee et al., 1994). Other sources of eolian hematite might be Permian and Triassic redbeds and surficial sediments derived from them in the Rolling Plains area, east of the southern High Plains. The presence of quartz in the lake sediment and in surficial sediment, detected using XRD, is consistent with an eolian source for some hematite, because of the common association of quartz and hematite in the red clastic sedimentary rocks and surficial deposits of the western plains of Texas.

The frequency-dependent MS vs. depth profile is very similar to that of MS (Figure 7D). FDMS values are nearly constant in sediment deposited before the mid-1930s, but they increase overall in sediment deposited during the late-1930s to about 1960. High FDMS in the upper part of the core (mostly between 6 and 8 percent) varies little, and it corresponds in time to rapid suburbanization following World War II. One possibility is that high FDMS is related to pedogenic oxides in soil that was imported to the watershed for housing developments and landscaping. Or, high FDMS may be characteristic of anthropogenic ferrites, about which we know little in terms of magnetic domain states and responses to different inductions and frequencies used for MS measurements.

#### *Variations related to post-depositional alteration*

The IRM/MS ratio is considered to be an indicator of greigite content relative to other magnetic minerals. This inference is based on petrographic observations of dominant greigite in samples that have high IRM/MS (about  $10\,000\text{ A m}^{-1}$  and higher) and lesser greigite content in samples that have low ratio values (less than about  $7000\text{ A m}^{-1}$ ).

Different explanations can be considered for the occurrence of greigite. Any viable possibility must explain not only its presence and its preservation, but also its increased concentration in certain intervals. A major control on greigite formation and preservation

is the redox state that would determine the valence states of iron and sulfur in iron sulfide minerals. For example, greigite contains iron in both the  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  states (Sherman, 1990) and sulfur as  $\text{S}^{-}$  and  $\text{S}^{2-}$ , whereas pyrite contains iron as  $\text{Fe}^{2+}$  and sulfur as  $\text{S}^{2-}$ . Whatever the exact states of redox potential and pH, the conditions at White Rock Lake have produced and preserved greigite throughout the sediment. The main question is what caused variations in the amount of greigite. The variable greigite contents may be related to the availability of the reactants-sulfur (as sulfate), iron, and organic matter as the food source for bacterial metabolism. Changes in these reactants, with addition of elemental sulfur, would have the potential to produce more or less greigite initially or to drive reactions, along with redox changes, to pyrite at the expense of greigite (see Berner, 1981, 1984). The elemental data imply no lack of available iron (Figure 2) or organic matter (on the basis of organic carbon contents of about 2 percent). The content of sulfate is thus a likely control on the type and amount of sulfide mineral produced in this setting. Short-term increases in sulfate over very low initial levels might have favored the production of more greigite for a short time. Alternatively, zones of greigite concentration might be related to short-term depletions of sulfate in an otherwise sulfate-rich environment that favored the authigenesis of large amounts of pyrite.

Contents of total sulfur, which are uniformly low ( $<0.16$  wt percent), do not help resolve these possibilities. Total sulfur increases in sediment deposited since about 1950, along with the increase in calcium (Figure 2) and inorganic carbon (van Metre & Callender, 1997: 245, Figure 4). The main variation in total sulfur apparently reflects the input of detrital pyrite, along with the related increase in detrital calcite from the Austin Chalk or less weathered parts of the surficial deposit.

These possibilities can be tested, however, by petrographic observations. Absence or small amounts of authigenic pyrite in association with greigite would favor the possibility that high greigite contents were related to the addition of sulfate in a sulfate-poor environment. Large amounts of such pyrite through much of the sediment, with thin, interspersed intervals of concentrated greigite, would imply greigite production during times of relative sulfate limitation and (or) brief shifts in redox conditions.

Petrographic examination reveals a lack of authigenic pyrite; it is not associated with detrital iron-bearing minerals in any sample and is rare in asso-

ciation with greigite. Sparse pyritic framboids, many partly oxidized, are the dominant form of pyrite in these sediments; such partly oxidized framboids resemble those in the bedrock and in the surficial mantle and thus are interpreted as detrital. These observations suggest that bacterial sulfate reduction took place in a sulfate-limited environment, so that additional sulfate produced more greigite but was not enough to produce much pyrite. Such sulfate buildups might be related, at least partly, to arid periods accompanied by long periods of water residence, high levels of evaporation, and (or) relatively high inflow of sulfate-bearing groundwater. The sulfate is most likely from the oxidation of pyrite in the Austin Chalk.

### Comparison of local and regional climate change with greigite occurrence

#### *Historical climate records*

A test for this possibility – that greigite is related to a long residence time of water in the reservoir during periods of aridity – would come from records of White Rock Creek flow and reservoir outflow since 1914, when the reservoir filled. Flow data from the creek are available, however, for only the last 35 years, and thus were not useful for evaluating the older zones of greigite enrichment. Related tests would include long-term monitoring of sulfate concentrations in the lake water compared to flow and climatic data.

Another approach is to compare the distribution of greigite with records of local and regional precipitation and drought, as well as with the discharge history of the nearby Trinity River, into which White Rock Creek flows. Partial historical records of precipitation in the Dallas area are available for comparison to greigite content, interpreted from the shape of the IRM/MS vs. age curve. None of three nearby meteorological stations took measurements from the mid-1930s to early 1940s. The most complete record of precipitation, from Collin County north of White Rock Lake, is expressed as the difference between the average ( $96.7 \text{ cm yr}^{-1}$ ) and the annual precipitation, so that a positive difference indicates below-average precipitation (Figure 8A).

A regional climate record was obtained from Climatic Division Data derived from numerous stations in the north central Texas division (Weather Disk Assoc., 1994). This record is illustrated in two ways: (1) The Palmer Drought Severity Index (PDSI), a hydrological drought index used to assess the severity of dry or

wet spells on the basis of a balance between moisture supply and demand (Palmer, 1965; PDSI values less than  $-1$  reflect drought, less than  $-3$ , severe drought) (Figure 8B); and (2) the difference between the regional average ( $86.4 \text{ cm yr}^{-1}$ ) and annual precipitation (Figure 8C), as with the data from the station in Collin County near the lake. A final measure of regional hydrologic balance is illustrated by nearby discharge in the Trinity River (Figure 8D).

#### *Climate records compared to IRM/MS ratio*

A close correspondence between climate and greigite occurrence is found in the record of the early and mid-1950s (Figure 8). This arid period is expressed by six consecutive years of below-average precipitation and by severe drought. During this time, discharge in the Trinity River was extremely low. This period matches closely with a sediment interval in which greigite is the predominant magnetic mineral as indicated by high IRM/MS values and confirmed by petrographic examination. It is perhaps significant that the interval of high IRM/MS represents a shorter duration than the period of aridity and that the peak (highest value) in the IRM/MS profile is displaced downward with respect to maxima in the measures of aridity. These differences might be related to lag times between aridity and limnologic conditions such as sulfate buildup, as well as between limnologic conditions and the production of greigite tied to diffusion of sulfate into sediment pore water. In this way greigite may have started to form in sediment that was deposited before the onset of drought. Similarly, highly favorable conditions for sulfidization leading to high contents of greigite may have been generated in sediment layers deposited before the most severe years of drought.

Another period of drought, the dust-bowl years of the mid- to late 1930s, appears to be associated with a zone of greigite enrichment. In north central Texas, the drought of the thirties was not as severe as that of the fifties. The regional record (Figure 8C) shows four consecutive years of below-average precipitation, with the lowest precipitation in 1939, the last year of this dry period. A peak in IRM/MS, caused by abundant greigite relative to titanomagnetite (Figure 3), is found in a sediment interval centered at year 1936, according to the age model.

Between 1912 and the early twenties, the shapes of the precipitation records and the IRM/MS profile are remarkably similar. For the period between mid-1920s and mid-1930s, however, there are no clear-cut

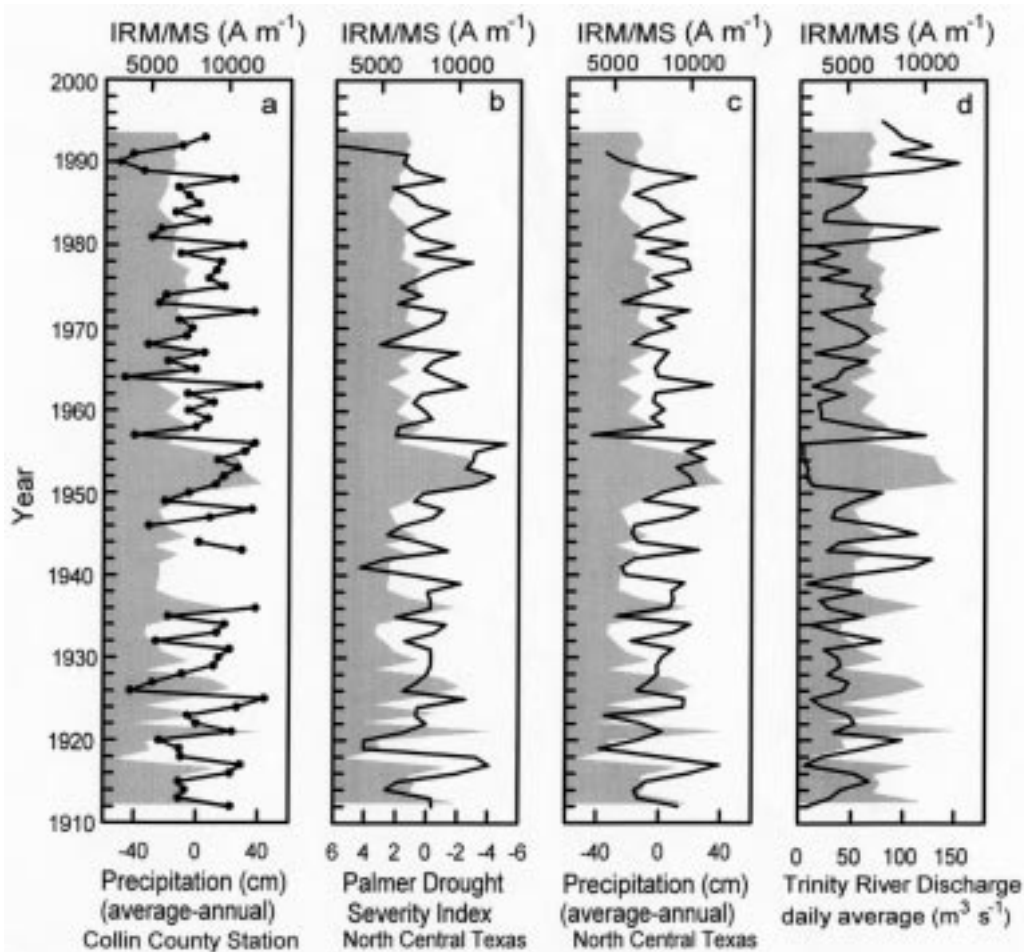


Figure 8. Comparisons between IRM/MS ratio (an indicator of greigite content; shaded) and records of precipitation, drought, and runoff in the Trinity River (solid lines). (a) precipitation from a station in Collin County (Figure 1), expressed as the difference between the average and the annual precipitation so that positive values indicate conditions drier than average. (b) Palmer Drought Severity Index (PDSI) for north central Texas, negative values indicating drought (Weather Disc Assoc., 1994). (c) precipitation expressed as in (a) for the region of north central Texas using the stations on which the PDSI is based. (d) discharge in the Trinity River from a station in the Dallas area.

associations among the precipitation, drought, runoff, and IRM/MS ratio values. Sharp variations characterize all parameters without a consistent pattern, so that it is not possible to relate, with any confidence, one peak to any other.

After about 1960, there were few prolonged periods of aridity in the area, and sediments deposited since then are characterized by only small variations in IRM/MS. Locally, the driest period within the last several decades was 1975 to 1978, four consecutive years of below-average precipitation. Slightly elevated IRM/MS values, higher than any other interval of the last 30 years, appear to be associated with this period (Figure 8a). The lack of correspondence between precipitation and greigite occurrence after 1960 may be

related to the lack of prolonged drought, to the influence of increasing anthropogenic material on IRM/MS values, or to limits on greigite production (or the destruction of early diagenetic greigite) in an increasingly shallower lake with perhaps stronger mixing. Destruction of greigite is not supported on the basis of petrographic examination that shows no evidence for more intense oxidation of greigite in the post-1960 sediment than seen in older sediment. Furthermore, the lack of intense oxidative alteration of greigite in any part of the core suggests that the observed distribution of greigite is related closely to the amount originally produced rather than to a residual amount remaining after selective *in situ* oxidation of nearly constant original amounts.

On the basis of these comparisons, we conclude that greigite concentrations in the lake sediment are at least partly associated with conditions of aridity and that the formation of greigite was promoted by such conditions. The interpreted link between greigite and aridity is most strongly indicated by the records of the early to mid-1950s. It is clear, though, that not every spike in IRM/MS is associated with a climatic event and that not every dry spell lasting a few years (less than about four) is associated with a zone of greigite concentration.

#### *Sources of uncertainty*

As noted, the IRM/MS record does not match exactly the climate records through the entire core. Two factors introduce uncertainties that warrant caution when comparing historical climate records with magnetic-property profiles. One factor is the lake-sediment chronology that is based on assumed constant sedimentation rates; the chronology is most uncertain over the interval of the 1920s to about 1950, for which the record lacks independent control. This uncertainty makes it difficult to assess the timing (or final 'stratigraphic position') of greigite formation with respect to the timing of drought. Nevertheless, our results strongly suggest rapid crystallization relative to the inferred causative climate conditions. This point is indicated from the record of the 1950s that has both tight chronologic control and the strongest association of drought and greigite content. Another complicating factor arises from the presence of multiple types of magnetic minerals and likely variations in their physical as well as magnetic grain sizes (i.e., magnetic domain states). The IRM/MS ratios are not solely controlled by greigite content; other minerals and their magnetic domain states can affect the ratio (see Thompson & Oldfield, 1986; Banerjee & Moskowitz, 1986).

#### **Importance for paleoclimate studies of lacustrine sediment**

The interpreted connection between greigite and drought in modern sediments suggests that greigite concentrations in older lacustrine sediments may similarly reflect long residence time of water and possibly arid conditions. As an example, Pleistocene and late Pliocene sediments in a 100-meter core from Butte Valley, northern California, contain several zones

of greigite concentrations that may reflect dry periods (Roberts et al., 1996). Other origins for lacustrine greigite are likely, depending on the chemical-hydrologic system. For example, greigite in late Pleistocene sediments from Owens Lake, southern California, was attributed to diagenetic replacement of detrital magnetite transported to the lake basin during high runoff from glaciers (Benson et al., 1996). Alternatively, the greigite might characterize sediment deposited during transitional periods of chemical regimes between flushing, open (magnetite present; greigite and pyrite absent) and closed (pyrite dominant; magnetite altered) hydrologic conditions. Greigite occurrences in Holocene sediments of terminal Lake Manas, in western China, appear to be related to anoxic bottom conditions during times of relatively high lake levels caused by high runoff levels; greigite apparently did not form during drier periods when the lake was shallow and better mixed (Jelinowska et al., 1995).

Our results indicate rapid formation of greigite in White Rock Lake in response to environmental change. The uncertainty introduced by offsets in the timing of drought and the timing of greigite crystallization in the White Rock Lake sediments is not important for the paleoclimatic interpretation of greigite occurrences in older lake sediments, in which resolutions of a few years are not critical. The evidence for rapid buildups of abundant greigite is also important for paleomagnetic interpretation of greigite-bearing sediments, in which the variations in paleomagnetic direction may reflect magnetic-field secular variation.

As a final cautionary note, we emphasize that factors other than climate can exert important influences on the production of greigite and other iron sulfide minerals in lake sediments. Several processes can lead to changing amounts of sulfate and changing chemical redox conditions that may strongly influence the type of sulfide mineral (Tuttle et al., 1993). As one example, the preservation of greigite is at least partly favored by low amounts of sulfate, larger amounts leading to disulfide minerals. Variations in organic matter and available iron are other potentially important factors. Changes in pore-water sulfate may vary not only in response to limnologic processes but also in response to changing sources. For example, fallout of sulfur-bearing volcanic ash, not climate, might strongly influence sulfide mineralogy. Such a condition likely explains the source of sulfur for abundant pyrite in the Oligocene Creede Formation composed

of lake beds that fill the Creede caldera of the San Juan Volcanic Field, Colorado (Reynolds et al., 1994a).

## Summary

Magnetic-property and petrographic studies of sediment from a reservoir in Dallas, Texas, reveal the presence of authigenic greigite ( $\text{Fe}_3\text{S}_4$ ). Greigite is strongly enriched in sediments that date close to the prolonged drought in the early 1950s. Sediments deposited during or shortly before some other, briefer droughts also contain concentrations of greigite. The possible association between greigite formation and drought may be related to buildups of pore-water sulfate because of low through-flow of reservoir water. Such sulfate was reduced by heterotrophic bacteria in near-surface sediment. In paleoclimate studies of older lake sediments, concentrations of greigite may similarly reflect arid conditions.

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## References

- Ariztegui, D. & D. Dobson, 1996. Magnetic investigations of framboidal greigite formation: a record of anthropogenic environmental changes in eutrophic lake St Moritz, Switzerland. *The Holocene* 6: 235–241.
- Banerjee, S. K. & B. M. Moskowitz, 1985. Ferrimagnetic properties of magnetite. In Kirschvink, J., D. S. Jones & B. J. MacFadden, (eds), *Magnetite Biomineralization and Magnetoreception in Organisms*. Plenum Press, N.Y.: 17–41.
- Beckwith, P. R., J. B. Ellis & D. M. Revitt, 1986. Heavy metal and magnetic relationships for urban source sediments. *Phys. Earth Planet. Sci.* 42: 67–75.
- Benson, L. V., J. W. Burdett, M. Kashgarian, S. P. Lund, F. M. Phillips & R. O. Rye, 1996. Climatic and hydrologic oscillations in the Owens Lake basin and adjacent Sierra Nevada, California. *Science*, 274, 746–749.
- Berner, R. A., 1970. Sedimentary pyrite formation. *Am. J. Sci.* 268: 1–23.
- Berner, R. A., 1974. Iron sulphides in Pleistocene deep Black Sea sediments and their paleoceanographic significance. In Degens, E. T. & D. A. Ross, (eds), *The Black Sea-Geology, Chemistry, Biology*. Am. Assoc. Petrol. Geol. Memoir 20: 523–531.
- Berner, R. A., 1978. Sulfate reduction and the rate of deposition of marine sediments. *Earth Planet. Sci. Letts.* 37: 492–498.
- Berner, R. A., 1981. Authigenic mineral formation resulting from organic matter decomposition in modern sediments. *Fortschritte der mineralogie* 59: 117–135.
- Berner, R. A., 1984. Sedimentary pyrite formation: An update. *Geochim. Cosmochim. Acta* 8: 605–615.
- Bradbury, J. P. & P. C. van Metre, 1997. A land-use and water-quality history of White Rock Lake reservoir, Dallas, Texas, based on paleolimnological analyses. *J. Paleolimnol.* 17: 227–237.
- Canfield, D. E. & R. Raiswell, 1991. Pyrite formation and fossil preservation. In P. Allison & D. E. Briggs (eds), *Taphonomy, Releasing the Information Locked in the Fossil Record*. Plenum Press, N.Y.: 337–387.
- Cloud, K. W., 1975. The diagenesis of the Austin Chalk. Master's thesis, Univ. of Texas at Dallas, Dallas, Texas: 70 pp.
- Dell, C. I., 1972. An occurrence of greigite in Lake Superior sediments: *Am. Mineral.* 7: 1303–1304.
- Durham, C. O., 1957. The Austin group in central Texas. Ph.D. dissertation, Columbia Univ., N.Y.: 130 pp.
- Finnell, H. H., 1954. The dust storms of 1954: *Sci. Am.* 191: 25–29.
- Flanders, P. J., 1994. Collection, measurement, and analysis of airborne magnetic particulates from pollution in the environment. *J. appl. Phys.* 75: 5931–5936.
- Giovanoli, F., 1979. A comparison of the magnetization of detrital and chemical sediments from Lake Zurich. *Geophys. Res. Letts.* 6: 233–235.
- Hilton, J., 1990. Greigite and the magnetic properties of sediments. *Limnol. Oceanogr.* 35: 509–520.
- Hoffmann, V., 1992. Greigite ( $\text{Fe}_3\text{S}_4$ ): magnetic properties and first domain observations. *Physics Earth Planet. Int.* 70: 288–301.
- Holliday, V. T., 1990. Soils and landscape evolution of eolian plains: The Southern High Plains of Texas and New Mexico. *Geomorphology* 3: 489–515.
- Holliday, V. T., 1991. The geologic record of wind erosion, eolian deposition, and aridity on the Southern High Plains. *Great Plains Research* 1: 6–25.
- Jackson, L. L., F. W. Brown & S. T. Neil, 1987. Major and minor elements requiring individual determination, classical whole rock analysis, and rapid rock analysis. In P. A. Baeckecker (ed.), *Methods for Geochemical Analysis*. U.S. Geol. Surv. Bulletin 1770: G1–G23.
- Jedwab, J., 1967. Minéralisation en greigite de débris végétaux d'une vase récente (Grote Geul). *Bulletin Société Belge de Géologie Paléontologie et d'Hydrologie* 76: 27–38.
- Jelinowska, A., P. Tucholka, F. Gasse & J. C. Fontes, 1995. Mineral magnetic record of environment in Late Pleistocene and Holocene sediments, Lake Manas, Xinjiang, China. *Geophys. Res. Letts.* 22: 953–956.
- Kodama, K. L., J. C. Lyons, P. A. Siver & A. Lott, 1997. A mineral magnetic and scaled chrysophyte paleolimnological study of two northeastern Pennsylvania lakes: Records of fly ash deposition, land-use change and paleorainfall variation. *J. Paleolimnol.* 17: 173–189.
- Krs, M., M. Krsová, P. Pruner, A. Zeman, F. Novák & J. Jansa, 1990. A petromagnetic study of Miocene rocks bearing micro-organic material and the magnetic mineral greigite (Sokolov and Cheb basins, Czechoslovakia). *Physics Earth Planet. Ints.* 63: 98–112.
- Lee, J. A., B. L. Allen, R. E. Peterson & K. E. Moffett, 1994. Environmental controls on blowing dust direction at Lubbock, Texas, U.S.A. *Earth Surface Processes and Landforms* 19: 437–449.

- Lee, J. A. & V. P. Tchakerian, 1995. Magnitude and frequency of blowing dust on the Southern High Plains of the United States, 1947–1989. *Annals Assoc. Am. Geogr.* 85: 684–693.
- Lee, J. A., K. A. Wigner & J. M. Gregory, 1993. Drought, wind, and blowing dust on the Southern High Plains of the United States. *Physical Geography* 14: 56–67.
- Lichte, F. E., D. W. Golightly & P. J. Lamothe, 1987. Inductively coupled plasma atomic emission spectrometry. In P. A. Baeckecker (ed.), *Methods for Geochemical Analysis*. U.S. Geol. Surv. Bulletin 1770: B1–B10.
- Mann, S., N. H. C. Sparks, R. B. Frankel, D. A. Bazylinski & H. W. Jannasch, 1990. Biomineralization of ferrimagnetic greigite ( $\text{Fe}_3\text{S}_4$ ) and iron pyrite ( $\text{FeS}_2$ ) in a magnetotactic bacterium. *Nature* 343: 258–261.
- Marshall, R. M. & C. B. Brown, 1939. Erosion and related land-use conditions on the watershed of the White Rock reservoir near Dallas, Texas. U.S. Dept. Agriculture: 29 pp.
- Palmer, W. C., 1965. Meteorological Drought. Weather Bureau Research Paper 45. U.S. Dept. Commerce, Washington, D.C. U.S. Gov. Printing Office 48–334/269.
- Patterson, M., 1942. A study of the seasonal distribution of plankton in White Rock Lake. *Trans. Tex. Acad. Sci.* 25: 72–75.
- Petersen, N., T. Von Dobonek & H. Vali, 1986. Fossil bacterial magnetite in deep-sea sediments from the South Atlantic Ocean. *Nature* 320: 611–615.
- Puffer, J. H., E. W. B. Russell & M. R. Rampino, 1980. Distribution and origin of magnetite spherules in air, water, and sediments of the greater New York City area and the North Atlantic Ocean. *J. Sed. Pet.* 50: 247–256.
- Reynolds, R. L., M. B. Goldhaber & M. L. Tuttle, 1993. Sulfidization and magnetization above hydrocarbon reservoirs. In Aissoui, D. M., D. F. McNeill & N. F. Hurley (eds), *Applications of Paleomagnetism to Sedimentary Geology*. Soc. Econ. Pet. Min. Spec. Publ. 49: 167–179.
- Reynolds, R. L. & J. W. King, 1995. Magnetic records of climate change. *Rev. Geophys., Suppl.*: U.S. National Rept to International Union of Geodesy and Geophysics 1991–1994: 101–110.
- Reynolds, R. L., J. G. Rosenbaum, D. S. Sweetkind, M. A. Lanphere, C. A. Rice & M. L. Tuttle, 1994a. Rock magnetic studies of the Oligocene Creede Formation and prospects for a polarity stratigraphy. U.S. Geol. Surv. Open-file Rept 94–260: 42 pp.
- Reynolds, R. L., M. L. Tuttle, C. A. Rice, N. S. Fishman, J. A. Karachewski & D. M. Sherman, 1994b. Magnetization and geochemistry of greigite-bearing Cretaceous strata, North Slope, Alaska. *Am. J. Sci.* 294: 485–528.
- Roberts, A. P., 1995. Magnetic properties of sedimentary greigite ( $\text{Fe}_3\text{S}_4$ ). *Earth Planet. Sci. Lett.* 134: 227–236.
- Roberts, A. P., R. L. Reynolds, K. L. Verosub & D. P. Adam, 1996. Environmental magnetic implications of greigite ( $\text{Fe}_3\text{S}_4$ ) formation in a 3 m.y. lake sediment record from Butte Valley, northern California. *Geophys. Res. Letts.* 23: 2859–2862.
- Rosenbaum, J. G., R. L. Reynolds, D. P. Adam, J. Drexler, A. M. Sarna-Wojcicki & G. C. Whitney, 1996. Record of middle Pleistocene climate change from Buck Lake, Cascade Range, southern Oregon – Evidence from sediment magnetism, trace-element geochemistry, and pollen. *Geol. Soc. Am. Bull.* 108: 1328–1341.
- Thompson, R. & F. Oldfield, 1986. *Environmental Magnetism*. Allen & Unwin, London: 227 pp.
- Sherman, D. M., 1990. Mössbauer spectra, crystal chemistry, and electronic structure of greigite,  $\text{Fe}_3\text{S}_4$ . *EOS Trans. Am. Geophys. Union* 71: 1649 pp.
- Skinner, B. J., R. C. Erd & F. S. Grimaldi, 1964. Greigite, the thio-spinel of iron; a new mineral. *Am. Mineral.* 49: 543–555.
- Snowball, I. F., 1991. Magnetic hysteresis properties of greigite ( $\text{Fe}_3\text{S}_4$ ) and a new occurrence in Holocene sediments from Swedish Lapland. *Physics Earth Planet. Ints.* 68: 32–40.
- Snowball, I. F. & R. Thompson, 1990. A stable chemical remanence in Holocene sediments. *J. Geophys. Res.* 95: 4471–4479.
- Stanjek, H., J. W. E. Fassbinder, H. Vali, H. Wägele & W. Graf, 1994. Evidence of biogenic greigite (ferrimagnetic  $\text{Fe}_3\text{S}_4$ ) in soil. *European J. Soil Sci.* 45: 97–103.
- Tuttle, M. L. & M. B. Goldhaber, 1993. Sedimentary sulfur geochemistry of the Paleogene Green River Formation, western USA: Implications for interpreting depositional and diagenetic process in saline alkaline lakes. *Geochim. Cosmochim. Acta* 57: 3023–3039.
- Tuttle, M. L., C. A. Rice & M. B. Goldhaber, 1990. Geochemistry of organic and inorganic sulfur in ancient and modern lacustrine environments. In Orr, W. L. & C. M. White (eds), *Geochemistry of Sulfur in Fossil Fuels*. Am. Chem. Soc. Symposium Series 429: 114–148.
- Van Metre, P. C. & E. Callender, 1997. Water-quality trends in White Rock Creek Basin from 1912–1994 identified using sediment cores from White Rock Lake reservoir, Dallas, Texas. *J. Paleolimnol.* 17: 239–249.
- Verosub, K. L. & A. P. Roberts, 1995. Environmental magnetism: Past, present, and future. *J. Geophys. Res.* 100: 2175–2192.
- Weather Disc Assoc., 1994. *World Weather Disc*: Seattle, WA.
- Wigner, K. A. & R. E. Peterson, 1987. Synoptic climatology of blowing dust on the Texas South Plains. *J. Arid Environ.* 13: 199–209.