Assessing the timing of greigite formation and the reliability of the Upper Olduvai polarity transition record from the Crostolo River, Italy

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Received 2 December 2004; revised 1 February 2005; accepted 7 February 2005; published 11 March 2005.

[1] The Crostolo River section in Italy yielded a detailed record of the Upper Olduvai geomagnetic polarity transition that has been used to support the hypothesis of deep mantle control on the transitional geomagnetic field. The paleomagnetic record is carried by the authigenic iron sulphide, greigite, which was interpreted to have formed shortly after deposition. Our detailed scanning electron microscope investigations indicate the presence of at least 3 generations of pyrite, which usually forms with greigite as a precursor. This suggests that the total magnetization is a complex composite that produced a smoothed record of transitional field behaviour. **Citation:** Roberts, A. P., W.-T. Jiang, F. Florindo, C.-S. Horng, and C. Laj (2005), Assessing the timing of greigite formation and the reliability of the Upper Olduvai polarity transition record from the Crostolo River, Italy, *Geophys. Res. Lett.*, *32*, L05307, doi:10.1029/2004GL022137.

1. Introduction

[2] The ~11-m-thick record of the Upper Olduvai polarity transition from marine sediments exposed by the Crostolo River, Italy [*Tric et al.*, 1991], is the thickest published polarity transition record. It is part of a database of records used to support the hypothesis of long-term lower mantle control on the reversal process [*Laj et al.*, 1991]. Understanding major geophysical phenomena, such as the geomagnetic field reversal process, depends on the reliability of such databases. The reliability of this Upper Olduvai record is, by definition, less clear than for other records because the paleomagnetic signal is carried by authigenic greigite (Fe_3S_4) that grew after deposition. Detrital magnetite (Fe_3O_4) should provide a syn-depositional paleomagnetic signal, but the reliability of a polarity transition recorded by greigite requires strong evidence for early diagenetic growth with minimal delay between deposition and remanence acquisition.

[3] Greigite can rapidly grow as a precursor to pyrite in the laboratory at 25°C [e.g., *Sweeney and Kaplan*, 1973; *Benning et al.*, 2000], in the water column of euxinic marine waters [e.g., *Cutter and Kluckhohn*, 1999], or in anoxic natural sediments within decades or less [e.g., *Pye*, 1981; *Reynolds et al.*, 1999]. Greigite formation in an anoxic water column and subsequent burial would provide ideal magnetic recording, but this would only occur in stagnant bottom waters. Greigite formation within years or decades would also be suitable for high-resolution paleomagnetic studies if remanence acquisition progressed sequentially with burial.

[4] *Tric et al.* [1991] argued that greigite in the Crostolo River sequence formed during early diagenesis within 500 years (possibly 100 years) of deposition. Such interpretations, with relatively short time lags between deposition and authigenic greigite formation, were relatively widely accepted at the time [e.g., *Roberts and Turner*, 1993], but have only been demonstrated in a few modern settings [e.g., *Pye*, 1981; *Reynolds et al.*, 1999]. *Tric et al.* [1991] documented strong field evidence for their interpretation. First, the position and duration of the Olduvai Subchron is consistent with biostratigraphy. Second, smooth variation in transitional paleomagnetic directions within the Upper Olduvai transition is abruptly disrupted by a ~60° angular jump on either side of an apparently brief depositional hiatus. They argued that, if the greigite grew substantially later than deposition, the magnetic direction would not jump at the hiatus. *Tric et al.* [1991] sampled fresh outcrops with minimal delay between sampling and measurement (1–2 weeks) to avoid greigite oxidation and concomitant degradation of the paleomagnetic signal.

[5] Many studies demonstrate that greigite can grow during later diagenesis, thereby producing polarity records that are inconsistent with robust independent age control [e.g., *Florindo and Sagnotti*, 1995; *Horng et al.*, 1998; *Roberts and Weaver*, 2005]. Sister samples from the same horizon sometimes record both polarities as a result of greigite growth at different times [e.g., *Jiang et al.*, 2001]. In other cases, geochemical observations provide evidence for greigite formation at multiple stages during diagenesis [e.g., *Reynolds et al.*, 1994]. *Liu et al.* [2004] demonstrated in a modern depositional setting that greigite can grow 3–30 m below the sediment surface as a result of ongoing diagenesis. While greigite can compromise paleomagnetic studies, we are satisfied at face value by the claims of *Tric et al.* [1991] that their Upper Olduvai transition could have been recorded during early burial. However, widespread documentation of complex magnetizations carried by greigite in similar sediments indicates that closer examination of these sediments is warranted.

2. Sampling and Methods

[6] Paleomagnetic samples were collected from fresh outcrops at three sites from the Crostolo River after cleaning

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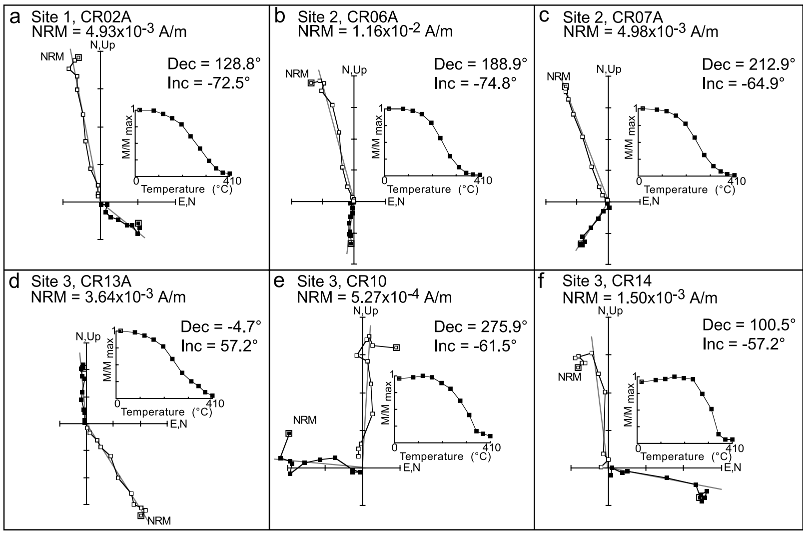

Figure 1. Demagnetization plots for representative samples from greigite-bearing sediments from the Crostolo River. (a) Site 1—reversed polarity; (b and c) site 2—reversed polarity; (d) site 3—normal polarity; (e and f) site 3—inconsistent reversed polarity.

weathered surficial material to depths of >0.5 m. The stratigraphically lowest site was sampled ~80 m from the small dam on the Vendina River upstream of its confluence with the Crostolo River. This site lies within the reversed polarity Matuyama Chron below the normal polarity Olduvai Subchron of *Tric et al.* [1991]. Site 2 was also sampled below the Olduvai Subchron, at the confluence of the Vendina River and the Crostolo River. Site 3 was sampled ~200 m downstream of site 2 and lies within the Olduvai Subchron of *Tric et al.* [1991]. No samples were taken from the Upper Olduvai transition because the outcrop was under water when we sampled.

[7] Samples were subjected to static and tumbling alternating field (AF) demagnetization and to thermal demagnetization. Remanence measurements were made with a 2-G Enterprises magnetometer. Paleomagnetic analyses were made within 1 week of sampling to avoid the problem of progressive oxidation reported by *Tric et al.* [1991]. Results of AF and thermal demagnetization were equivalent; as was the case for *Tric et al.* [1991], thermal demagnetization yielded the cleanest results.

[8] Resin-impregnated polished sections were made from fresh sediment samples. They were subjected to scanning electron microscope (SEM) analysis using a LEO 1450VP SEM, operated at 15 keV at the Southampton Oceanography Centre. Elemental analyses were made with an X-ray energy-dispersive spectrometer (EDS). Point analyses of mineral grains, or clusters of grains (2–3 μm beam diameter), were made using a Princeton Gamma Tech (IMIX-PTS) system. Analyses were calibrated to a pyrite standard. EDS spectra have a high iron to sulphur ratio for greigite (44% (atomic %) Fe; 56% S) compared to pyrite (34% Fe; 66% S), which makes it straightforward to identify the two phases.

3. Results

[9] Our extensive rock magnetic and mineralogical analyses are consistent [cf. *Roberts*, 1995] with the interpretation of *Tric et al.* [1991] that greigite is the dominant magnetic mineral in the studied sediments. Detailed bulk mineralogical results are presented by *Tric et al.* [1991] and are not reproduced here. Representative paleomagnetic results for the 3 sites (Figure 1) are consistent with the results of *Tric et al.* [1991], where sites 1 and 2 have reversed polarity (Figures 1a–1c), and site 3 has normal polarity (Figure 1d). For sites 1 and 2, the mean paleomagnetic directions (uncorrected for minor northward tilt) are Dec. = 113.8°, Inc. = −68.9° (n = 8; α_{95} = 10.4°) and Dec. = 203.4°, Inc. = −76.0° (n = 16, α_{95} = 5.7°), respectively. These site-mean declinations are variable, but together with the inclinations they clearly indicate reversed polarity. In contrast, of the 9 samples analysed from site 3, seven have scattered normal polarity directions (e.g., Figure 1d), and two have reversed polarity (Figures 1e and 1f). Site 3 lies within the Olduvai Subchron of *Tric et al.* [1991], so the samples with contradictory polarities are the 2 reversed polarity samples (Figures 1e and 1f). *Tric et al.* [1991] also observed contradictory polarities (see their Figure 7), which they attributed to post-depositional oxidation because polarities became consistent for multiple samples from all stratigraphic levels after using a bulldozer to dig deeper into the outcrop (see their Figure 8). Our anomalous reversed polarity magnetizations suggest that Brunhes Chron oxidation is not responsible, and, because all samples were handled identically, post-sampling oxidation also seems less likely than a geological origin for the spurious magnetizations. However, it is not possible to rule out the interpretation of *Tric et al.* [1991] that anomalous results are due to laboratory alteration.

[10] SEM observations of microtextural relationships can help to assess the origin of magnetizations carried by magnetic iron sulphides [*Jiang et al.*, 2001; *Roberts and Weaver*, 2005]. Pyrite (P) and greigite (G) occur in a range of contexts in the Crostolo samples, including large polyframboidal aggregates within foraminifer tests (Figures 2a and 2b), variably sized polyframboidal aggregates in the sediment matrix (Figures 2c–2h), individual framboids and other crystals in the matrix, and as individual grains that

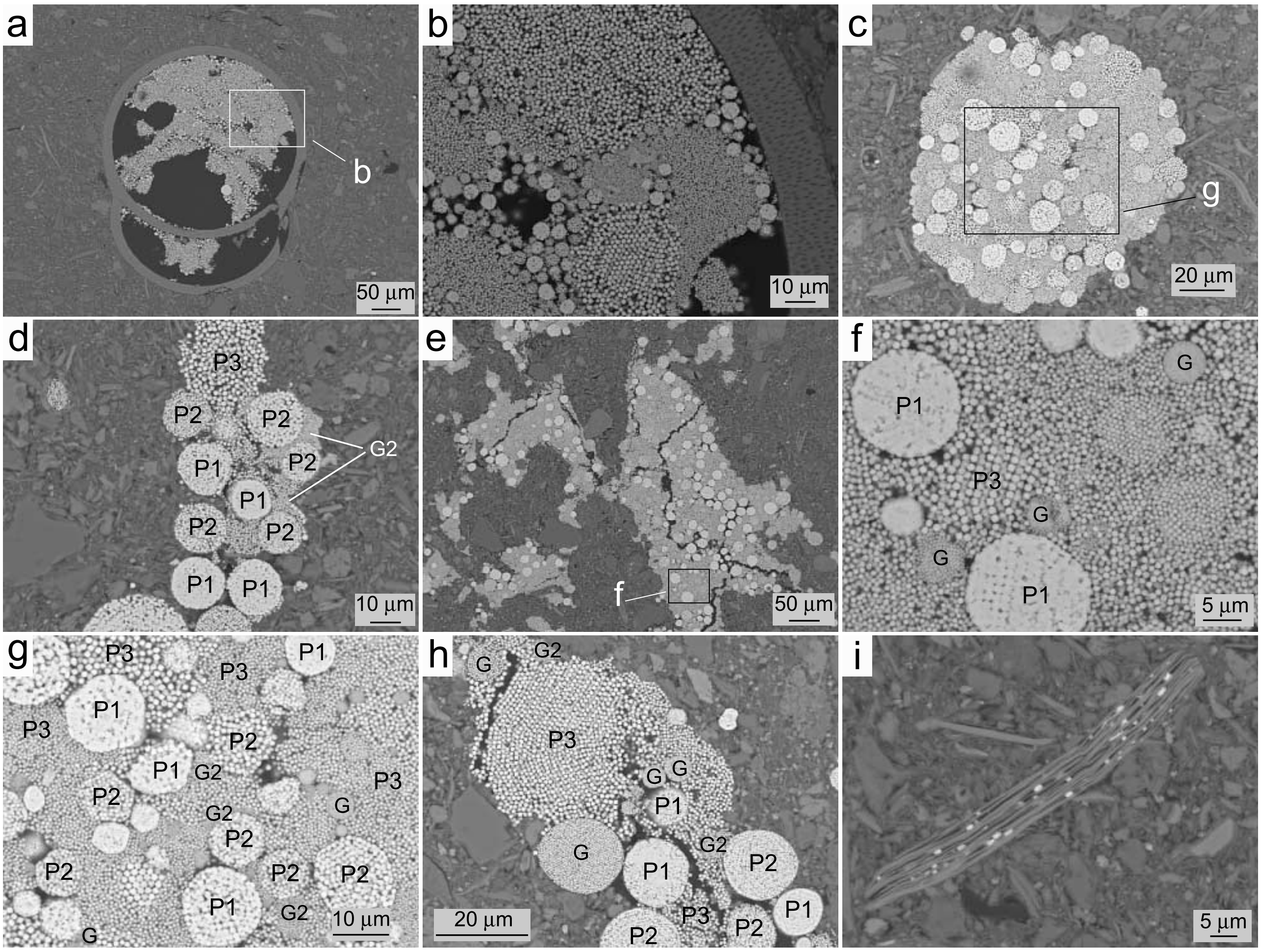

Figure 2. Back-scattered electron images illustrating microtextures and authigenic growth sequences of pyrite and greigite. (a) Polyframboidal aggregate filling space inside a foraminifer (sample CR07B; site 2). (b) Close-up of pyrite and greigite shown in Figure 2a. (c) Polyframboidal aggregate (probably remineralized organic matter) within sediment matrix (sample CR11B; site 3). (d) Smaller polyframboidal aggregate within sediment matrix (sample CR08B; site 2). (e) Large, irregular polyframboidal aggregate within sediment matrix (sample CR08B; site 2). Cracks probably formed during sample preparation. (f) Close-up indicated in Figure 2e. (g) Close-up indicated in Figure 2c. (h) Close-up of polyframboidal aggregate from sample CR13B (site 3). (i) Phyllosilicate with iron sulphides on sheet surfaces within the grain (sample CR08B; site 2). P1: earliest (overgrown) framboidal pyrite; P2: 2nd generation non-overgrown framboidal pyrite; P3: 3rd generation space filling pyrite; G: greigite framboids with unconstrained timing of formation; G2: late greigite generation that grew on surfaces of P1 and P2 framboids. G2 either grew before, or at the same time as, the P3 pyrite.

grew on the surfaces of inter-layer sheets of phyllosilicate grains (Figure 2i). The iron sulphides give stoichiometrically correct Fe/S ratios. Oxidation (before or after sampling) would not result in a correct stoichiometry because it produces an oxygen peak in EDS analyses as well as higher concentrations of Fe compared to S. These factors suggest that the observed sulphides are unaltered. Several generations of iron sulphide are indicated by SEM observations (Figure 2), which have important implications for the Crostolo River paleomagnetic record.

[11] The polyframboidal aggregates in Figures 2a–2h contain large (~10–20 μm) pyrite framboids in which individual crystals are partially obscured by pyrite overgrowths (P1). Such overgrowths are a common early diagenetic feature in anoxic sediments and reflect a paragenetic product of more evolved pore waters [*Raiswell*, 1982]. Pyrite framboids that lack overgrowths are interpreted to have formed next in the authigenic sequence (P2). Finally, a third generation of non-framboidal space filling pyrite (P3) occurs in interstices between the two framboidal generations. Greigite (G) framboids always contain the smallest crystals, but it is not clear when they formed except that they pre-date P3 pyrite (because P3 pyrite grew around G framboids). Greigite also occurs as less regular aggregates that fill space between framboids (G2). This greigite gives the best evidence for timing of formation because it grew on surfaces of P1 and P2 framboids (Figures 2d, 2g, and 2h). Greigite growth upon existing framboids is consistent with the neoformation mechanism suggested by *Jiang et al.* [2001]. G2 probably formed at the same time as, or as a precursor to, the P3 generation. It is unclear why this greigite did not become pyritized since nearby grains were later transformed to pyrite. We assume that this resulted from localized exhaustion of dissolved sulphide.

[12] In addition to evidence for several generations of iron sulphide growth within polyframboidal aggregates, all

of the studied samples contain sulphides that grew within phyllosilicate sheets (e.g., Figure 2i). This evidence has important implications for the time duration of iron sulphide formation. *Canfield et al.* [1992] showed that common sheet silicates (biotite, chlorite, smectite, illite) react slowly, with a half-life of 120,000 years when in contact with 1 mM concentrations of pore water sulphide (i.e., typical dissolved sulphide concentrations during sulphate reduction). Iron sulphide formation is then limited by availability of reactive iron. The large surface area of sheet silicate layers, and their slow reactivity, provide abundant sites for sulphide formation over long time spans. *Jiang et al.* [2001] and *Roberts and Weaver* [2005] argued that preservation of greigite within sheet silicates has major implications for paleomagnetic records. The fact that this is so commonly observed in our Crostolo River samples indicates that they were exposed to sulphidic pore waters for considerable time periods.

4. Discussion and Conclusions

[13] Pyrite and greigite formed at various times after deposition of the studied marine sediments. We have no constraints on the timing of formation of various generations of sulphide, and it is possible that they all formed during early diagenesis, as suggested by the strong field evidence of *Tric et al.* [1991]. Nevertheless, the presence of several sulphide generations suggests that the total magnetization is a complex composite of contributions from each generation. Widespread sulphidization of phyllosilicates suggests that sulphide growth occurred over a prolonged period because time intervals in excess of thousands of years seem necessary for partial dissolution of phyllosilicates [*Canfield et al.*, 1992]. Inconsistent polarities within the same stratigraphic horizon (e.g., Figures 1d–1f) can be explained by variable contributions from different generations of greigite that formed at times of different polarity, the sum of which can vary within short distances [e.g., *Jiang et al.*, 2001]. These inconsistent reversed polarities probably formed during the Matuyama Chron, after the Olduvai Subchron. This suggests time delays of 10's to 100's of kyr for the dominant greigite generation. Many forcing mechanisms can change pore water conditions and produce late sulphide growth [*Roberts and Weaver*, 2005].

[14] The presence of several sulphide generations in all of the studied samples raises questions about how *Tric et al.* [1991] documented such generally consistent magnetic polarities and field evidence suggestive of early diagenetic greigite formation. The field and paleomagnetic evidence suggests that any later diagenetic greigite must generally be volumetrically dominated by early greigite. Also, the paleomagnetic record must have generally been locked in within some fraction of the time taken for the field to reverse polarity. Despite apparent domination of early diagenetic greigite, this composite magnetization will have been smoothed with each later generation of greigite growth. Smoothing would have suppressed fine details of transitional field behaviour, as suggested by the lack of "stop and go" geomagnetic features observed in other high-resolution transition records. This Upper Olduvai transition record appears to be a "best-case" recording involving greigite, with dominance of early diagenetic greigite. Nevertheless, there was also considerable potential for growth of much later greigite and associated inconsistent polarities. We conclude that this Upper Olduvai polarity transition record suffers from recording complexities and that considerable caution should be exercised in interpreting its details as representing real transitional field characteristics.

[15] **Acknowledgment.** We thank the Royal Society of London and the National Science Council of the ROC for funding, Jaume Dinarès-Turell for help with sampling, Giuliana Villa for hospitality, Richard Pearce for SEM assistance and Rich Reynolds and an anonymous reviewer for constructive comments.

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