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# Greigite from carbonate concretions of the Ediacaran Doushantuo Formation in South China and its environmental implications

Jin Dong[a,b], Shihong Zhang[a,*], Ganqing Jiang[c], Haiyan Li[a], Rui Gao[b]

[a] State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences, Beijing 100083, PR China
[b] Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, PR China
[c] Department of Geoscience, University of Nevada, Las Vegas, NV 89154-4010, USA

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ABSTRACT

Greigite ($Fe_3S_4$) is a ferrimagnetic iron sulfide that commonly forms as a precursor of pyrite in anoxic environments where the supply of reactive Fe outpaces that of sulfide ($H_2S$ and $HS^-$). Because of its metastability and sensitivity to redox changes during burial, greigite has been rarely documented in rocks older than the Cretaceous. Here we report well-preserved greigite in carbonate concretions of the upper Doushantuo Formation (ca. 551 Ma) in the Yangtze Gorge area, South China. Greigite in the carbonate concretions coexists with anhedral and framboidal pyrite, and is distributed in clay-rich carbonates with card-house microtextures and dolomitic spherical structures indicative of early diagenetic formation during shallow burial. Preservation of greigite in carbonate concretions of the upper Doushantuo Formation implies that these concretions maintained a closed micro-system since their formation and that they provide information about the ancient depositional and early diagenetic environments.



## 1. Introduction

Greigite is a ferrimagnetic iron sulfide mineral that has a similar spinel crystal structure to magnetite (Skinner et al., 1964). It usually forms as a metastable precursor of pyrite in anoxic sedimentary environments where dissolved iron provided by reduction of reactive iron oxides outpaces sulfide supply (Karlin and Levi, 1983; Berner, 1984; Canfield and Berner, 1987; Karlin, 1990a,b; Kao et al., 2004). Because of its ferrimagnetic attributes, greigite has been widely documented in paleomagnetic and paleoenvironmental studies (e.g. Snowball and Thompson, 1988; Snowball, 1991; Roberts and Turner, 1993; Florindo and Sagnotti, 1995; Horng et al., 1998; Jiang et al., 2001; Roberts et al., 2005; Rowan and Roberts, 2005, 2006, 2008; Sagnotti et al., 2005). In Cenozoic successions, greigite has been found in a wide range of depositional environments, such as estuaries and deep-sea fans (Kasten et al., 1998), hemipelagic deposits on continental shelves and deep-water basins (Berner, 1984; Horng et al., 1992; Lee and Jin, 1995; Sagnotti and Winkler, 1999; Oda and Torri, 2004), and gas hydrate systems (Housen and Musgrave, 1996; Larrasoaña et al., 2007). However, because greigite can be poorly crystalline and sensitive to redox changes and to elevated temperatures during deeper burial, its preservation and identification in old sedimentary successions is often difficult.

It has been inferred that greigite was part of an iron monosulfide membrane that served as a catalyst between fluids in a Hadean submarine hydrothermal redox front that may have enabled emergence of life on Earth (Russell et al., 1994; Russell and Hall, 1997), but either such early greigite has not been preserved in the geological record or it has not been discovered. The oldest strata reported to host hydrothermal greigite within siderite nodules are of Permo-Carboniferous age (Krupp, 1991, 1994). In this case, the preservation of greigite suggested that siderite nodules could provide protection from later oxidation (Krupp, 1994). Greigite has also been reported from Cretaceous strata of northern Alaska (Reynolds et al., 1994) and Peru (Linder and Gilder, 2011), but some of those reported greigites might have formed during late diagenesis, much younger than Cretaceous.

In this paper, we report the occurrence of greigite in carbonate concretions of the Ediacaran Doushantuo Formation in South China. These carbonate concretions are hosted in the black shales of the uppermost Doushantuo Formation that has been dated at ca. 551 Ma (Condon et al., 2005; Zhang et al., 2005). If the greigite in these concretions were formed close to the time of deposition, this would be the oldest documented occurrence of greigite in the geological record. We test this possibility and the potential paleoenvironmental information that can be provided by the occurrence of greigite.

* Corresponding author at: China University of Geosciences, Beijing, 29 Xueyuan Road, Haidian, Beijing 100083, PR China. Tel.: +86 10 82322257; fax: +86 10 82321983.
*E-mail address:* shzhang@cugb.edu.cn (S. Zhang).

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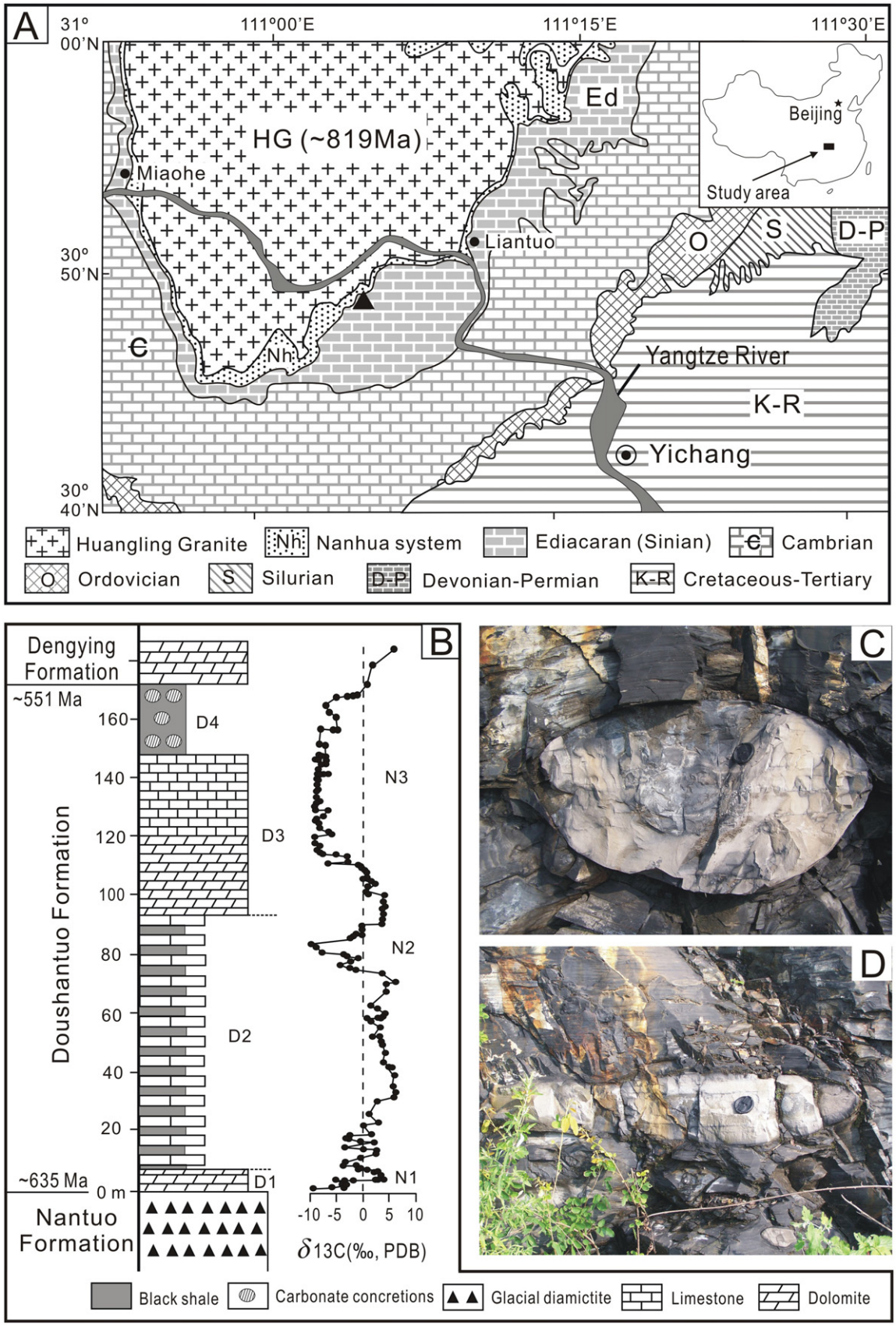


**Fig. 1.** (A) Simplified geological map of the Yangtze Gorge area (after Zhang et al., 2005) with location of the studied section (closed triangle). (B) Stratigraphic column of the Doushantuo Formation (after Jiang et al., 2007). (C and D) Field photographs of concretions (Camera lens cap in C and D is 65 mm across).