

Environmental magnetic implications of greigite (Fe₃S₄) formation in a 3 m.y. lake sediment record from Butte Valley, northern California

Andrew P. Roberts,¹ Richard L. Reynolds,² Kenneth L. Verosub,¹ and David P. Adam³

Abstract. Authigenic greigite (Fe₃S₄) has been identified in several horizons of lake beds in a 102-m core from Butte Valley, northern California, using mineral magnetic methods and x-ray diffraction analysis. The presence of greigite has several implications for the paleoenvironmental record from Butte Valley. First, its occurrence in 2.5 - 3.0 Ma strata confirms that greigite can persist in the geological record for long periods of time. Second, the detrital mineral magnetic record may be partially obscured by the presence of authigenic greigite and care must be taken in interpreting magnetic variations in the greigite-bearing zones as paleoclimate proxies. Third, differences in the timing of remanence acquisition for authigenic and detrital phases may compromise studies of high-frequency geomagnetic field variations. Fourth, greigite may also be significant as a paleoenvironmental indicator of lake and sediment chemistry. The magnetic detection of greigite may therefore provide important information about paleolimnological conditions.

Introduction

Environmental magnetism can be useful in studies of lake sediments because temporal variations in magnetic parameters often covary with biological indicators of paleoclimate. Magnetic parameters can therefore be sensitive indicators of catchment responses to climate change [e.g., Verosub and Roberts, 1995; Reynolds and King, 1995]. However, there can be numerous sources of fine-grained magnetic particles in lacustrine settings and it is necessary to distinguish between different potential sources before interpreting environmental magnetic results as paleoclimate records. In particular, *in situ* dissolution of detrital grains and authigenic formation of secondary magnetic phases, such as greigite (Fe₃S₄), can seriously obscure a detrital magnetic record [e.g., Reynolds et al., 1994].

The importance of greigite has been widely underestimated because it has often been assumed that greigite will convert to pyrite in most sediments [e.g., Berner, 1984]. The documentation of greigite in Pleistocene and older sedimentary sequences [e.g., Skinner et al., 1964; Krs et al. 1990; Tric et al., 1991; Horng et

al. 1992; Roberts and Turner, 1993; Hallam and Maher, 1993; Reynolds et al., 1994] demonstrates that greigite can persist in the geological record for long periods of time. It is therefore necessary to screen sedimentary samples for the presence of authigenic phases such as greigite before making interpretations that rely on a strictly detrital origin of magnetic minerals. Roberts [1995] proposed a set of diagnostic magnetic properties for fingerprinting sediments for the presence of greigite. These criteria have been applied to lake sediments from Butte Valley, northern California, to assess the appropriateness of interpreting the environmental magnetic record in terms of paleoclimate change.

Geological setting

Butte Valley is a topographically closed basin, 25 km in length and 8-15 km in width (elevation of 1290 m), that lies in the upper Klamath River drainage basin in northern California. The Klamath basin is well-suited for studies of paleolimnology and paleoclimatology because it lies in the rain shadow of the Cascade Range where it catches and stores much precipitation. Long-lived lakes have existed in several sub-basins of the Klamath basin for much of the last several m.y. The sedimentary sequences in these sub-basins contain rich records of long-term climate variation that have been targeted by the U.S. Geological Survey Global Change Program [Adam et al., 1989; Rieck et al., 1992; Rosenbaum et al., 1996].

Upper Miocene and Pliocene basalts and basaltic andesites make up the catchment bedrock in the Butte Valley basin [Wood, 1960]. The Butte Valley core comprises 102 m of fine-grained lake beds which were recovered with a rotary drilling rig in 1991 (see Adam et al. [1994] for details and lithological descriptions).

Methods

Samples were collected in plastic boxes (9.4 cm³) at 15 cm intervals, where possible, from depths of 2 m to 102 m. After measurement of the natural remanent magnetization, stepwise alternating field (AF) demagnetization was conducted, with at least 5 steps (10, 20, 30, 40, 50 mT). Mass-specific magnetic susceptibility (χ) was measured for each sample and the saturation isothermal remanent magnetization (M_{rs}) was estimated by applying a field of 1.2 T to the samples. Hysteresis parameters were measured on bulk sediment subsamples (20-40 mg), up to fields of 1 T. Temperature-dependence of magnetic susceptibility was measured on selected samples, to temperatures of 720°C. Magnetization acquired in a 0.2 T inducing field was measured during heating to 640°C. Low-temperature analyses were made on several samples by imparting a saturation remanence with an applied field of 2.5 T at 5 K, followed by measurements of M_{rs} at regular intervals up to room temperature. In some intervals, magnetic minerals were extracted from the sediment by pumping a sedi-

1. Dept of Geology, University of California, Davis, CA 95616.
2. U.S. Geological Survey (U.S.G.S.), Box 25046, MS 964, Denver Federal Center, Denver, CO 80225.
3. U.S.G.S., 345 Middlefield Rd, Menlo Park, CA 94025.

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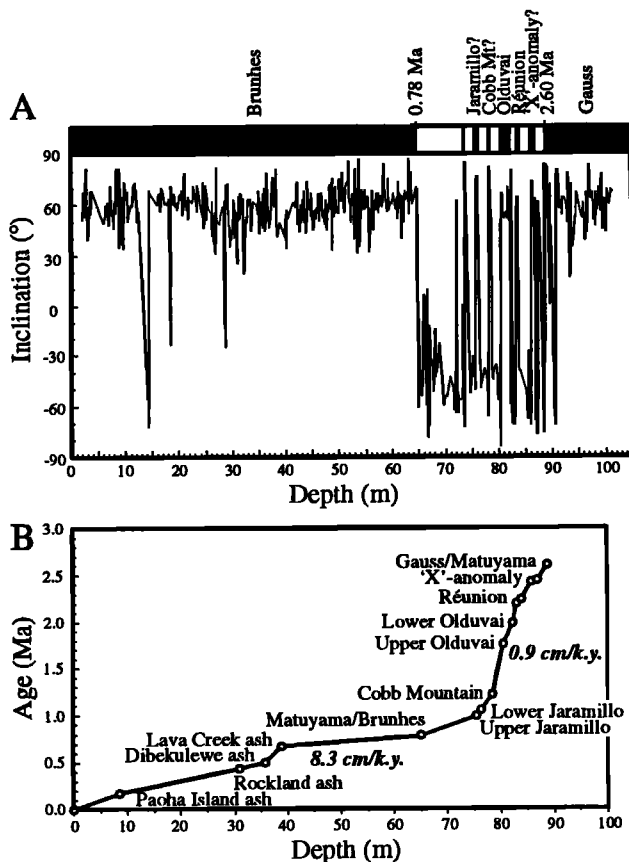


Figure 1 Magnetostratigraphy of the Butte Valley core. A. Inclination versus depth with interpreted polarity log. Remanence directions are plotted only for stably-magnetized samples (determined from straight-line fits to at least 3, and up to 6, points). Anomalous inclinations, possibly representing Brunhes Chron geomagnetic excursions, are recorded at 14 m, 18.5 m, and 29 m. Several anomalous inclinations are also recorded below the Matuyama/Brunhes boundary. We make no interpretations concerning these possible excursions. B. Sedimentation rate diagram. Detailed lithological descriptions are given by *Adam et al.* [1994].

ment slurry at low velocity past a permanent magnet, using a technique similar to that of *Petersen et al.* [1986]. The extracts were subjected to thermomagnetic analysis and polished grain mounts were examined by reflected-light petrography.

Results

Magnetostratigraphy

The Butte Valley sequence is dominated by muds and silty muds, with occasional thin sand beds [*Adam et al.*, 1994]. The fine-grained sediments consistently record stable magnetizations and the magnetic reversal stratigraphy indicates that the core spans almost 3 m.y. of lake history (Figure 1). Sedimentation rates were uniform (ca 0.9 cm/k.y.) from the Gauss Chron to the Jaramillo subchron (ca 3 - 1 Ma), with an almost ten-fold acceleration (to uniform rates of ca 8.3 cm/k.y.) from the Jaramillo subchron to the uppermost Brunhes Chron (ca 1 - 0 Ma). Several tephra layers [*Sarna-Wojcicki et al.*, 1991] provide temporal control within the Brunhes Chron. The magnetostratigraphy indicates that this record is one of the longest continuous records of lacustrine environmental change in the western United States, comparable to that of the nearby Tulelake record [*Adam et al.*, 1989; *Rieck et al.*, 1992].

Mineral magnetic detection of sedimentary greigite

Sedimentary greigite typically has high relative ratios of M_{rs}/χ , that are accompanied by hysteresis ratios of $M_{rs}/M_s \approx 0.5$ and $B_{cr}/B_c \approx 1.5$ (M_s is the saturation magnetization; B_c is the coercive force; B_{cr} is the coercivity of remanence) [*Roberts*, 1995]. M_{rs}/χ is largely a measure of magnetic grain size: fine grains have higher ratios while coarser grains have lower ratios. *Snowball and Thompson* [1990a,b], *Roberts and Turner* [1993], and *Reynolds et al.* [1994] all report high M_{rs}/χ ratios for greigite-bearing samples relative to those for magnetite- or titanomagnetite-bearing samples in the same sequences. While these parameters are nonunique with regard to greigite identification, they provide an excellent indicator which can be confirmed by ancillary analyses.

Greigite undergoes no low-temperature magnetic transitions, therefore low-temperature measurements may prove valuable in distinguishing among magnetite (Verwey transition at 118 K; *Özdemir et al.* [1993]), pyrrhotite (magnetic transition at ca 34 K; *Dekkers et al.* [1989]) and greigite. The absence of a low-temperature transition cannot, however, be taken as definitive evidence for the presence of greigite. Greigite also displays characteristic high-temperature behaviour, with a major drop in magnetization between 270 and 350°C [*Roberts*, 1995].

Magnetic screening of the Butte Valley sediments for greigite indicates that there are several peaks in M_{rs}/χ at discrete stratigraphic horizons, particularly at 2 m, 14-15 m, 68-69 m, 76 m, 78 m, 91 m, 93-95 m, 97 m, and 100 m (Figure 2). M_{rs}/χ ratios display low amplitude variations about a constant value throughout the remainder of the core. Thermomagnetic analyses of bulk sediment samples from the majority of the sediments indicate that titanomagnetite is the dominant magnetic mineral (Figure 3a). The dominance of titanomagnetite is easily explained because it is a common constituent of the basaltic bedrock that surrounds the catchment. This interpretation is confirmed by the presence of basaltic rock fragments and magnetic iron oxides of volcanic origin in magnetic separates from the Butte Valley core.

Magnetic mineral separates were obtained from sample depths of 2.3 m, 14.4 m, 90.9 m, 93.6 m, 94.5 m, 96.3 m, and 100.25 m. Magnetic iron sulphides were observed petrographically in polished grain mounts from all samples except those from 2.3 m and 14.4 m. Petrographic observations of the magnetic separates from 2.3 m and 14.4 m indicate that they are dominated by volcanic rock fragments that contain ferrimagnetic ilmeno-hematites and titanomagnetites. Notably, the lithology of these two horizons (medium to fine volcanic sand) differs significantly from that of the greigite-bearing zones (mud and silty mud). Hysteresis parameters from bulk sediment and magnetic separates from the vol-

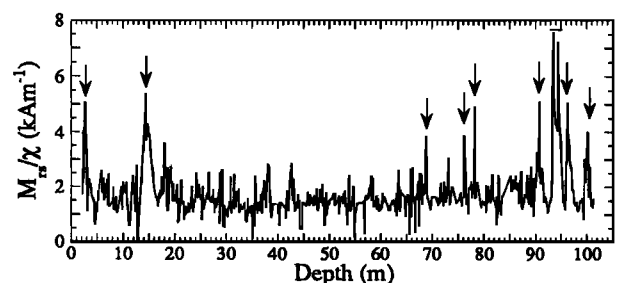


Figure 2 M_{rs}/χ versus depth for the Butte Valley core. Relatively uniform values of 1.5 kAm⁻¹ are recorded throughout most of the core. The large spikes (indicated by arrows) were identified as possible locations for greigite preservation and have been studied in greater detail using magnetic mineral separates.

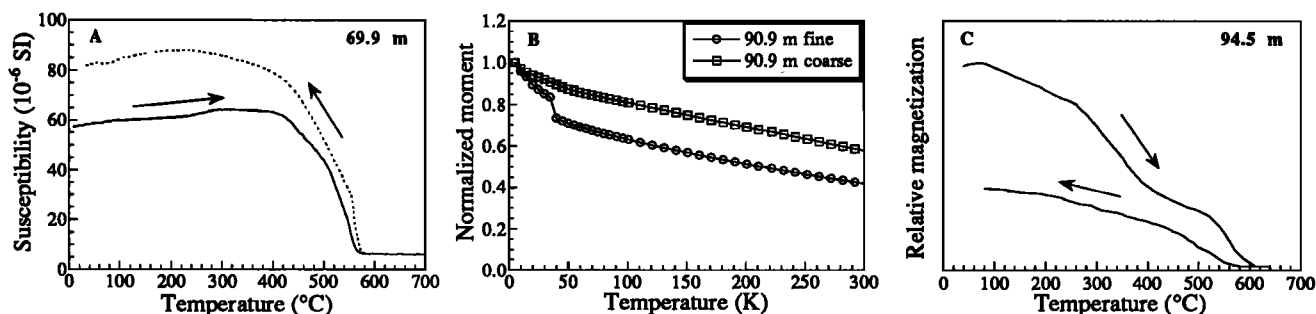


Figure 3 A. Low-field susceptibility versus temperature for a titanomagnetite-dominated bulk sediment sample (depth 69.9 m); B. M_{rs} versus temperature from 5 K to room temperature. Data are from fine (extracted from a pumped slurry) and coarse (rock fragments extracted with a hand-held magnet) particles, respectively, in a magnetic extract from 90.9 m; C. Magnetization versus temperature for a sample containing greigite and titanomagnetite (depth 94.5 m).

canic sand beds at 2.3 m and 14.4 m indicate a dominance of pseudo-single domain grains ($M_{rs}/M_s \approx 0.2 - 0.3$) which makes it difficult to explain the high M_{rs}/χ ratios recorded from these horizons. Further magnetic mineral separates and petrological observations are necessary to provide clues as to why the M_{rs}/χ ratio is high for these horizons. Nevertheless, as stated by Roberts [1995], high ratios of M_{rs}/χ are not unique to greigite-bearing sediments and ancillary methods should be used to identify zones of greigite mineralization.

Greigite is difficult to identify optically because it is usually extremely fine-grained; however, the magnetic iron sulphides in separates from 90.9 m, 93.6 m, 94.5 m, 96.3 m, and 100.25 m look identical to aggregates of fine-grained greigite associated with pyrite from the Simpson oil field, Alaska [Reynolds *et al.*, 1994]. Some samples, particularly that from 94.5 m, contain rare euhedral iron sulphide particles that display strong optical anisotropy which is characteristic of pyrrhotite. Despite this, the 34 K magnetic transition for pyrrhotite is absent in low-temperature measurements (Figure 3b), and pyrrhotite is not evident in the x-ray diffraction (XRD) data, as discussed below. It is likely that pyrrhotite represents a minor component and that greigite is the dominant magnetic iron sulphide mineral in these sediments.

A distinct magnetic transition is evident at 40 - 50 K in some of the low temperature M_{rs} data (Figure 3b). Measurements of M_s verified that this magnetic transition is due to thermal unblocking at 40 K (the Néel temperature of ilmenite, cf. Hunt *et al.* [1995]). Ilmenite was identified petrographically in all of the separates in which this unblocking is evident.

Even though titanomagnetite is present, as indicated by high-temperature analyses and by petrographic observations, the Verwey transition is not observed in the range of temperatures expected for titanomagnetite [cf. Hunt *et al.*, 1995]. This suggests that the surfaces of any fine titanomagnetite grains are probably oxidized [cf. Özdemir *et al.*, 1993]. This interpretation is consistent with petrographic and XRD (see below) observations of oxidized magnetic phases. No other low-temperature transitions were observed in these samples (Figure 3b), which is consistent with, but not diagnostic of, the presence of greigite.

High-temperature data from the potential greigite-bearing horizons contain a break in slope at about 260 - 270°C (Figure 3c), which may be indicative of greigite [Snowball and Thompson, 1990a; Roberts and Turner, 1993; Reynolds *et al.*, 1994; Roberts, 1995]. However, the high-temperature behaviour normally expected for greigite-dominated samples is obscured by the presence of a detrital titanomagnetite component as well as by the probable high-temperature oxidation of the greigite to a magnetic iron oxide phase (Figure 3c). The presence of detrital titanomag-

netite has been confirmed by petrographic examination of the same separates. Thus, while several lines of evidence point toward the presence of greigite, clear identification of greigite was not possible on the basis of magnetic and petrographic methods alone because the presence of several magnetic minerals partially obscures the the identification criteria of Roberts [1995]. In contrast to these ambiguous indicators of greigite, x-ray diffractograms clearly indicate the presence of greigite, as well as magnetite, hematite, and possible maghemite (Figure 4).

Discussion and conclusions

Despite the non-uniqueness of the magnetic criteria for detection of sedimentary greigite, these criteria are clearly useful for identifying intervals of greigite-bearing sediment, even in environments with complex magnetic mineralogy. For the Butte Valley sediments, it was necessary to use XRD to unambiguously detect greigite; nevertheless, the magnetic criteria were all consistent with the presence of greigite and they provided the primary evidence that pointed to its occurrence.

Identification of greigite in these sediments has important implications for interpretation of the paleoenvironmental record. First, much of the greigite in the Butte Valley record occurs in 2.5 - 3.0 Ma strata (i.e., 90 - 100 m). If the Butte Valley greigite formed soon after deposition, it confirms previous studies which indicate that greigite can persist for long periods in the geological record [e.g., Skinner *et al.*, 1964; Krs *et al.* 1990; Tric *et al.*, 1991; Horg *et al.* 1992; Roberts and Turner, 1993; Hallam and Maher, 1993; Reynolds *et al.*, 1994]. Second, the detrital mineral magnetic record will be partially obscured by the presence of authigenic greigite and care must be exercised in interpreting the

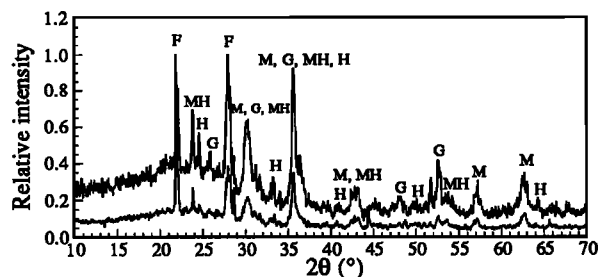


Figure 4 XRD data (Cu-K α radiation) from magnetic separates from 94.5 m and 96.3 m (upper and lower curves, respectively), with the most intense reflections normalized to unity for each data set. G is greigite, M is magnetite, MH is possible maghemite, H is hematite, F is feldspar.

mineral magnetic record of greigite-bearing horizons at Butte Valley as a paleoclimate proxy. Third, greigite carries a stable chemical remanent magnetization which is usually acquired post-depositionally during shallow burial. Time lags between remanence acquisition for authigenic and detrital phases may not be large, but this possibility adds complexity to the interpretation of high-frequency geomagnetic field variations in sedimentary records. Fourth, the presence of greigite may have significance as a paleoenvironmental indicator. Greigite often forms as a precursor to pyrite in a series of reactions which are limited by three principal factors [Bernier, 1984], including the availability of: dissolved sulphate in the sediment pore waters, microbially metabolizable organic matter, and iron in detrital minerals which reacts with H₂S to form iron sulphide minerals. At Butte Valley, detrital iron-bearing minerals are clearly abundant. Similarly, reactive organic matter should not be a limiting factor here. Dissolved sulphate concentrations are typically low in lake sediments and sulphate is usually consumed during bacterial sulphate reduction at depths of a few centimeters [Bernier, 1984]. The key factor is therefore likely to be the availability of dissolved sulphate, with greigite preservation being favoured by consumption of sulphate before full reaction to pyrite occurs. The amount and availability of sulphate may be related to limnological conditions such as whether the lake basin was open or closed.

All of the zones of greigite mineralization detected in the Butte Valley record occur below 69 m. A major change in lake conditions, as indicated by the marked change in sedimentation rate (Figure 1), occurred near this depth. The observation that greigite occurs only in the lower part of the sequence suggests a major difference in water chemistry, at least periodically, between the earlier and latter parts (i.e., pre- and post- ca 1 Ma) of the history of the lake. Greater residence times of lake water would favour sulphate accumulation which is a critical factor in authigenic formation of iron sulphide minerals. Such information is clearly important in reconstructing paleoenvironments. Although firm conclusions of this nature are not yet possible for the Butte Valley record, further work on microfossil assemblages should provide important paleolimnological information that may clarify the environmental implications of the presence of greigite. Nevertheless, the potential of easily detectable mineral phases, such as greigite, as paleoenvironmental indicators underscores the importance of joint magnetic, paleontological, and geochemical studies of lake sediments.

Although greigite is considered to be a minor magnetic mineral, it is clearly important in magnetic studies of anoxic sediments. Greigite may also prove to be an important paleoenvironmental indicator in its own right.

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David P. Adam, U.S.G.S., 345 Middlefield Rd, Menlo Park, CA 94025, USA.

Richard L. Reynolds, U.S.G.S., Box 25046, MS 964, Denver Federal Center, Denver, CO 80225, USA.

Andrew P. Roberts and Kenneth L. Verosub, Department of Geology, University of California, Davis, CA 95616, USA.

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