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Greigite formed in early Pleistocene lacustrine sediments from the Heqing Basin, southwest China, and its paleoenvironmental implications



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ABSTRACT

The ferrimagnetic iron sulfide greigite (Fe₃S₄) occurs widely in sulfidic lacustrine and marine sedimentary environments. Knowledge of its formation and persistence is important for both magnetostratigraphic and paleoenvironmental studies. Although the formation mechanism of greigite has been widely demonstrated, the sedimentary environments associated with greigite formation in lakes, especially on relatively long timescales, are poorly understood. A long and continuous sequence of Pleistocene lacustrine sediments was recovered in the Heqing drill core from southwestern China, which provides an outstanding record of continental climate and environment. Integrated magnetic, geochemical, and paleoclimatic analysis of the lacustrine sequence provides an opportunity to improve our understanding of the environmental controls on greigite formation. Rock magnetic and scanning electron microscope analyses of selected samples from the core reveal that greigite is present in the lower part of the core (part 1, 665.8-372.5 m). Greigite occurs throughout this interval and is the dominant magnetic mineral, irrespective of the climatic state. The magnetic susceptibility (χ) record, which is mainly controlled by the concentration of greigite, matches well with variations in the Indian Summer Monsoon (ISM) index and total organic carbon (TOC) content, with no significant time lag. This indicates that the greigite formed during early diagenesis. In greigite-bearing intervals, with the χ increase, B_c value increase and tends to be stable at about 50 mT. Therefore, we suggest that χ values could estimate the variation of greigite concentration approximately in the Heqing core. Greigite favored more abundant in terrigenous-rich and organicpoor layers associated with weak summer monsoon which are characterized by high χ values, high Fe content, high Rb/Sr ratio and low TOC content. Greigite enhancement can be explained by variations in terrigenous inputs. Our studies demonstrate that, not only the greigite formation, but also its concentration changes could be useful for studying climatic and environmental variability in sulfidic environments.

1. Introduction

Lake sediments provide continuous, high-resolution records of past climatic and environmental changes and, thus, are increasingly important for studies of past global change and regional environmental evolution (Dearing et al., 2006; Fagel et al., 2007; Liu et al., 2012; Oldfield, 2013; Just et al., 2016). Variations in the mineralogy, concentration, and grain size of magnetic minerals in lake sediments are a sensitive indicator of environmental processes within the terrestrial catchment and can also provide information about the depositional environment and post-depositional processes (Ao et al., 2010; Oldfield, 2013; Chang et al., 2014; Fu et al., 2015; Roberts, 2015; Just et al., 2016). However, the origin of magnetic property variations in lake sediments may be complex. An important primary control is the input of detrital iron oxides, which may reflect variations in weathering, erosion, and sediment transport, as well as other processes (Thompson and Morton, 1979; Oldfield et al., 1985; Evans et al., 1997). However, post-depositional alteration can modify or obscure detrital magnetic signals (Reynolds et al., 1999; Robinson and Sahota, 2000; Roberts and Weaver, 2005; Roberts, 2015).

Post-depositional diagenesis in lake sediments is relatively common and well documented (Snowball and Thompson, 1988; Roberts et al., 1996; Nolan et al., 1999; Reynolds et al., 1999; Demorya et al., 2005; Babinszki et al., 2007; Frank et al., 2007; Ron et al., 2007; Ao et al., 2010; Bol'shakov and Dolotov, 2011; Murdock et al., 2013; Roberts, 2015; Just et al., 2016). In iron-reducing sedimentary environments,

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Fig. 1. Location of the study area, wind directions associated with the Asian monsoon systems, and bedrock and surficial geology of the Heqing Basin (An et al., 2011).

microbes utilize iron oxides and dissolve fine-grained detrital ferrimagnetic iron oxide minerals such as magnetite and maghemite. Subsequently, authigenesis of iron sulfides (e.g., greigite) occurs during the process of pyritization (Snowball and Thompson, 1988; Roberts, 1995; Robinson and Sahota, 2000; Kao et al., 2004; Rowan and Roberts, 2006; Chang et al., 2014; Fu et al., 2015; Just et al., 2016).

Greigite (Fe₃S₄) is a widespread ferrimagnetic iron sulfide mineral in sulfidic marine and lacustrine sedimentary environments. During early diagenesis, greigite forms as a precursor to pyrite (FeS₂) in sulfatereducing environments, and it can also be produced directly by magnetotactic bacteria. Roberts and Weaver (2005) argued that greigite can form at any time during diagenesis if dissolved sulfide and reactive iron are available. Therefore, knowledge of the formation and geological persistence of greigite are important for both magnetostratigraphic and paleoenvironmental studies.

The sulfate content in lakes is much lower than in marine environments and, therefore, sulfate will be exhausted at shallow depths in the sediment or even within the water column. Methanic magnetic mineral diagenesis is thus likely to be more important than sulfidic diagenesis in lake sediments than in marine sediments, although iron sulfide formation is commonplace in lake sediments and thus, sulfidic diagenesis remains important (Roberts, 2015). Overall, the lacustrine sedimentary environments linked to greigite formation, especially in the geological past, are relatively poorly understood. For example, in Lake Qinghai in North China, greigite is present in interglacial sediments with a relatively high total organic carbon (TOC) content (Fu et al., 2015). Conversely, in Lake Ohrid in Macedonia, greigite is present within glacial sediments with a relatively low TOC content (Just et al., 2016).

The Heqing drill core is a long and continuous lacustrine sediment

core from Heqing Basin in southwestern China with a basal age of about 2.78 Ma (An et al., 2011 (Supporting Online Material)). Well-characterized climatic cycles, revealed by analysis of environmental proxies indicate that the core provides an exceptional record of continental climate and environment that documents the evolution of the Indian summer monsoon (ISM) (Xiao et al., 2010; An et al., 2011). The lower part of the core contains grayish-green-colored clay sediments, that are indicative of ferruginous and sulfidic diagenetic environments, and within which greigite is present. The aim of the present study is to determine the climatic and environmental control for the greigite formation and greigite concentration changes in these lacustrine sediments.

2. Study area

Heqing Basin $(26^{\circ}27'-26^{\circ}46'N, 100^{\circ}08'-100^{\circ}17'E)$ is a faultbounded basin in northwestern Yunnan Province, southwestern China (Fig. 1), situated at the southeastern margin of the Tibetan Plateau, at the terminus of the Hengduan Mountains. It is a closed basin surrounded by mountains with altitudes up to 2500 m. The basin has an N-S orientation and is 22 km in length. The width in the E-W direction is 5–10 km, and the basin area is 144 km². The basin receives drainage from the surrounding rivers and streams, and Caohai Lake is located in the current center of the basin. The Yanggong River, which originates in the Yulong Mountains, flows across the basin from north to south and then flows eastward into the Jinsha River. The catchment bedrock consists of Triassic limestone in the west, and Paleogene calcareous conglomerate, sandstone, and silty shale, in the east.

The Heqing drill core (26°33′43.1″N, 100°10′14.2″E, 2190 m) was obtained in 2002 from the center of Heqing Basin. The calibrated depth

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