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Questioning the Biogenicity of Neoproterozoic Superheavy Pyrite by SIMS

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ABSTRACT

The Neoproterozoic sulfur isotope ($\delta^{34}S$) record is characterized by anomalously high $\delta^{34}S_{pyrite}$ values. Many $\delta^{34}S_{pyrite}$ values are higher than the contemporaneous $\delta^{34}S_{sulfate}$ (i.e., $\delta^{34}S_{pyrite}>\delta^{34}S_{sulfate}$), showing reversed fractionation. This phenomenon has been reported from the Neoproterozoic post-glacial strata globally and is called "Neoproterozoic superheavy pyrite". The commonly assumed biogenic genesis of superheavy pyrite conflicts with current understanding of the marine sulfur cycle. Various models have been proposed to interpret this phenomenon, including extremely low concentrations of sulfate in seawaters or porewaters, or the existence of a geographically isolated and geochemically stratified ocean. Implicit and fundamental in all these published models is the assumption of a biogenic origin for pyrite genesis, which hypothesizes that the superheavy pyrite is syngenetic (in water column) or early diagenetic (in shallow marine sediments) in origin and formed via microbial sulfate reduction (MSR). In this study, the Cryogenian Datangpo Formation in South China, which preserves some of the highest $\delta^{34}S_{pyrite}$ values up to +70‰, is studied by secondary ion mass spectrometry (SIMS) at unprecedented spatial resolutions (2 μm). Based on textures and the new sulfur isotope results, we propose that the Datangpo superheavy pyrite formed via thermochemical sulfate reduction (TSR) in hydrothermal fluids during late burial diagenesis, and therefore lacks a biogeochemical connection to the Neoproterozoic sulfur cycle. Our study demonstrates that SEM-SIMS is an effective approach to assess the genesis of sedimentary pyrite using combined SEM petrography and μm-scale $\delta^{34}S$ measurements by SIMS. The possibility that pervasive TSR has overprinted the primary $\delta^{34}S_{pyrite}$ signals during late diagenesis in other localities may necessitate the reappraisal of some of the $\delta^{34}S_{pyrite}$ profiles associated with superheavy pyrite throughout Earth's history.

Key words: microbial sulfate reduction (MSR), thermochemical sulfate reduction (TSR), secondary ion mass spectrometry (SIMS), scanning electron microscopy (SEM), sulfur isotopes, framboidal pyrite

INTRODUCTION

The Neoproterozoic Era (1000–541 Ma) marks a transitional period in Earth's history that is characterized by a considerable rise in atmospheric oxygen, a gradual transformation in ocean redox conditions, and the rise of animal life (Halverson and Shields-Zhou, 2011; Narbonne et al., 2012; Shields-Zhou et al., 2012; Xiao, 2014). Notably, the Cryogenian Period (ca. 720–635 Ma) witnessed two episodes

of global-scale low-latitude glaciation: the Sturtian glaciation (717–660 Ma) and the Marinoan glaciation (>639–635 Ma) (Hoffman et al., 1998; Rooney et al., 2015; Hoffman et al., 2017). These glaciations have been widely regarded as among the most profound ice ages in Earth's history. Sedimentological and paleomagnetic studies suggest that glaciers during the Cryogenian glaciations may have approached the equatorial latitudes, forming a "Snowball Earth" (Kirschvink, 1992; Hoffman et al., 1998; Hoffman and Schrag, 2002). Although the Neoproterozoic fossil record shows an Ediacaran (635–541 Ma) emergence of early animal life (Xiao et al., 2016), molecular clock studies suggest that the origin of the animal phyla may have occurred in early Neoproterozoic (Runnegar, 1982; Peterson et al., 2004). Therefore, a precise biogeochemical reconstruction of the Neoproterozoic Era is critical to understanding the environmental context of early animal life evolution.

A remarkable feature of the Neoproterozoic chemostratigraphy is the anomalously high pyrite sulfur isotope ($\delta^{34}S_{pyrite}$) values, many of which are higher than the inferred contemporaneous seawater $\delta^{34}S_{sulfate}$ values (i.e., $\delta^{34}S_{pyrite} > \delta^{34}S_{sulfate}$) that are reconstructed from coexisting sulfate phases (e.g., anhydrite, carbonate-associated sulfate) (Fig. 1; Appendix 1). These pyrites are commonly known as "superheavy pyrite" (Liu et al., 2006; Ries et al., 2009; Fike et al., 2015). The biogeochemical origin and palaeoenvironmental implications of the Neoproterozoic superheavy pyrite have puzzled geochemists for decades (Hayes et al., 1992; Fike et al., 2015). In marine sulfur cycles, $\delta^{34}S_{pyrite}$ signals can never be higher than coexisting $\delta^{34}S_{sulfate}$ signals (Canfield, 2001a; Böttcher, 2011; Canfield and Farquhar, 2012), therefore the occurrence of superheavy pyrite challenges the canonical understanding of the sulfur isotope systems.

Multiple studies have reported anomalously high $\delta^{34}S$ values in the Cryogenian Period (Fig. 1; Appendix 1), including the Datangpo Formation in South China (Wu et al., 2016 and references therein), the Tapley Hill Formation in Australia (Hayes et al., 1992; Gorjan et al., 2000), the Court and Rasthof formations in Namibia (Hurtgen et al., 2002; Gorjan et al., 2003), the Bonahaven Dolomite Formation in Scotland (Parnell and Boyce, 2017), and the Arena Formation in East Greenland (Scheller et al., 2018). Notably, reported superheavy pyrites in these formations all overlie the Sturtian glacial diamictite, leading to the speculation of a potential linkage between the superheavy pyrite and the Sturtian glaciation (Gorjan et al., 2000; Hurtgen et al., 2002).

Largely based on the post-glacial occurrence of the superheavy pyrites, a tantalizing hypothesis links the genesis of superheavy pyrite to a Snowball Earth glaciation (Gorjan et al., 2000; Hurtgen et al., 2002). In this scenario, the ocean during the Sturtian glaciation was covered with a thick ice sheet, therefore terrestrial sulfate input by riverine fluxes was significantly reduced or shut off. Continuous pyrite burial via microbial sulfate reduction (MSR) in the subglacial ocean drove seawater $\delta^{34}S_{sulfate}$ to extremely high values. During deglaciation, the high-$\delta^{34}S_{sulfate}$ water mass generated and maintained during the Snowball Earth upwelled onto continental shelf environments, causing the precipitation of superheavy pyrite in post-glacial successions at a global scale.

The above hypothesis is attractive in that it links the genesis of superheavy pyrites to the Sturtian glaciation. If correct, then extremely high seawater $\delta^{34}S_{sulfate}$ values hypothesized in the terminal Sturtian oceans are expected to be reflected in syngenetic or early authigenic pyrite in diamictite intervals assuming a certain fractionation between $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{sulfide}$. Insofar as pyrite authigenesis could represent a broad spectrum of conditions from syndepositional to postdepositional, pyrites can be remarkably zoned or heterogeneous. Therefore, conventional >mm-scale $\delta^{34}S_{pyrite}$ analysis of mineral concentrates extracted from bulk samples may be useful in constraining the $\delta^{34}S_{sulfate}$ signals of contemporaneous seawater. To test this hypothesis, it is critical to target early authigenic pyrite in diamictite samples and analyze the $\delta^{34}S_{pyrite}$ values in situ at micron-scale.

The focus of this study is the Cryogenian strata in South China (Fig. 2). Superheavy pyrite has been widely reported from the Cryogenian Datangpo Formation in South China with anomalously high

$\delta^{34}S_{pyrite}$ values up to ca. +70‰ (Liu et al., 2006; Li et al., 2012; Wu et al., 2016). The post-Sturtian seawater $\delta^{34}S_{sulfate}$ value is estimated to be ca. +26‰ based on nodular and "chicken wire" anhydrite in Australia (Gorjan et al., 2000), or no more than ca. +50‰ based on carbonate-associated sulfate (CAS) analysis of the Cryogenian carbonates in Australia, Namibia (Hurtgen et al., 2005) and South China (Lang, 2016). Based on these $\delta^{34}S_{sulfate}$ constraints, many of the published $\delta^{34}S_{pyrite}$ values from the Cryogenian Datangpo Formation are much higher than the inferred coeval seawater $\delta^{34}S_{sulfate}$ values (Fig. 1; Appendix 1).

INTERROGATING THE SUPERHEAVY PYRITE

To understand the origin of the superheavy pyrite, two outstanding questions should be addressed. First, how to create and maintain a high-$\delta^{34}S_{sulfate}$ reservoir? Based on current knowledge of sulfur isotope systems, to generate high-$\delta^{34}S_{pyrite}$ values requires a sulfate reservoir with even higher $\delta^{34}S_{sulfate}$. Therefore, the existence of a sulfate reservoir with extremely high-$\delta^{34}S_{sulfate}$ has been invoked in multiple models. Models for such high-$\delta^{34}S_{sulfate}$ reservoirs show a wide spectrum of geological settings: an ice-covered ocean during a hard snowball-Earth glaciation (Gorjan et al., 2000; Walter et al., 2000; Gorjan et al., 2003; Parnell and Boyce, 2017), a restricted basin with limited access to the open ocean (Li et al., 2012), an isolated porewater system (Chen et al., 2008), a sulfate minimum zone in the water column (Logan et al., 1995), a stratified ocean with substantial burial of pyrite in the euxinic deep ocean (Logan et al., 1995; Canfield, 2004), or a local euxinic water mass with active emissions of low-$\delta^{34}S_{org}$ organic sulfur (Lang, 2016; Lang et al., 2016).

Second, how to reverse sulfur isotope fractionations ($\Delta^{34}S_{sulfate\text{-}sulfide}$) to negative values? During microbial sulfate reduction (MSR), $\delta^{34}S_{pyrite}$ can approach, but not be higher than, the coexisting $\delta^{34}S_{sulfate}$ signals. Therefore, to produce reversed $\Delta^{34}S_{sulfate\text{-}sulfide}$ values, the sulfur reservoirs of $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{sulfide}$, respectively, have to be decoupled. In other words, two coexisting, but separated, sulfur reservoirs are needed to explain the reversed values of $\Delta^{34}S_{sulfate\text{-}sulfide}$. Such conditions are uncommon in marine environments.

Implicit among most of the published models is the notion that the superheavy pyrite formed via MSR. However, this assumption has not been tested. To test this assumption and reevaluate published models, an integrated approach that combines both basin-scale field observation and µm-scale SIMS $\delta^{34}S_{pyrite}$ analysis coupled to SEM-based petrography is required. For example, pyrite formed in seawater (i.e., open system) vs. in pore waters (i.e., restricted system) could result in different patterns of $\delta^{34}S_{pyrite}$ at µm scale when Rayleigh fractionation occurs. Higher $\delta^{34}S_{pyrite}$ values are expected to be strongly zoned in late-stage overgrowths of pyrite if it forms in an increasingly fractionated pore-water system. In contrast, pyrite formed in the marine water column should record relatively low $\delta^{34}S_{pyrite}$ values without strong heterogeneity in $\delta^{34}S_{pyrite}$ at µm scale. In addition, pyrite formed during early syndepositional diagenesis vs. late burial diagenesis could also be reflected in paragenesis, and revealed by petrography.

In this study, we aim to test published models for the genesis of Neoproterozoic superheavy pyrite in South China using the novel SEM-SIMS approach. Detailed petrographic observations by scanning electron microscopy (SEM) and in situ µm-scale $\delta^{34}S_{pyrite}$ analysis by secondary ion mass spectrometry (SIMS) were performed for the pyrite samples. The SIMS $\delta^{34}S_{pyrite}$ analyses are coupled with detailed petrographic observations by scanning electron microscopy (SEM) and trace elements by electron-probe microanalysis (EPMA). Based on these new results, a $\delta^{34}S_{sulfide}$ constraint that is directly based on early authigenic pyrites for the Sturtian glacial ocean was achieved for the first time. These data evaluate if the seawater $\delta^{34}S_{sulfide}$ signal during the terminal Sturtian glaciation was as heavy as inferred by previous studies (Gorjan et al., 2000; Hurtgen et al., 2002). Alternatively, we will test if superheavy pyrite formed via thermochemical sulfate reduction (TSR) during a post-depositional hydrothermal event. This is in strong contrast with the widely accepted assumption, held for decades, of a microbial sulfate reduction (MSR) origin for the Neoproterozoic superheavy pyrite in South China.

BACKGROUND

Current interpretations of the deep-time $\delta^{34}S$ records apply fractionations of sulfur isotopes between sulfate and sulfide ($\Delta^{34}S_{sulfate\text{-}sulfide} = \delta^{34}S_{sulfate} - \delta^{34}S_{sulfide}$). Before fully investigating the Neoproterozoic superheavy pyrite, a brief review of sulfur isotopes is necessary.

Microbial sulfate reduction (MSR)

Microbial sulfate reduction is the dominant mechanism that fractionates sulfur isotopes in marine environments. It is often expressed as the following simplified reactions:

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \quad (1)$$

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \quad (2)$$

Most MSR occurs at temperatures lower than ~100 ºC (Jørgensen et al., 1992). During MSR, sulfate-reducing bacteria reduce sulfate to sulfide and form pyrite with $\delta^{34}S$ values lower than the coexisting sulfate (i.e., $\delta^{34}S_{sulfide} < \delta^{34}S_{sulfate}$) (Kaplan and Rafter, 1958; Kaplan and Rittenberg, 1964; Canfield, 2001a; Böttcher, 2011). MSR-induced sulfur isotope fractionation $\Delta^{34}S_{sulfate\text{-}sulfide}$ up to +40‰ has been produced in lab experiments (Canfield, 2001b). More recently, experiments with pure cultures of sulfate reducers show a maximal $\Delta^{34}S_{sulfate\text{-}sulfide}$ of +66‰ at sulfate concentrations ($[SO_4^{2-}]$) similar to modern seawater at 28 mM (Sim et al., 2011a). Even larger $\Delta^{34}S_{sulfate\text{-}sulfide}$ values of up to +72‰ have been found in natural samples (Wortmann et al., 2001; Canfield et al., 2010; Sim et al., 2011a).

Sulfate concentrations ($[SO_4^{2-}]$) in solutions can strongly influence the magnitude of $\Delta^{34}S_{sulfate\text{-}sulfide}$. Experimental studies of microbial cultures demonstrate that the degree of MSR-induced sulfur isotope fractionation in both seawater and freshwater can be increasingly suppressed as $[SO_4^{2-}]$ decreases, and $\Delta^{34}S_{sulfate\text{-}sulfide}$ approaches zero when $[SO_4^{2-}]$ is less than 200 μM (Habicht et al., 2002). However, a more recent study based on Lake Matano (Indonesia) suggests large fractionations (>20‰) at sulfate levels below 200 μM (Crowe et al., 2014).

In addition, environmentally controlled experiments suggest that the magnitude of MSR-induced sulfur isotope fractionation is also related to strain-specific factors (Fike et al., 2015; Bradley et al., 2016), intracellular metabolite levels (Wing and Halevy, 2014), and sulfate reduction rate that is dependent on the availability of organic substrates as electron donors (Canfield et al., 2010; Leavitt et al., 2013; Leavitt, 2014; Fike et al., 2015; Gomes and Hurtgen, 2015). The magnitude of $\Delta^{34}S_{sulfate\text{-}sulfide}$ is found to be inversely proportional to the cell-specific sulfate reduction rate (csSRR) (Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Chambers et al., 1975; Sim et al., 2011a; Sim et al., 2011b; Sim et al., 2012; Leavitt et al., 2013; Fike et al., 2015). This inverse relationship between $\Delta^{34}S_{sulfate\text{-}sulfide}$ and csSRR is consistent with observations in modern marine sediments, particularly in the sulfate–methane transition zone (SMTZ) where MSR rate reaches a maximum in the presence of an upward methane flux and a downward sulfate flux (Jørgensen et al., 2004; Lin et al., 2016b). Additionally, sedimentation rate could also play a role in controlling the expression of $\Delta^{34}S_{sulfate\text{-}sulfide}$. Studies suggest that higher sedimentation rate could cause smaller $\Delta^{34}S_{sulfate\text{-}sulfide}$ and higher $\delta^{34}S_{pyrite}$ values, and conversely, lower sedimentation rate could cause larger $\Delta^{34}S_{sulfate\text{-}sulfide}$ and lower $\delta^{34}S_{pyrite}$ values (Goldhaber and Kaplan, 1975; Claypool, 2004; Pasquier et al., 2017).

In marine environments, bacterial sulfur disproportionation (BSD) could also play a significant role in fractionating the sulfur isotopes. During BSD, sulfides produced through MSR are re-oxidized to elemental sulfur, and then subsequently disproportionated to sulfate and sulfide, by coupling with the reduction of O_2, NO_3^-, iron or manganese compounds (Canfield and Thamdrup, 1994; Canfield and Teske, 1996; Canfield, 2001a; Fike et al., 2015). Disproportionation reactions can significantly augment the

fractionation of sulfur isotopes, resulting in isotopic contrasts between reactant sulfate and product sulfide with $\Delta^{34}S_{sulfate\text{-}sulfide}$ greater than +70‰. The involvement of BSD has been proposed to occur in the rock record of multiple geological intervals (Canfield and Teske, 1996; Johnston et al., 2005; Fike et al., 2006; Wu et al., 2015b; Cui et al., 2016b; Kunzmann et al., 2017).

Published studies of MSR-derived pyrite in sedimentary rocks typically show strong heterogeneity in $\delta^{34}S_{pyrite}$ values at μm scales (Machel et al., 1997; Kohn et al., 1998; Machel, 2001; Wacey et al., 2010; Williford et al., 2011; Lin et al., 2016b; Meyer et al., 2017; Peng et al., 2017; Gomes et al., 2018; Marin-Carbonne et al., 2018). This is largely due to a biogenic nature of MSR and the involvement of Rayleigh fractionation in restricted pore waters (Kohn et al., 1998; McLoughlin et al., 2012; Wacey et al., 2015). As MSR proceeds in pore water environments, the restricted flow of porewaters and Rayleigh fractionation causes progressively lower $\Delta^{34}S_{sulfate\text{-}sulfide}$, higher $\delta^{34}S_{sulfate}$, and consequently higher $\delta^{34}S_{sulfide}$ values (Kaplan and Rafter, 1958; Kaplan and Rittenberg, 1964; Canfield, 2001a).

Rayleigh fractionation of sulfur isotopes can be expressed at both stratigraphic meter-to-kilometer- and micrometer-scales. (1) Stratigraphically, $\delta^{34}S$ values of both porewater sulfate and authigenic pyrite typically increase with greater burial depth (Goldhaber and Kaplan, 1980; Borowski et al., 2000; Canfield, 2001a; Fike et al., 2015); (2) At micrometer scales, as pyrite grains continuously grow during diagenesis, the late-stage pyrite overgrowth typically records higher $\delta^{34}S_{pyrite}$ values than the early-stage pyrite (e.g., Raiswell, 1982; McKibben and Riciputi, 1998; Ferrini et al., 2010; Williford et al., 2011; Fischer et al., 2014; Drake et al., 2015; Lin et al., 2016b; Drake et al., 2017). Both phenomena reflect the occurrence of Rayleigh fractionation in the broad spectrum of post-depositional process. Therefore, strong heterogeneity in $\delta^{34}S_{pyrite}$ is predicted to be common in MSR-dominated environments.

Taken together, MSR could cause significant fractionation between sulfate and sulfide. The controlling factors of $\Delta^{34}S_{sulfate\text{-}sulfide}$ in marine environments are non-unique. Multiple factors may play a role, including sulfate concentration, MSR rate, organic carbon availability, and sulfide re-oxidation. Rayleigh fractionation of sulfur isotopes in restricted pore waters could cause strong $\delta^{34}S$ heterogeneity at both stratigraphic and mineral scales.

Thermochemical sulfate reduction (TSR)

Thermochemical sulfate reduction is an abiotic process by which sulfate is reduced by organic matter during heating. The temperatures of TSR are typically higher than 110 °C (Goldstein and Aizenshtat, 1994; Machel et al., 1995; Worden et al., 1995; Machel, 2001; Jiang et al., 2015). The reactants and products of TSR and MSR can be very similar, therefore distinguishing these two sulfate-reduction pathways is not straightforward and often requires multiple lines of evidence (Machel et al., 1995; Machel, 2001).

The $\Delta^{34}S_{sulfate\text{-}sulfide}$ induced by TSR remains poorly constrained compared with that of the MSR. Lab experiments show that the TSR rate is strongly dependent on temperatures (Kiyosu, 1980; Kiyosu and Krouse, 1990). The TSR-induced values of $\Delta^{34}S_{sulfate\text{-}sulfide}$ caused by hydrocarbons at T > 200°C are typically around 25‰ (Ohmoto and Goldhaber, 1997). However, disequilibrium $\Delta^{34}S_{sulfate\text{-}sulfide}$ values ranging from +20.8‰ to –5.0‰ have also been reported in TSR experiments using amino acids (Watanabe et al., 2009). Published lab experiments suggest that the $\Delta^{34}S_{sulfate\text{-}sulfide}$ value at equilibrium is ~40‰ (Friedman and O'Neil, 1977) or ~30‰ (Ohmoto and Lasaga, 1982; Ohmoto, 1986; Ohmoto and Goldhaber, 1997; Seal, 2006) at the temperature of ~200 °C.

The occurrence of TSR has been widely reported in hydrocarbon reservoirs (Orr, 1974; Orr, 1977; Machel, 1987; Heydari and Moore, 1989; Worden et al., 1995; Riciputi et al., 1996; Worden and Smalley, 1996; Worden et al., 2000; Cai et al., 2001; Cai et al., 2003; Cai et al., 2004; Zhu et al., 2007a; Zhu et al.,

2007b; Hao et al., 2008; Machel and Buschkuehle, 2008; Jiang et al., 2014; King et al., 2014; Cai et al., 2015; Jia et al., 2015; Jiang et al., 2015; Zhu et al., 2015; Biehl et al., 2016; Fu et al., 2016; Liu et al., 2016; Olanipekun and Azmy, 2018). It was revealed that TSR can play a significant role in enhancing the secondary porosity and permeability of carbonate reservoirs (Jiang et al., 2018).

TSR has also been invoked as an important process in ore deposits (Rye and Ohmoto, 1974; Powell and Macqueen, 1984; Ghazban et al., 1990; Tompkins et al., 1994; Randell and Anderson, 1996; Alonso et al., 1999; Cooke et al., 2000; Peevler et al., 2003; Kelley et al., 2004a; Kelley et al., 2004b; Basuki et al., 2008; Gadd et al., 2017; Sośnicka and Lüders, 2018). Hydrothermal sulfate-bearing fluids that percolated through preexisting evaporites could react with organic matter and form pyrite deposits.

TSR could also be critical in interpreting the sulfur isotope records of the early Earth. It has been found that TSR could produce anomalous mass-independent fractionation (MIF) signals of sulfur isotopes ($\Delta^{33}S$ = +0.1 to +2.1‰ and $\Delta^{36}S$= –1.1 to +1.1‰) by using specific amino acids (Watanabe et al., 2009; Oduro et al., 2011), which may have been largely overlooked in the study of the early Earth (Watanabe et al., 2009; Ohmoto et al., 2014). In a more recent study, $\delta^{34}S_{pyrite}$ signals up to +90‰ have been found in the early Paleoproterozoic succession (2.415 Ga) in South Africa, which have been interpreted as resulting from late fluids during burial metamorphism and late diagenesis (Johnson et al., 2013).

In summary, the occurrence of TSR has been widely reported from hydrocarbon reservoirs and ore deposits. TSR has also been invoked in the study of sulfur isotope signals of the deep-time records. The TSR-induced $\Delta^{34}S_{sulfate\text{-}sulfide}$ is relatively less constrained than that of the MSR, but $\Delta^{34}S_{sulfate\text{-}sulfide}$ are dependent on temperatures with smaller fractionations in higher temperatures.

GEOLOGICAL SETTINGS

Stratigraphy and paleogeography

The focus of this study is the Cryogenian Tiesi'ao and Datangpo formations in South China (Fig. 2A–C). The Tiesi'ao and Datangpo formations have been widely regarded as a glacial-postglacial transition in South China. The Tiesi'ao Formation is a glacial diamictite interval of the Sturtian glaciation. The overlying Datangpo Formation is typically subdivided into three members by local mining companies, which are, in ascending order, Member 1 black shale with basal Mn-rich carbonate intervals, Member 2 gray shale, and Member 3 siltstone (Fig. 2C) (Xu et al., 1990; Zhou et al., 2004; Qin et al., 2013; Zhu et al., 2013; Xie et al., 2014; Wu et al., 2016). The Mn-rich carbonate interval in the basal Datangpo Formation has been proposed to be the Sturtian "cap carbonate" (Yu et al., 2017) and is the main target for Mn mining in South China (Wu et al., 2016).

Paleogeographic reconstructions in previous studies reveal that a southeast facing (present direction) passive margin on the Yangtze block was developed during the breakup of the Rodinia supercontinent (Fig. 2A, B) (Jiang et al., 2003; Wang and Li, 2003; Hoffman and Li, 2009; Li et al., 2013). Therefore a rift basin was formed in South China during the Cryogenian Period (Fig. 2C). The Datangpo Formation is mainly distributed in the slope and basinal facies (Xu et al., 1990; Xiao et al., 2014; Wu et al., 2016).

Age constraints

The ages of the Neoproterozoic strata in South China are relatively well constrained. Based on a TIMS U–Pb age of 662.9 ± 4.3 Ma (Zhou et al., 2004) and a SIMS U–Pb age of 667.3 ± 9. 9 Ma (Yin et al., 2006) analyzed from zircons in the tuff beds within the Mn-rich carbonate interval of the basal Datangpo Formation (Fig. 2C), the Tiesi'ao diamictite and Mn-rich carbonate couplet is constrained to be of the Sturtian age (Zhou et al., 2004; Yin et al., 2006).

Stratigraphically upward, the Datangpo Formation is overlain by the Cryogenian Nantuo diamictite, and then the Ediacaran Doushantuo (635–551 Ma) and Dengying (551–541 Ma) formations. A SIMS U–Pb age of 654.5 ± 3.8 Ma from an ash bed immediately below the Nantuo Formation provides a maximum age for the upper boundary of the Datangpo Formation (Zhang et al., 2008). Based on a TIMS U–Pb age of 635.2 ± 0.6 Ma analyzed from a tuff bed within the cap dolostone right above the Nantuo diamictite, the Nantuo Formation is constrained to be a Marinoan counterpart (Condon et al., 2005). The ages from South China and other basins suggest that the Cryogenian glaciations are synchronous at a global scale (Calver et al., 2013; Lan et al., 2015a; Lan et al., 2015b; Rooney et al., 2015; Song et al., 2017).

Distribution of the superheavy pyrite

Superheavy pyrites with bulk $\delta^{34}S$ values up to ca. +70‰ have been reported in the postglacial Datangpo Formation (Fig. 1) (Wang et al., 1985; Tang, 1990; Li et al., 1996; Chu et al., 1998; Li et al., 1999a; Tang and Liu, 1999; Chu et al., 2001; Yang et al., 2002; Chu et al., 2003; Liu et al., 2006; Zhou et al., 2007; Chen et al., 2008; Feng et al., 2010; Li et al., 2012; Zhang et al., 2013; Zhu et al., 2013; Zhang, 2014; Wu et al., 2015a; Wang et al., 2016; Wu et al., 2016). A comprehensive compilation of the distributions of the Datangpo superheavy pyrite at a basin scale reveals a close association with ancient faults (see Fig. 12 in Wu et al., 2016). Similarly, the Datangpo manganese deposits are also associated with ancient faults (Qin et al., 2013; Zhou et al., 2013). Field studies of the Datangpo Formation show abundant textures that suggest pervasive overprint by hydrothermal fluids triggered by tectonic events. These textures include faulting, host rock breccia, sharp-sided quartz veins, calcite, gypsum, and barite infillings and veins (Xu et al., 1990; Chen and Chen, 1992; He et al., 2013a; He et al., 2013b; Zhang et al., 2013; Pan et al., 2016).

SAMPLES

Most chemostratigraphic studies analyze $\delta^{34}S_{pyrite}$ from mg-size aliquots of powder obtained at >mm-scale by crushing or drilling samples. These procedures homogenize samples that may be zoned or heterogeneous at µm-to-mm scale. In contrast, the SIMS analysis of this study sputtered 2-µm diameter pits (~1-µm deep) in situ from polished surfaces that had been imaged by SEM, representing samples over a million times smaller than in conventional analysis (<ng vs. >mg). By SIMS, it is only practical to examine a relatively small number of hand samples, but SEM examination makes it possible to select representative or critical regions and a large amount of data can be efficiently obtained at this scale. The information density per sample can be extraordinarily high by SIMS yielding information that is inaccessible by other means (Eldridge et al., 1989; Valley and Kita, 2009; Williford et al., 2016; Cui et al., 2018). Thus, the best-preserved, most-representative samples were selected for detailed analysis in this study.

The studied drill core (ZK1105, drilled in September 2015) is composed of the Cryogenian Tiesi'ao Formation and Datangpo Formation at the Daotuo mine (28°07'04"N, 108°52'26"E), Songtao County, eastern Guizhou Province in South China (Fig. 2B). The Daotuo mine represents the largest known Mn ore reserve (up to 142 Mt in carbonates) in China (Qin et al., 2013; Zhu et al., 2013; Wu et al., 2016), and records bulk $\delta^{34}S_{pyrite}$ values as high as ca. +70‰ (Fig. 1) (Zhu et al., 2013; Wu et al., 2016), providing a good opportunity for the study of superheavy pyrite and Mn metallogenesis.

Four samples were selected from the ZK1105 drill core for detailed SEM-SIMS $\delta^{34}S_{pyrite}$ study (Figs. 2C, 3, 4). Sample 1 (drill core Hy59) is a diamictite specimen from the uppermost Tiesi'ao Formation. Sample 2 (drill core Hy55) is a Mn-rich carbonate specimen from the lower Member 1 of the Datangpo Formation. Sample 3 (drill core Hy31) is black shale from the upper Member 1 of the Datangpo Formation. Sample 4 (drill core Hy1) is from lower Member 2 of the Datangpo Formation. These four samples cover the main lithologies (diamictite, Mn-rich carbonates, and shale) and pyrite morphology

(including pyrite framboids, pyrite overgrowth, and euhedral to subhedral pyrite grains, respectively) (Fig. 4). Individual pyrite grains were imaged by SEM with back-scattered electrons (BSE) and secondary electrons (SE) prior to SIMS analysis. Mineral chemistry was verified by SEM energy-dispersive spectrometry (EDS) and electron-probe microanalysis (EPMA).

METHODS

SIMS analysis

Samples in this study were analyzed by a CAMECA IMS 1280 at the WiscSIMS (Wisconsin Secondary Ion Mass Spectrometry) Lab, Department of Geoscience, University of Wisconsin–Madison. The analyses include three SIMS sessions. During session 1 (Oct. 18-19, 2018) and session 3 (June 8, 2017), sulfur two-isotopes (^{32}S, ^{34}S) were measured with a 2-µm-diameter beam size. During session 2 (May 22, 2017), sulfur three isotopes (^{32}S, ^{33}S, ^{34}S) were measured with a 10-µm-diameter beam size.

The UWPy–1 standard (pyrite from the Balmat Mine, NY, $\delta^{34}S = 16.04 \pm 0.18‰$, $\Delta^{33}S = -0.003 \pm 0.009‰$, 2SD, V-CDT) (Ushikubo et al., 2014) was used to calibrate analyses of pyrite. Sulfur isotope ratios are reported in standard per mil (‰) notation relative to V-CDT, calculated as $\delta^{34}S_{unknown} = [(^{34}S/^{32}S)_{unknown} / (^{34}S/^{32}S)_{VCDT} - 1] \times 1000$. Measured ratios of $^{34}S/^{32}S$, were divided by the V-CDT value of $^{34}S/^{32}S = 1/22.6436$ (Ding et al., 2001), and were calculated as "raw" δ-values $\delta^{34}S_{raw}$ before converting to the V-CDT scale based on eight analyses of UWPy-1 that bracket each group of 10-15 sample analyses. All the data can be found in the online appendices (Appendices 2–6).

SIMS sessions 1 and 3 (^{32}S, ^{34}S analysis; 2-µm beam size). Measurements of $^{34}S/^{32}S$ were made using a $^{133}Cs^+$ primary ion beam with an intensity of ~30 pA in session 3, which was focused to approximately 2×1 µm at the surface of the sample. The secondary $^{32}S^-$, $^{34}S^-$ and $^{32}S^1H^-$ ions were simultaneously collected by detectors L'2, FC2, and C, respectively, using three Faraday cups. The secondary ion intensity of $^{32}S^-$ was ~6×10^7 cps and ~2.2×10^7 cps for in session 1 and session 3, respectively. $^{32}S^1H^-$ was analyzed to evaluate the effect of hydrogen that might be in the form of organic matter on the SIMS results. An electron flood gun in combination with a gold coat (~40 nm) was used for charge compensation. The total analytical time per spot was about 4 minutes including presputtering (60 s), automatic centering of the secondary ion beam in the field aperture (90 s), and analysis (80 s). The baseline noise level of the Faraday cups was monitored during presputtering. The spot to spot precision of $\delta^{34}S_{raw}$ values based on all bracketing analyses of 2-µm spots on standard UWPy–1 is ±0.91‰ and ±0.87‰, respectively, in session 1 and session 3 (2SD, Appendix 7).

SIMS session 2 (^{32}S, ^{33}S, ^{34}S analysis; 10-µm beam size). During session 2, the secondary ion intensity was ~1.4×10^9 cps for $^{32}S^-$ and ~1.7×10^6 cps for $^{33}S^-$. The ions ^{32}S, ^{33}S, ^{34}S were simultaneously analyzed by detector L'2, C, FC2, respectively, using three Faraday cups. Mass resolving power (M/ΔM, measured at 10% peak height) was set to ~5000. Analysis time consisted of 30 s for presputtering, 80 s for centering of secondary ions in the field aperture, and 80 s for analysis. $^{32}S^1H^-$ was analyzed by detector C at the end of each spot analysis. The ratio of the $^{32}S^1H^-$ tail at the $^{33}S^-$ peak position relative to the $^{32}S^1H^-$ peak ($^{32}S^1H_{tail}/^{32}S^1H_{peak}$) was determined (6.95E–6) at the beginning of the session, which was used to correct the contribution of the $^{32}S^1H^-$ tail signal to the $^{33}S^-$ peak during each spot analysis. $^{32}S^1H^-$ was measured by using a deflector (DSP2X, which is located after the magnet) and detector C at end of each analysis. The contribution of $^{32}S^1H^-$ to the $^{33}S^-$ peak in all the spots (9.7×10^{-4} ‰ at most, 6.6×10^{-4} ‰ on average) is negligible. The $\Delta^{33}S$ values were calculated as $\Delta^{33}S_{unknown} = \delta^{33}S_{unknown} - 10^3 \times [(1 + \delta^{34}S_{unknown}/10^3)^{0.515} - 1]$. The spot to spot precision of $\delta^{34}S$ and $\Delta^{33}S$ (values based on all bracketing analyses of 10-µm spots on standard UWPy–1) is ±0.18‰ and ±0.06‰, respectively (2SD, Appendix 7).

Gold-coat removal and SEM imaging

After SIMS analysis, gold coating was removed from samples by chemical dissolution of gold using a saturated solution of potassium iodide (Jones et al., 2012). The gold-removing solution is a 0.02 mol/L solution of iodine in ethaline. Ethaline is prepared as a 1:2 molar mixture of choline chloride ($C_5H_{14}ClNO$) and ethylene glycol ($C_2H_6O_2$). The rinse solutions are potassium iodide solution and deionized water, respectively. The potassium iodide solution is prepared by adding potassium iodide (KI) to water until saturation. Samples were placed in the gold-removing solution on a hot plate at ~60 °C for 10 to 15 minutes, and then rinsed by potassium iodide saturated solution. The samples were rinsed again by deionized water before further analysis.

SEM imaging was performed in the Ray and Mary Wilcox Scanning Electron Microscopy Laboratory, Department of Geoscience, University of Wisconsin–Madison. BSE images of carbon-coated samples were acquired with a Hitachi S3400 VP SEM with EDS using a Thermo Fisher thin window detector. Each pit was investigated by SEM for possible irregularities. SEM images were acquired using an accelerating voltage of 15 keV or 20 keV at a working distance of 10 mm. All the SIMS pits were imaged by SEM and are shown with corresponding $\delta^{34}S_{pyrite}$ values in the online appendices (Appendices 2–5).

EPMA analysis

EPMA analysis was conducted in the Eugene Cameron Electron Microbeam Lab, Department of Geoscience, University of Wisconsin–Madison. EPMA was performed with the CAMECA SXFive field emission electron probe, operated at 20 kV and 50 nA, and either a focused beam or a 3-4 micron defocused beam, using wavelength dispersive crystal spectrometers (Appendix 8). Counting times were 10 seconds on peak, and a total of 10 on backgrounds, for all elements except those noted in the following listing. Al Ka (20 sec) and Si Ka (20 sec) were acquired on a large TAP crystal; As Ka (20 sec) and Se Ka (20 sec) on LIF; S Ka and Ca Ka (27 sec) on large PET; Fe Ka, Mn Ka and Co Ka on LIF; and Ni Ka, Cu Ka and Zn Ka on large LIF. Standards used were Balmat pyrite (Fe, S), NBS glass K412 (Si, Al, Ca), arsenopyrite (As) and freshly polished metals for the balance. PHA modes used were integral, except for Al and Si which were differential mode. Software used was Probe for EPMA (Donovan et al., 2018). Off peak backgrounds were acquired, and matrix correction was conducted by using the Armstrong/Love Scott algorithm (Armstrong, 1988). Minimum detection levels are shown in Appendix 8.

RESULTS

All the SIMS results in this study are shown with petrographic context in online Appendices 2–5 and tabulated in online Appendix 7. SIMS analyses of each spot that were off the correct target, with large internal error (2SE > 2‰), or with yield values (^{32}S count rate divided by primary beam intensity, Mcps/pA) that are beyond the range from 90 to 110% of the mean yield values for UWPy-1 are considered unreliable. A total of 258 SIMS analyses (6 data points are unreliable) were made during session 1, including 182 analyses of unknown samples and 76 analyses of the UWPy-1 standard. A total of 18 SIMS analyses (0 data filtered) were made during session 2, including 10 analyses of unknown samples and 8 analyses of the UWPy-1 standard. A total of 138 analyses (10 data filtered) were made during session 3, including 87 analyses of the unknown samples and 41 analyses of the UWPy-1 standard.

Integrated SEM–SIMS results of the studied samples show distinct patterns in pyrite paragenesis, S isotope ratios and spatial distributions at μm scale (Table 1; Figs. 4–23; Appendices 2–5). These results are described below.

Sample 1 (Hy59, glacial diamictite)

SEM petrography. The pyrite phases in Sample 1 typically show two types of texture: pyrite framboids (up to 30 μm in diameter) (Figs. 4F, 4G, 5–7; Appendix 2) and pyrite nodules (Fig. 4H, 4I, 8; Appendix 2). (1) The pyrite framboids are mostly assemblages of smaller pyrite microcrystals (Figs. 4F, 4G, 5–7). Sometimes, pyrite microcrystals may also occur outside the pyrite framboids as individual microcrystals surrounded by pyrite cement (Figs. 4G, 7A). BSE investigations at high magnification reveal that individual pyrite microcrystals are typically defined by a darker (lower average atomic number) rim (Fig. 5; Appendix 2). The shape and size of the pyrite microcrystals are similar within individual framboids, but may vary among different framboids. Octahedral, subhedral, and rounded pyrite microcrystals have all been observed within different pyrite framboids (Fig. 5; Appendix 2). (2) The pyrite nodules are mostly at mm scale, and consist of multiple zoned pyrite crystals at μm scales (Fig. 4H, 4I, 8; Appendix 2).

SIMS results. A total of 90 spots were analyzed by SIMS in different textures, including framboidal pyrite (n = 76), pyrite cements outside framboids (n = 4), and pyrite nodules (n = 10) (Appendix 2). The $\delta^{34}S$ values measured from pyrite nodules range from +9.8‰ to +52.2‰. The $\delta^{34}S$ values measured from pyrite framboids range from +11.2‰ to +28.3‰. Pyrite cements outside the framboids show $\delta^{34}S$ ranging from +22.7‰ to +36.7‰ (Table 1; Figs. 22, 23). Generally, the pyrite cements outside the framboids (+30.9‰ in average) have much higher $\delta^{34}S$ values than was measured within pyrite framboids (+16.4‰ on average) (Figs. 7A, 22, 23).

Data evaluation. SEM investigation of Sample 1 shows that both the framboidal pyrite and the pyrite nodules are very heterogeneous at μm scale (Figs. 4F–I, 5–8; Appendix 2). The SIMS spots within the framboids may have covered both pyrite microcrystals that are smaller than the 2-μm beam spot and pyrite cements between the microcrystals (Fig. 5). Similarly, closer views of the pyrite crystals within nodules show zoned pyrite overgrowths (Fig. 4I; 8C–J; Appendix 2). Therefore, the measured $\delta^{34}S$ data from SIMS spots that include multiple phases should represent an averaged value of pyrite formed in different phases.

Sample 2 (Hy55, Mn-rich carbonates)

SEM petrography. Sample 2 is mainly composed of laminated Mn-rich carbonate layers and siliciclastic-rich layers (Figs. 9–14). The Mn-rich carbonate layers are mostly granular rhodochrosite [$MnCO_3$] (Fig. 10) and often show nodule- or sausage-shaped textures (Figs. 9, 12; Appendix 3). Trace amounts of euhedral kutnohorite [$CaMn(CO_3)_2$] were also found. Lath-shaped illite crystals are abundant in Sample 2 (Figs. 12, 13; Appendix 3). The pyrite in Sample 2 shows intermittent sausage-shaped textures (Fig. 9A–F) that occur within the Mn-rich carbonate layers and preferentially replace the pre-existing carbonates (Figs. 9–13; Appendix 3). The nodule- or sausage-shaped texture of pyrite is largely inherited from that of the hosting Mn-rich carbonates (Appendix 3).

Under BSE (typically with decreased color brightness), pyrite in Sample 2 shows at least two textures: individual pyrite framboids and lacy pyrite overgrowth/cements (Figs. 11, 13, 14). In contrast with the framboidal pyrite in Sample 1 that shows a wide range in size (up to 30 μm in diameter), all the pyrite framboids in Sample 2 are smaller than 7 μm in diameter (Appendix 3).

The pyrite framboids and the lacy pyrite "veins" within an overgrowth are typically brighter (higher average atomic number) than the pyrite overgrowth under BSE (Figs. 11A, 11I, 13H, 13G, 13L, 14; Appendix 3). The detailed causes of this zoning are still unclear, but preliminary EPMA shows that the darker pyrite overgrowths yield lower analytical totals than the brighter pyrite framboids and lacy pyrite veins (Appendix 8), suggesting that porosity or C/N-rich inclusions may have played a role in causing this effect.

Paragenesis. Detailed SEM investigation allows reconstruction of the paragenesis of different minerals in Sample 2. Multiple lines of evidence suggest that pyrite in this sample postdates rhodochrosite and illite. Supporting evidence includes: (1) petrographic overviews showing that pyrite grains in this sample are nodule- or sausage-shaped and preserved exclusively within rhodochrosite lamina (Fig. 9); (2) rhodochrosite granules with ring-shaped pyrite cements (Fig. 10); (3) pyrite with abundant inclusions of granular rhodochrosite (Fig. 11); (4) magnified views showing that pyrite in Sample 2, either individual pyrite framboids (Fig. 13A–D) or framboidal pyrite with lacy pyrite overgrowths (Fig. 13E–L), are replacing both rhodochrosite and illite. More detailed petrographic evidence is available in the online Appendix 3. Taken together, these textures indicate that pyrite in this sample is relatively late, postdating the mineralization of rhodochrosite and illite.

SIMS results. Both disseminated pyrite framboids and lacy pyrite overgrowth have been analyzed for $\delta^{34}S$ by SIMS. In total of 28 spots were analyzed in Sample 2 (Appendix 3). The range of SIMS $\delta^{34}S$ values is from +56.3‰ to +60.4‰. These values are remarkably homogeneous regardless of heterogeneous textures under BSE (Figs. 14, 22, 23; Table 1).

Sample 3 (Hy31, black shale)

SEM petrography. In Sample 3, no framboidal pyrite was found. Instead, pyrite mostly shows disseminated subhedral grains ranging from 20 to 100 µm in size (Figs. 15, 16; Appendix 4). It is notable that some pyrite grains are relatively large (up to 2 mm), composed of multiple µm-size pyrite sub-grains cemented by later-stage pyrite (Fig. 17; Appendix 4). The µm-size pyrite sub-grains mimic the disseminated pyrite in the shale matrix, suggesting that pyrite sub-grains were formed earlier, and were then cemented by pervasive pyrite cement.

SIMS results. A total of 108 spots were measured by SIMS from Sample 3 (Appendix 4), including both µm-size sub-grains (n = 85; Fig. 16, 17) and mm-size pyrite cements (n = 23; Fig. 17). The range of the SIMS $\delta^{34}S$ values of individual pyrite sub-grains is from +60.3 to +71.2‰, with an average value of +66.3‰ (Figs. 16, 17, 22, 23). The pyrite cements show homogeneous $\delta^{34}S$ values ranging from +60.2‰ to +64.8‰ (Figs. 17, 22, 23). Notably, the µm-scale SIMS $\delta^{34}S$ analysis reveals a consistently decreasing $\delta^{34}S$ trend from the core (ca. +70‰) to the edge (ca. +60‰) of individual pyrite grains (Figs. 16, 17; Appendix 4).

Sample 4 (Hy1, shale)

SEM petrography. Two pyrite textures are found in Sample 4 (Fig. 18–21; Appendix 5). The first type of pyrite, named "pyrite flowers" here, is characterized by framboidal pyrite cores with a zoned pyrite overgrowth (Figs. 18C, 19). The second texture is characterized by "Fe-oxide coronas" with pyrite cores and thin pyrite rims (Figs. 18D, 20, 21). The pyrite cores inside the "Fe-oxide coronas" typically show framboidal textures in the center with fibrous textures in the outer surface (Figs. 18D, 20, 21), which was likely marcasite initially (e.g., Zhang et al., 2014; Lin et al., 2016a).

SIMS results. Both pyrite textures have been analyzed by SIMS in this study. A total of 25 spots were analyzed in the "pyrite flowers" and 21 spots were analyzed in the pyrite cores of the "Fe-oxide coronas" (Fig. 19; Appendix 5). For the first time, a bimodal distribution of $\delta^{34}S$ values is found within a single sample at cm-scale (Figs. 22, 23). SIMS $\delta^{34}S$ results of the "pyrite flowers" show remarkably homogeneous and high values ranging from +59.9‰ to +62.8‰, regardless of zoned textures under BSE (Figs. 18C, 19, 22, 23; Appendix 5). In contrast, the pyrite cores within the "Fe-oxide coronas" show a much wider range with much lower $\delta^{34}S$ values, ranging from ca. +16.6‰ to ca. +32.7‰ with an average value of +22.2‰ (Figs. 18D, 20–23; Appendix 5).

Pyrite $^{32}S^{1}H/^{32}S$ values

During SIMS analysis, mass $^{32}S^{1}H^{-}$ was also measured in order to check the irregularity of each spot. The mean value of $^{32}S^{1}H/^{32}S$ in UWPy-1 is 4.6E–4 during the three sessions. Among the studied four samples, only pyrite analyses of Sample 3 show similar level (mean: 7.4E–4) of $^{32}S^{1}H/^{32}S$. Notably, pyrite analyses of Samples 1, 2 and 4 show $^{32}S^{1}H/^{32}S$ values that are around two orders of magnitude higher than those of the UWPy-1 standard indicating the presence of a second hydrogen-bearing phase (Appendix 6).

Except for the $\delta^{34}S$ values analyzed from a single pyrite nodule in Sample 1 that show a weak correlation with the $^{32}S^{1}H/^{32}S$ values, most of the measured $\delta^{34}S$ values in this study do not show apparent correlation with corresponding $^{32}S^{1}H/^{32}S$ values (Appendix 6). For example, $\delta^{34}S$ data measured from Sample 4 show a bimodal distribution (mean $\delta^{34}S$ of superheavy pyrite flowers: +61.6‰; mean $\delta^{34}S$ of pyrite cores within Fe-oxide coronas: +22.2‰), but all these data are coupled with $^{32}S^{1}H/^{32}S$ values (mean $^{32}S^{1}H/^{32}S$ of superheavy pyrite flowers: 9.7E–3; mean $^{32}S^{1}H/^{32}S$ of pyrite cores within Fe-oxide coronas: 1.3E–2) that are around two orders of magnitude higher than the mean $^{32}S^{1}H/^{32}S$ values of the UWPy-1 standard. It is also notable that among superheavy pyrites, $^{32}S^{1}H/^{32}S$ values can be very different. For example, superheavy pyrites in Samples 2 and 4 show $^{32}S^{1}H/^{32}S$ values that are two orders of magnitude higher than the mean $^{32}S^{1}H/^{32}S$ values of the UWPy-1 standard, while superheavy pyrite in Sample 3 show $^{32}S^{1}H/^{32}S$ values that are similar to those measured from UWPy-1.

Integrated SEM-SIMS results show that the $^{32}S^{1}H/^{32}S$ values correlate with the pyrite textures under BSE. Pyrites in Sample 1, 2, and 4 show strong heterogeneity in brightness under BSE and have relatively high $^{32}S^{1}H/^{32}S$ values, while pyrites in Sample 3 show relatively homogeneous in brightness under BSE and have relatively low $^{32}S^{1}H/^{32}S$ values. It is possible that fluid inclusions or organic matter inclusions that are rich in hydrogen (leading to higher $^{32}S^{1}H/^{32}S$ values) within pyrite in Samples 1, 2, and 4 may have played a role in the BSE brightness and $^{32}S^{1}H/^{32}S$ values.

In summary, the $^{32}S^{1}H/^{32}S$ values measured during the SIMS sessions provide valuable information on the studied pyrite. No apparent correlation was found between $^{32}S^{1}H/^{32}S$ and $\delta^{34}S$ values. $^{32}S^{1}H/^{32}S$ values show an overall correlation with the pyrite brightness under BSE, which we regard can be explained by the contribution of fluid or organic inclusions mixed within pyrite.

DISCUSSION

A viable model for the genesis of the studied superheavy pyrite should be able to explain sedimentological and geochemical observations at both basin and micrometer scales. We will evaluate multiple models for the superheavy pyrite below.

Superheavy pyrite formed via microbial sulfate reduction (MSR)?

All the previously published biogeochemical models for the superheavy pyrite in South China assume a biogenic origin by microbial sulfate reduction (MSR) (Liu et al., 2006; Chen et al., 2008; Li et al., 2012; Lang et al., 2016; Wu et al., 2016; Wang et al., 2017). This assumption hypothesizes that superheavy pyrite formed in the marine water column or shallow sediments with different degrees of access to seawater sulfate. However, based on detailed SIMS-SEM study, the superheavy pyrite in the Datangpo Formation is found replacing preexisting rhodochrosite and illite (Figs. 9–13), and therefore formed after deep burial.

Supporting evidence for a non-MSR origin of the Datangpo superheavy pyrite also comes from its µm-scale $\delta^{34}S$ patterns. Sample 2 shows remarkably homogenous $\delta^{34}S$ values regardless of heterogeneous textures (Fig. 14); and Sample 3 shows a decreasing $\delta^{34}S$ trend from the core to the edge of individual pyrite grains (Figs. 16, 17). These µm-scale $\delta^{34}S$ patterns are inconsistent with a MSR origin

considering that progressive MSR in restricted pore waters would only increase, instead of decrease, the pyrite $\delta^{34}S$ values. Therefore, previous models based on a MSR assumption cannot explain the textures or $\delta^{34}S$ values of studied superheavy pyrite either, and a non-MSR model is needed.

Superheavy pyrite formed in a sulfide-rich fluid flow?

It is possible that flow of a reducing hydrothermal fluid that is rich in sulfide, instead of sulfate, may have caused the mineralization of the studied superheavy pyrite. In this scenario, iron that may be available in the sediments reacts with external hydrogen sulfide and forms pyrite in the absence of simultaneous sulfate reduction. The flow of sulfide-rich fluid can be hypothesized to come from an underlying magmatic source. However, multiple lines of evidence suggest that this scenario is unlikely.

First, given the typically near-0 $\delta^{34}S_{sulfide}$ values (0 ± 5‰) of magmatic sulfur reservoirs (Marini et al., 2011), it would be extremely difficult for such a sulfur reservoir to generate $\delta^{34}S_{sulfide}$ values as high as +70‰ at a basinal scale in South China.

Second, a sulfide-rich source is inconsistent with the SIMS $\delta^{34}S$ data shown in Sample 3, where decreasing $\delta^{34}S$ trends with a magnitude of ca. 10‰ are consistently registered from core to edge of each individual subhedral pyrite grain (Figs. 16, 17). Previous study shows that sulfur isotope fractionations between hydrogen sulfide and iron sulfide ($\Delta^{34}S_{FeS-H2S}$) are small (~ 1‰) (Böttcher et al., 1998), in strong contrast with MSR-induced fractionation ($\Delta^{34}S_{sulfate-sulfide}$). Such small fractionation ($\Delta^{34}S_{FeS-H2S}$) cannot readily explain the $\delta^{34}S_{pyrite}$ heterogeneity in Sample 3 revealed by the SIMS data at a μm scale (Figs. 16, 17).

Third, the discovery of barite and gypsum veins or infillings in the Datangpo Formation (Xu et al., 1990; Chen and Chen, 1992; He et al., 2013a; He et al., 2013b; Zhang et al., 2013; Pan et al., 2016) indicate the involvement of sulfate-rich, instead of sulfide-rich, fluids. Therefore, based on the above discussion, it is more likely that a non-MSR type sulfate reduction caused the mineralization of the studied superheavy pyrite. We will fully explore this scenario in the next section.

Reinterpretation: superheavy pyrite formed by thermochemical sulfate reduction (TSR)

In this study, we propose that the studied superheavy pyrite formed by thermochemical sulfate reduction (TSR) in hydrothermal fluids. This revised interpretation is supported by multiple lines of sedimentological and geochemical evidence listed below.

Superheavy pyrite associated with ancient faults. In South China, the superheavy pyrite in the Datangpo Formation is found closely associated with ancient faults (Wu et al., 2016). This distinct pattern suggests that the genesis of the Datangpo superheavy pyrite was controlled by external fluids that flowed along the faults. It is possible that an external sulfate-rich hydrothermal fluid intruded the Datangpo Formation along ancient faults, and caused the mineralization of the superheavy pyrite via TSR.

Superheavy pyrite associated with Mn-rich carbonates. In South China, most of the superheavy pyrites were found near or within the Mn-rich carbonate intervals in the basal Datangpo Formation. Detailed petrographic investigation in this study shows preferential replacement of carbonate by superheavy pyrite (Figs. 9–13; Appendix 3). Given that TSR is a process that produces hydrogen sulfide and increases pore-water acidity (Machel et al., 1995; Jiang et al., 2018), carbonate host rocks would be preferentially dissolved and then replaced by pyrite when TSR occurs (Kelley et al., 2004a). This process has also been reported in many other carbonate-dominated strata worldwide (e.g., Krouse et al., 1988; Worden and Smalley, 1996; Cai et al., 2001; Biehl et al., 2016; Jiang et al., 2018). Therefore, the reinterpretation of a TSR origin for the studied superheavy pyrite is consistent with the close coupling between superheavy pyrite and Mn-rich carbonates.

Paragenesis. In contrast with MSR that dominantly occurs in the water column or shallow marine sediments (Jørgensen and Kasten, 2006; Bowles et al., 2014), TSR usually occurs relatively late, typically in temperatures higher than 100 °C during deep burial diagenesis. Integrated SEM-SIMS results in Sample 2 show pervasive replacement of rhodochrosite and illite by superheavy pyrite (Figs. 9–13; Appendix 3), suggesting that superheavy pyrite is a late diagenetic product. The reinterpretation of a TSR origin for the studied superheavy pyrite is consistent with independent paragenesis revealed by SEM petrography.

Barite and gypsum veins and infillings. Field observations of the Datangpo Formation show abundant textures that suggest pervasive overprint by hydrothermal fluids, including host-rock breccia, quartz veins, calcite, gypsum, and barite infillings and veins (Xu et al., 1990; Chen and Chen, 1992; He et al., 2013a; He et al., 2013b; Zhang et al., 2013; Pan et al., 2016). The preservation of barite and gypsum veins indicates that the hydrothermal fluids were rich in sulfate, which would trigger TSR to occur given that organic matter is abundant in the Datangpo shale.

Homogeneous $\delta^{34}S$ in heterogeneous pyrite textures. In this study, superheavy pyrite in some samples shows remarkably homogenous $\delta^{34}S_{pyrite}$ values in zoned pyrite grains (Figs. 22, 23). In Sample 2, the $\delta^{34}S_{pyrite}$ values of 28 SIMS spots in framboidal pyrite and lacy pyrite overgrowth range from +56.3‰ to +60.4‰ (Fig. 14). In Sample 4, the $\delta^{34}S_{pyrite}$ values of 25 SIMS spots in zoned "pyrite flowers" range from +59.9‰ to +62.8‰ (Fig. 19). Such homogeneous $\delta^{34}S_{pyrite}$ patterns are difficult to explain by MSR. Typically, MSR-derived pyrite shows considerable $\delta^{34}S$ zoning at μm scale due to a biogenic nature of MSR and the effect of Rayleigh fractionation in an increasingly restricted pore water environment (Kohn et al., 1998; Williford et al., 2011). Alternatively, it is likely that these relatively invariant $\delta^{34}S_{pyrite}$ values result from TSR in hydrothermal fluids. The superheavy pyrite of different textures may have precipitated in response to a hydrothermal fluid flow when it intruded into the host rocks.

Decreasing $\delta^{34}S$ trend from core to edge of individual pyrite grains. In this study, μm-scale $\delta^{34}S$ analysis reveals decreasing $\delta^{34}S$ trends in core-to-edge traverses of individual pyrite grains from Sample 3 (Figs. 16, 17). This phenomenon is inconsistent with MSR, which typically leads to an increasing trend at μm-scales. Alternatively, the core-to-rim traverses in Sample 3 can be explained by TSR when the temperature of the hydrothermal fluid cools. Lab experiments on kinetic sulfur isotope fractionation during TSR have demonstrated that as temperature decreases, $\Delta^{34}S_{sulfate\text{-}sulfide}$ would increase, and consequently $\delta^{34}S_{pyrite}$ would decrease (Kiyosu and Krouse, 1990). As a result, a gradient with decreasing $\delta^{34}S_{pyrite}$ values would be recorded in individual TSR-derived pyrite grains.

Varying $\delta^{34}S_{pyrite}$ at a basin scale. Published chemostratigraphic $\delta^{34}S_{pyrite}$ profiles of the Datangpo Formation at different sections in South China show remarkably different values (Fig. 1) (Li et al., 1999a; Li et al., 2012; Zhou et al., 2013; Zhu et al., 2013; Wu et al., 2015a; Lang, 2016; Wu et al., 2016). For example, $\delta^{34}S_{pyrite}$ values in the lower Datangpo Formation at the Yangjiaping section range from +20‰ to +30‰, while $\delta^{34}S_{pyrite}$ values of the correlative Minle section range from +40‰ to +65‰ (Li et al., 2012). These different $\delta^{34}S_{pyrite}$ values among different sections have been interpreted to result from a stratified ocean controlled by dynamic influx of sulfate and nutrient (Li et al., 2012). However, sedimentological observations show that most of the high-$\delta^{34}S_{pyrite}$ values are associated with Mn-rich carbonate intervals and ancient faults (e.g., Minle section in Li et al., 2012), while siliciclastic-dominated sections (e.g., Yangjiaping section in Li et al., 2012) lack superheavy pyrite. We interpret this isotope-lithology pattern as resulting from preferential replacement of carbonates by superheavy pyrite via TSR. The occurrence of TSR may have caused a strong bias of superheavy pyrite preservation in carbonate-dominated intervals, and as a result, overprinted the primary $\delta^{34}S_{pyrite}$ signals.

Negative correlation between Fe content and bulk $\delta^{34}S_{pyrite}$ values. Previous studies have reported an overall negative correlation (correlation coefficient/R = –0.83, n = 8) between bulk Fe content and bulk $\delta^{34}S_{pyrite}$ values in the Datangpo Mn-rich carbonates (Fig. 15 of Wu et al., 2016). This

phenomenon has been interpreted as resulting from Rayleigh distillation in seawater. However, petrographic observations in this study suggest that the bulk Fe content in the Mn-rich carbonates is mainly post-depositional pyrite replacing pre-existing carbonates. Therefore, it is more likely that this overall negative correlation reflects Rayleigh distillation in restricted hydrothermal fluids within deeply buried sediments. If correct, then TSR would be the more likely pathway of sulfate reduction instead of MSR. As TSR progressively occurs with Rayleigh distillation, $\delta^{34}S_{pyrite}$ would evolve to higher values. Therefore, the Rayleigh distillation process would be characterized by a relatively larger amount of pyrite (therefore high bulk Fe content) with relatively low $\delta^{34}S_{pyrite}$ values at the early stage and a relatively smaller amount of pyrite (therefore low bulk Fe content) with high $\delta^{34}S_{pyrite}$ values (i.e., superheavy pyrite) at the very late stage. This process can cause a broad spectrum of $\delta^{34}S_{pyrite}$ values with an overall negative correlation between bulk Fe content and bulk $\delta^{34}S_{pyrite}$ values.

Negative correlation between total organic carbon and total sulfur. An overall negative correlation (correlation coefficient, R = –0.48, n = 29) between total organic carbon (TOC) and total sulfur (TS) was reported in the Datangpo Mn-rich carbonates (Wang et al., 2017). This pattern is in strong contrast with normal marine environments where TOC and TS typically show positive correlations (Berner, 1984; Berner, 1989; Cao et al., 2016). The negative TOC–TS correlation observed in the Datangpo Formation was interpreted to result from anomalous sulfur cycling during deposition (Wang et al., 2017). Petrographically, the low-TOC samples are mostly carbonates that are rich in superheavy pyrites (therefore high in TS). On the other hand, the high-TOC samples are mostly shales that have less pyrite abundance (therefore lower in TS). The new results of this study show that this overall negative TOC–TC correlation actually results from preferential replacement of carbonates by TSR-derived pyrite, therefore cannot be used to infer marine sulfur cycles.

Temperature data. Studies on vitrinite reflectance of the Datangpo Formation suggest that the Mn-rich carbonate interval experienced a maximum burial temperature of ca. 195 °C (Chen and Chen, 1992; Xie et al., 1999). Studies of fluid inclusions in authigenic quartz in the Datangpo Formation yield homogenization temperatures of 173–241 °C, with an average value of 194 °C (Wang et al., 1985). These temperatures are consistent with the scenario that the Datangpo Formation experienced a hydrothermal event.

Based on the current burial depth of the studied Datangpo drill core (Samples 1, 2, 3, 4 collected at depths of 1303.06 m, 1299.88 m and 1289.09 m, 1274.14 m, respectively) and the current geothermal gradient of 10–20 °C/km in the studied region (Yuan et al., 2006), assuming the surface temperature is ca. 20 °C, the current burial temperature is likely to be ca. 33–46 °C at the sampled depths. This shows that the Datangpo Formation should have experienced a cooling event from a hydrothermal or maximum burial temperature to the current burial temperature, which is consistent with the μm-scale $\delta^{34}S_{sulfide}$ spatial patterns shown in Sample 3.

Source and compositions of the TSR fluids

To allow TSR to occur, sulfate-rich hydrothermal fluids and organic-rich host rocks are both required. Given the high abundance of organic matter in the Datangpo Formation, sulfate-rich hydrothermal fluid is more likely to be the controlling factor. Typically, the fluids for TSR are derived from late dissolution of preexisting sulfate minerals (e.g., gypsum, anhydrite). Therefore, the deposition of sulfate has to predate the TSR event.

In South China, the oldest gypsum-bearing sedimentary bedding with a basin-scale distribution is the late-Ediacaran Dengying Formation. Distinct textures that point to the deposition of marine evaporites have been widely reported in this formation (Xi, 1987; Siegmund and Erdtmann, 1994; Lu et al., 2013; Wang et al., 2013; Duda et al., 2015; Cui et al., 2016b). Due to high solubility, evaporites in this formation are mostly shown as calcite pseudomorphs with distinct crystal shapes that are diagnostic of

preexisting gypsum (Duda et al., 2015; Cui et al., 2016b). The $\delta^{34}S_{sulfate}$ value of this gypsum-bearing interval has been constrained to be ca. +40‰ based on carbonate associated sulfate (CAS) analysis (Cui, 2015; Cui et al., 2016b), which is consistent with the $\delta^{34}S_{sulfate}$ constraints based on CAS analysis of coeval strata in Arctic Siberia (Cui et al., 2016a) and direct $\delta^{34}S_{sulfate}$ analyses of bedded anhydrite strata in Oman (Fike and Grotzinger, 2008; Fike and Grotzinger, 2010; Bergmann, 2013). We propose that this could be the source of hydrothermal sulfate for the Datangpo TSR event.

Rayleigh distillation model for superheavy pyrite

To generate superheavy pyrite with $\delta^{34}S_{pyrite}$ as high as +70‰, it is required that the $\delta^{34}S_{sulfate}$ values of an equilibrated TSR solution to be higher than +70‰. Figure 24 shows models of sulfide precipitation by batch precipitation in a closed system and by Rayleigh distillation. In these models, an initial $\delta^{34}S_{sulfate}$ value of +40‰ was adopted assuming that the sulfate source of this TSR fluid is the Ediacaran Dengying Formation in South China and an equilibrium value of $\Delta^{34}S_{sulfate\text{-}sulfide}$ = 40‰. These calculations show that $\delta^{34}S_{sulfide}$ values above +70‰ can be generated after precipitation of 80% of sulfate in closed system fluids.

It needs to be noted that the above calculation represents a simplified scenario with a constant $\Delta^{34}S_{sulfate\text{-}sulfide}$ of 40‰. Published lab experiments suggest that the $\Delta^{34}S_{sulfate\text{-}sulfide}$ value at equilibrium is ~ 40‰ (Friedman and O'Neil, 1977) or ~30‰ (Ohmoto and Lasaga, 1982; Ohmoto, 1986; Ohmoto and Goldhaber, 1997; Seal, 2006) at the temperature of ~200 °C. The $\Delta^{34}S_{sulfate\text{-}sulfide}$ value would be significantly higher at lower temperature. It is possible that the hydrothermal fluid temperatures vary as TSR occurs. In geological conditions, the precipitation of superheavy pyrite can be a dynamic process with varying $\delta^{34}S_{sulfate}$, temperatures, $\Delta^{34}S_{sulfate\text{-}sulfide}$ and $\delta^{34}S_{pyrite}$ values. Regardless, our model demonstrates that $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{sulfide}$ signals as high as +70‰ can be produced via TSR during the late stage of Rayleigh distillation. This process could occur when hydrothermal fluids flow along ancient faults, during which pyrite with a spectrum of $\delta^{34}S_{pyrite}$ values may have been produced via TSR.

IMPLICATIONS

Rethinking the Neoproterozoic sulfur cycle

The occurrence of the Neoproterozoic superheavy pyrite has led to the speculation of anomalously low sulfate concentrations in the ocean (Hayes et al., 1992; Hurtgen et al., 2002; Canfield, 2004; Li et al., 2012; Wu et al., 2016). However, in light of the petrographic and isotopic results in this study, we argue that the studied superheavy pyrite formed in deeply buried sediments by hydrothermal fluids and therefore cannot be used to infer the marine sulfur cycles during deposition. Similar SEM-SIMS studies have not yet been published for other localities. It is possible that the sulfate concentration in the Cryogenian ocean may not be as low as the previous studies suggested.

Cryogenian superheavy pyrite has been reported from five post-Sturtian successions worldwide: the Datangpo Formation in South China; the Tapley Hill and Aralka formations in Australia; the Court Formation in Namibia; and the Arena Formation in East Greenland (Fig. 1). In light of our study of the Datangpo Formation in South China, similar investigations are suggested in other localities to assess the nature of the high-$\delta^{34}S$ signals. It needs to be noted that the current time-series $\delta^{34}S$ compilation (Canfield, 2001a; Shen et al., 2001; Cui et al., 2016a; Cui et al., 2016b) is based on pyrite that has been regarded as early diagenetic in origin. TSR-derived superheavy pyrite can be much more abundant in geological record than the time-series $\delta^{34}S$ compilation shows.

The new data from South China suggest that at least some Neoproterozoic superheavy pyrite formed by late diagenetic alteration. If this observation applies to other localities, then an emerging question is, why is superheavy pyrite particularly notable in the Neoproterozoic interval? Here, we

propose that three potential factors may have played a role in contributing to the occurrence of the Neoproterozoic superheavy pyrite.

Increased diagenetic potential for TSR. Considering that bedded sulfate evaporites are increasingly deposited during and after the Neoproterozoic (Kah et al., 2004; Halverson and Hurtgen, 2007; Kah and Bartley, 2011; Cui et al., 2016b), it is likely that the considerable rise in seawater sulfate concentrations during the Neoproterozoic Oxygenation Event promoted evaporite deposition (Shields-Zhou and Och, 2011; Och and Shields-Zhou, 2012), which consequently enhanced the diagenetic potential for TSR during deep burial. When these evaporites are dissolved by hydrothermal fluids, TSR would occur if organic matter is also available in the host sedimentary strata.

High $\delta^{34}S_{sulfate}$ during the Neoproterozoic. It is notable that time-series $\delta^{34}S_{sulfate}$ values remain high during the Neoproterozoic and reach to the maximum (ca. +40‰) during the late Ediacaran Period (Fike and Grotzinger, 2008; Halverson et al., 2009; Halverson et al., 2010; Paytan and Gray, 2012; Cui et al., 2016a; Cui et al., 2016b). The high $\delta^{34}S_{sulfate}$ signals of the Neoproterozoic seawater may have been recycled after deposition (e.g., post-depositional dissolution of gypsum), facilitating the genesis of superheavy pyrite in the host rocks during a post-depositional TSR event.

Increased tectonic activity. The breakup of the Rodinia supercontinent and progressive formation of the Gondwana supercontinent during the Neoproterozoic Era (Li, 2011; Li et al., 2013) may have also played an active role in facilitating TSR in sedimentary strata. The process of continental reconfiguration may have enhanced the activity of hydrothermal fluids, and thus promoted TSR to occur in the Neoproterozoic.

We propose that the above factors may have played a role in facilitating TSR in the Neoproterozoic record in South China and possibly beyond. The Neoproterozoic superheavy pyrites in other localities are suggested to be examined in a similar way in order to better test the above hypotheses.

Diverse origins of framboidal pyrite

Framboidal pyrite in sedimentary records has been widely regarded as either formed in seawater or during diagenesis via MSR in low temperature conditions. Framboids often start to grow in the water column, followed by early diagenetic overgrowth in shallow marine sediments (Raiswell, 1982; Schallreuter, 1984; Wilkin et al., 1996; Wilkin and Barnes, 1997; Popa et al., 2004; Schieber, 2011). Based on the pioneering work by Wilkin et al. (1996) and then followed by Bond and Wignall (2010), the size distribution of pyrite framboids has been widely used to infer the redox conditions of seawater during deposition. However, more complexities are revealed in the samples of this study showing that origin, texture, size, and isotopic values of framboidal pyrite can be diverse.

First, the size of pyrite framboids can be significantly affected by late-stage pyrite overgrowth. Pyrite framboids can be partially or completely masked by late-stage pyrite overgrowth (Figs. 6, 7, 11–14), which cannot be detected without SEM imaging. Similar phenomena have also been reported from the Ediacaran samples (Wacey et al., 2015; Liu, 2016) and pyrites in modern marine sediments (Lin et al., 2016b; Lin et al., 2017).

Second, both MSR- and TSR-derived framboidal pyrites have been found in the studied samples. These two types of framboid have distinct characteristics in petrography, paragenesis and $\delta^{34}S_{pyrite}$ spatial patterns at μm scale. The framboidal pyrite in diamictite Sample 1 shows heterogeneous $\delta^{34}S_{pyrite}$ values (Figs. 7, 22, 23), and is interpreted to be syngenetic (in water column) or early diagenetic (in shallow marine sediments) in origin and formed by MSR. In contrast, the framboidal pyrite in Sample 2 and Sample 4 records remarkably homogeneous and superheavy $\delta^{34}S_{pyrite}$ values in spite of heterogeneous textures (Figs. 14, 19), which are interpreted to be formed via TSR by migrating hydrothermal fluids.

Supporting evidence for the existence of framboidal pyrite with a hydrothermal origin also comes from studies on both natural and synthetic pyrite framboids. Framboidal pyrites nucleated in hydrothermal veins or ores have been reported (Rust, 1935; Love and Amstutz, 1969; Ostwald and England, 1979; Scott et al., 2009). Additionally, lab experiments have demonstrated that framboidal pyrite can be synthesized at temperatures as high as 350 °C within a few hours (Sunagawa et al., 1971; Graham and Ohmoto, 1994; Ohfuji and Rickard, 2005). These studies suggest that framboidal pyrite of a high temperature origin is possible in both natural and lab environments.

Taken together, framboidal pyrite can be formed in both marine and hydrothermal (>100 °C) conditions. Observations by reflected light microscopy alone are insufficient to detect the origins of pyrite. Detailed SEM petrography and μm-scale $\delta^{34}S_{pyrite}$ analysis by SIMS are a powerful approach to interrogate the genesis of framboids.

CONCLUSIONS

(1) To interrogate the origins of the Neoproterozoic superheavy pyrite (Fig. 1), detailed petrographic and in situ $\delta^{34}S$ analyses (Figs. 3–21, Appendix 2–6) were conducted using scanning electron microscopy and secondary ion mass spectrometry (SEM-SIMS) for pyrite in the Cryogenian Tiesi'ao and Datangpo formations at unprecedented spatial resolution (2 μm spot size). Distinct spatial patterns of $\delta^{34}S_{pyrite}$ values at μm scale are found to be correlated with pyrite morphology and genesis (Table 1; Figs. 22, 23).

(2) Petrographic observations show that the Datangpo superheavy pyrite postdates the mineralization of rhodochrosite and illite (Figs. 9–13; Appendix 3) and thus is late diagenetic in origin. This refutes the long-held belief that these framboids are syngenetic (in water column) or early diagenetic (in shallow marine sediments).

(3) Framboidal pyrites of both marine and hydrothermal origins were found in this study. Framboidal pyrite in the Tiesi'ao diamictite (Sample 1) shows heterogeneous (+11.2‰ to +28.3‰), relatively low (+16.4‰ in average) $\delta^{34}S_{pyrite}$ values and a relatively wide range of grain sizes (up to 30 μm in diameter) (Fig. 5–7; Appendix 2). In contrast, the framboidal pyrite in Mn-rich carbonates (Sample 2) from the basal Datangpo Formation shows homogeneous (+56.3‰ to +60.4‰) and superheavy (+57.6‰ average) $\delta^{34}S_{pyrite}$ values and relatively small grain sizes (<7 μm diameter) (Figs. 11–14; Appendix 3). Sample 1 is interpreted to be syngenetic or early diagenetic in origin and formed by microbial sulfate reduction (MSR), while Sample 2 is interpreted to be hydrothermal in origin and formed by thermochemical sulfate reduction (TSR) (Table 1). The use of the size distribution of framboidal pyrite to infer paleo-redox conditions should be done with caution.

(4) Pyrite in one studied Datangpo shale sample from drill core (Sample 3) shows heterogeneous (+60.3‰ to +71.2‰) and superheavy (+66.3‰ average) $\delta^{34}S_{pyrite}$ values at μm scales (Figs. 16, 17; Appendix 4). It is notable that a decreasing $\delta^{34}S_{pyrite}$ trend is consistently recorded from the core to the edge of individual pyrite grains in Sample 3 (Figs. 16, 17; Appendix 4). This is in strong contrast with biogenic pyrite, which typically shows an increasing $\delta^{34}S_{pyrite}$ trend from the core to the edge of individual pyrite grains. It is proposed that the decreasing $\delta^{34}S_{pyrite}$ trend results from TSR with increasing sulfur isotope fractionations between sulfate and sulfide as hydrothermal fluids cool.

(5) Based on multiple lines of sedimentological and geochemical evidence at both basinal- and μm-scales, we argue that the superheavy pyrite in the Cryogenian strata in South China formed via thermochemical sulfate reduction (TSR), instead of microbial sulfate reduction (MSR). This is the first time that a post-depositional, hydrothermal origin is proposed for the superheavy pyrite in South China.

(6) We propose that post-depositional TSR plays an influential role in generating high $\delta^{34}S$ values. Consequently, interpretations of the high $\delta^{34}S$ values from the ancient geological record should reconsider

the influence that similar post-depositional processes may have in generating superheavy pyrite associated with noteworthy biogeochemical events in the Earth's history. Our study demonstrates that the integrated SEM-SIMS approach to $\delta^{34}S_{pyrite}$ analysis of individual pyrite grains is an effective tool to assess the veracity of sedimentary pyrite in chemostratigraphic studies.

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CONTRIBUTIONS

H.C. designed research; F.Z. provided samples; H.C. and K.K. performed SIMS analysis at J.W.V.'s WiscSIMS lab; H.C. and J.H.F. performed SEM and EPMA analyses; H.C. interpreted the data with contributions from all coauthors. H.C. wrote the manuscript with significant input from J.W.V. All authors contributed to discussion and manuscript revision.

APPENDIX 1

Compilation of the published $\delta^{34}S$ data measured from the Cryogenian post-glacial strata in China, UK, Namibia, and Australia.

APPENDIX 2

Integrated SEM-SIMS results of the drill core Sample 1 (Hy59, Sturtian glacial diamictite). Sample collected from the Cryogenian Tiesi'ao Formation, Daotuo mine, Guizhou Province, South China.

APPENDIX 3

Integrated SEM-SIMS results of the drill core Sample 2 (Hy55, Mn-rich carbonates). Sample collected from the Member 1 of the Cryogenian Datangpo Formation, Daotuo mine, Guizhou Province, South China.

APPENDIX 4

Integrated SEM-SIMS results data of the drill core Sample 3 (Hy31, black shale). Sample collected from the Member 1 of the Cryogenian Datangpo Formation, Daotuo mine, Guizhou Province, South China.

APPENDIX 5

Integrated SEM-SIMS results SIMS data of the drill core Sample 4 (Hy1, shale). Sample collected from the Member 2 of the Cryogenian Datangpo Formation, Daotuo mine, Guizhou Province, South China.

APPENDIX 6

Time-series plots and cross-plots of all the SIMS results in this study.

APPENDIX 7

Tables of all the SIMS $\delta^{34}S$ data in this study. The data were generated in three separate SIMS sessions: Session 1 (Oct. 18-19, 2016), Session 2 (May 22, 2017), and Session 3 (June 8, 2017). Sulfur two-isotopes (^{32}S, ^{34}S) were measured with a 2-µm-diameter beam size in Sessions 1 and 3. Sulfur three isotopes (^{32}S, ^{34}S, ^{33}S) were measured with a 10-µm-diameter beam size in Session 2.

APPENDIX 8

Table of all the elemental concentration data for pyrite by EPMA in this study.

TABLE 1

TABLE 1. Summary of SEM-SIMS results in this study of Cryogenian pyrite from Daotuo, South China. For the detailed petrographic context of all the geochemical data, the reader is referred to the online appendices (Appendices 2–5).

SIMS samples	**Sample 1 (Hy59)**	**Sample 2 (Hy55)**	**Sample 3 (Hy31)**	**Sample 4 (Hy1)**
Stratigraphic position	Uppermost Tiesi'ao Fm	Basal Mb 1, Datangpo Fm	Mb 1, Datangpo Fm	Mb 2, Datangpo Fm
Lithology	Terminal-Sturtian glacial diamictite	Post-Sturtian Mn-rich carbonates	Post-Sturtian black shale	Post-Sturtian shale
SEM-SIMS results	Figs. 5–8; Appendix 2	Figs. 9–14; Appendix 3	Figs. 15–17; Appendix 4	Figs. 18–21; Appendix 5
Pyrite morphology and grain size	Framboidal pyrite: up to ~30 µm; Pyrite nodules: ~1 to ~2 mm	Framboidal pyrite: up to 7 µm; Lacy pyrite overgrowth: µm to cm scale, showing lacy textures, metasomatic corrosion boundaries, and relatively darker color (compared with the framboids) under BSE	Subhedral pyrite: mostly 20 to 100 µm; Large pyrite with cemented individual pyrite grains: up to ~2 mm	Superheavy pyrite flowers (~15 µm in diameter): framboidal pyrite cores (~5 µm in diameter) with zoned pyrite overgrowth of ~5 µm in thickness; Fe-oxide coronas with pyrite rim (~35 µm in diameter) and pyrite cores (~10 µm in diameter)
Number of SIMS analyses (n)	Framboidal pyrite: n=76; Pyrite cements outside framboids: n=4; Pyrite nodules: n=10	Framboidal pyrite: n=5; Lacy pyrite overgrowth: n=15; Mixture between framboids and overgrowth: n=8	Subhedral pyrite grains: n=85; Later-stage pyrite cement: n=23	Superheavy pyrite flowers: n=25; Pyrite within Fe-oxide coronas: n=21
Range of SIMS $\delta^{34}S$ values ‰ V-CDT	Pyrite nodules: +9.8 to +52.2‰; Pyrite framboids: +11.2 to +28.3‰; Pyrite cements outside framboids: +22.7 to +36.7‰	Lacy pyrite overgrowth: +56.3 to +60.4‰; Mixture of framboids and overgrowth: +56.8 to +58.3‰; Pyrite framboids: +56.3 to +57.4‰	Individual pyrite grains: +60.3 to +71.2‰; Pyrite cements: +60.2 to +64.8‰	Superheavy pyrite flowers: +59.9 to +62.8‰; Pyrite cores within Fe-oxide coronas: +16.6 to +32.7‰
Mean $\delta^{34}S$ ‰ V-CDT	Pyrite nodules: +26.5‰; Pyrite framboids: +16.4‰; Pyrite cements outside	Lacy pyrite overgrowth: +57.8‰; Mixture of framboids and overgrowth: +57.4‰; Pyrite framboids:	Individual pyrite grains: +66.3‰; Pyrite cements: +62.0‰	Superheavy pyrite flowers: +61.6‰; Pyrite cores within Fe-oxide coronas: +22.2‰

	framboids: +30.9‰	+56.9‰		
Intra-grain $\delta^{34}S$ pattern	No systematic increasing or decreasing $\delta^{34}S$ trend	Not available	Systematic decreasing $\delta^{34}S$ trend from core to edge of each individual grain	Not available
$\delta^{34}S$ patterns on µm scales	Heterogeneous, mostly not superheavy	Homogeneous, superheavy	Individual pyrite grains: heterogeneous (in the range of ~10‰), superheavy; Pyrite cements: homogeneous, superheavy	Superheavy pyrite flowers: homogeneous, superheavy; Pyrite cores within Fe-oxide coronas: heterogeneous (in the range of ~16‰), not superheavy
Mean $^{32}S^{1}H/^{32}S$	Pyrite nodules: 8.7E–3 Pyrite framboids: 1.2E–2 Pyrite cements outside framboids: 1.0E–2	Lacy pyrite overgrowth: 1.6E–2 Mixture of framboids and overgrowth: 1.5E–2 Pyrite framboids: 1.3E–2	Individual pyrite grains: 7.0E–4 Pyrite cements: 8.5E–4	Superheavy pyrite flowers: 9.7E–3 Pyrite cores within Fe-oxide coronas: 1.3E–2
Paragenesis	Framboidal pyrite: syngenetic (water column) to early diagenesis; Pyrite nodules: early to late diagenesis	Framboidal pyrite: late diagenesis (petrographically replacing rhodochrosite and illite); Lacy pyrite overgrowth: postdating framboids	Disseminated subhedral pyrite: interpreted to be formed during late diagenesis; Pyrite cements: postdating individual pyrite grains	Superheavy pyrite flowers: late diagenesis; Pyrite cores within Fe-oxide coronas: syngenetic (water column) to early diagenesis
Interpretation in this study	Biogenic, microbial sulfate reduction	Abiogenic, thermochemical sulfate reduction	Abiogenic, thermochemical sulfate reduction	Superheavy pyrite flowers: abiogenic, thermochemical sulfate reduction; Pyrite cores within Fe-oxide coronas: biogenic, microbial sulfate reduction

FIGURE CAPTIONS

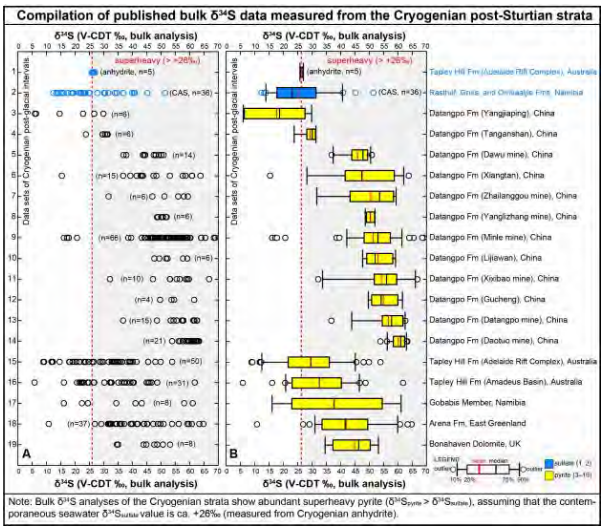


Figure 1. Compilation of published $\delta^{34}S$ data measured from the Cryogenian post-glacial strata in China, UK, Namibia, and Australia. X axis represents $\delta^{34}S$ values (V-CDT, ‰). Y axis represents different published data sets. (**A**) Individual data points of all the data sets. Numbers in parentheses representing the amount of data. (**B**) Box plots of corresponding data in **A**. Red line and black line within each box showing the mean value and the median value, respectively. Data sets 1 and 2 (blue) representing $\delta^{34}S_{sulfate}$ data measured from anhydrite and carbonate-associated sulfate (CAS), respectively. Data sets 3–19 (yellow in **B**) representing $\delta^{34}S_{pyrite}$ data. Red dash line represents Cryogenian seawater $\delta^{34}S_{sulfate}$ values based on data set 1. All plotted data were generated by conventional bulk analysis. Note that many $\delta^{34}S_{pyrite}$ data (up to +70‰) are much higher than the contemporaneous $\delta^{34}S_{sulfate}$ value (ca. +26‰, red dash line), commonly known as superheavy pyrite signals (i.e., $\delta^{34}S_{pyrite} > \delta^{34}S_{sulfate}$). Data source: (**1**) Tapley Hill Formation (Adelaide Rift Complex), Australia (Gorjan et al., 2000); (**2**) Rasthof, Gruis, and Ombaatjie formations of the Otavi Group, Namibia (Hurtgen et al., 2002); (**3–14**) Datangpo Formation in South China, including localities at (**3**) Yangjiaping, Hunan Province (Li et al., 2012), (**4**) Tanganshan, Hunan Province (Liu et al., 2006), (**5**) Dawu mine, Songtao County, Guizhou Province (Zhou et al., 2007; Wu et al., 2016), (**6**) Xiangtan, Hunan Province (Li et al., 1999a; Liu et al., 2006), (**7**) Zhailanggou mine, Songtao County, Guizhou Province (Chen et al., 2008), (**8**) Yanglizhang mine, Songtao County, Guizhou Province (Zhou et al., 2007), (**9**) Minle mine, Huayuan County, Hunan Province (Tang, 1990; Li et al., 1999a; Tang and Liu, 1999; Feng et al., 2010; Li et al., 2012; Wu et al., 2016), (**10**) Lijiawan, Songtao County, Guizhou Province (Wang et al., 2016), (**11**) Xixibao mine, Songtao County, Guizhou Province (Zhang et al., 2013; Wang et al., 2016), (**12**) Gucheng, Hubei Province (Wu et al., 2016), (**13**) Datangpo mine, Songtao County, Guizhou Province (Li et al., 1999a; Zhou et al., 2007; Wu et al., 2016), (**14**) Daotuo mine, Songtao County, Guizhou Province (Zhu et al., 2013; Wang et al., 2016); (**15**) Tapley Hill Formation in the Adelaide Rift Complex, Australia (Gorjan et al., 2000); (**16**) Tapley Hill Formation in the Amadeus Basin, Australia (Gorjan et al., 2000); (**17**) Gobabis Member, Namibia (Gorjan et al., 2003); (**18**) Arena Formation, East Greenland (Scheller et al., 2018); (**19**) Bonahaven Dolomite Formation, UK (Parnell and Boyce, 2017). All the compiled data are available in the online Appendix 1.

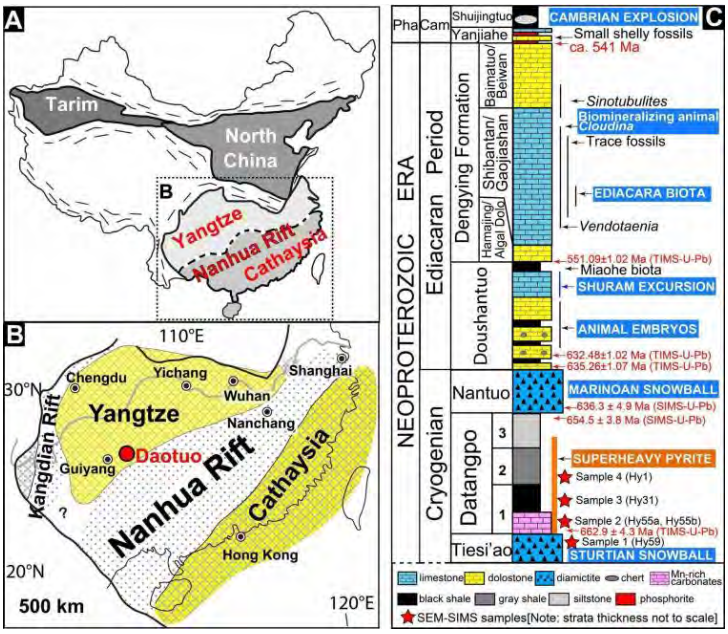


Figure 2. (**A**) Tectonic map of China. (**B**) Reconstructed Yangtze and Cathaysia blocks with the Nanhua rift in between (Li et al., 1999b; Jiang et al., 2003; Wang and Li, 2003; Zhang et al., 2008). Red dot indicates the location of the studied Daotuo mine at Songtao, eastern Guizhou Province. (**C**) Simplified litho-, bio-, and chrono-stratigraphy of the Neoproterozoic strata in South China. Source of the lithology and fossil record (Jiang et al., 2007; McFadden et al., 2008; Cai et al., 2010; Jiang et al., 2011; Chen et al., 2013; Chen et al., 2014; Cui, 2015; Cui et al., 2016b; Cui et al., 2017). Source of the radiometric ages (Zhou et al., 2004; Condon et al., 2005; Zhang et al., 2008; Schmitz, 2012; Chen et al., 2015). Superheavy pyrite has been widely reported from the post-glacial Datangpo Formation (see text). Thickness is not to scale. Cam = Cambrian; Pha = Phanerozoic.

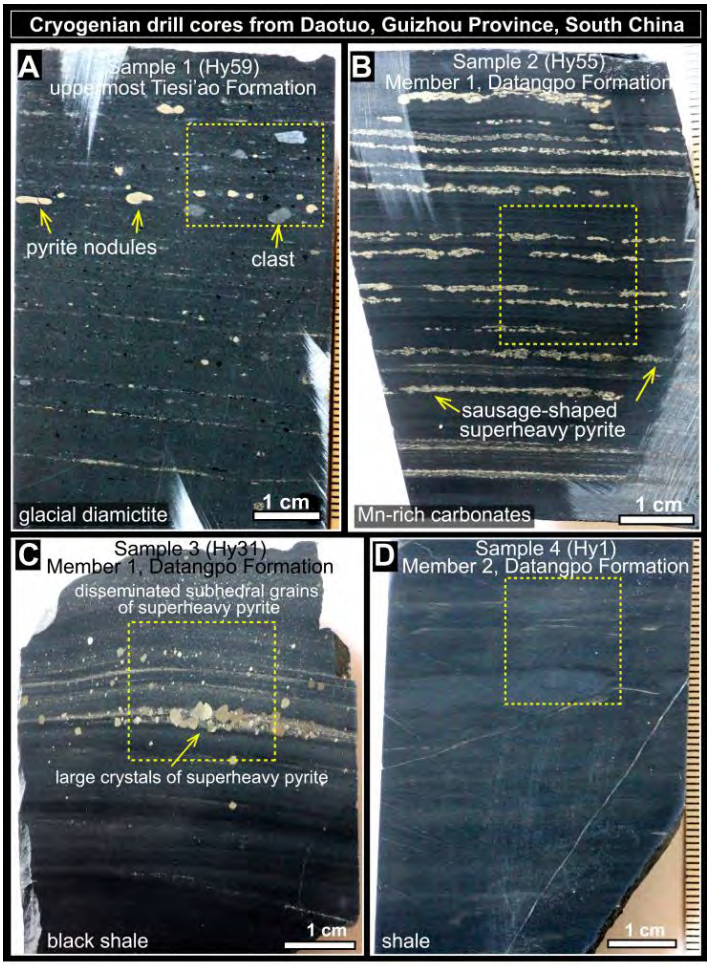


Figure 3. (A–D) Four drill core samples collected at Daotuo, Guizhou Province, South China. Marked zones of the surfaces were prepared as SIMS mounts for further studies. **A:** Sample 1 (Hy59, glacial diamictite) from the uppermost Tiesi'ao Formation. **B:** Sample 2 (Hy55, Mn-rich carbonates) from the Member 1 of the Datangpo Formation. **C:** Sample 3 (Hy31, shale) from the Member 1 of the Datangpo Formation. **D:** Sample 4 (Hy1, shale) from the Member 2 of the Datangpo Formation. All the drill cores are 4.5 cm in diameter.

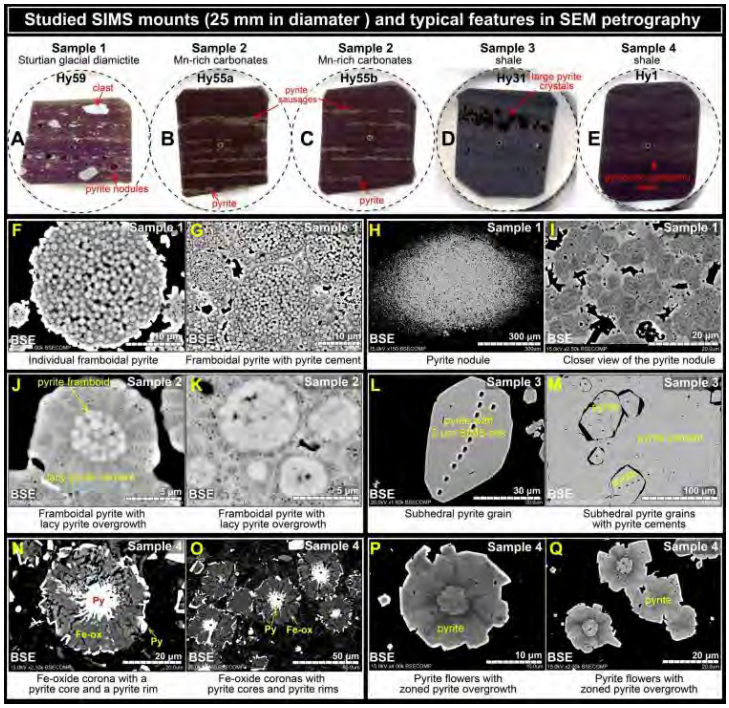


Figure 4. Studied SIMS mounts and typical petrographic features of each sample. **(A–E)** 25-mm-diameter SIMS mounts with in-house pyrite standard UWPy-1 (marked as yellow circles) mounted in the center of each mount. **(F–Q)** Typical features by SEM-BSE. **F–I** Sample 1 (Hy59); **J–K** Sample 2 (Hy55); **L–M** Sample 3 (Hy31); **N–Q** Sample 4 (Hy1). **(F)** Individual pyrite framboid in Sample 1. **(G)** Framboidal pyrite with pyrite cement in Sample 1. **(H)** A large pyrite nodule in Sample 1. **(I)** A magnified view of the individual zoned pyrite crystals within the pyrite nodule in Sample 1. **(J, K)** Framboidal pyrite with lacy pyrite overgrowth in Sample 2. **(L)** Subhedral pyrite grain in Sample 3. **(M)** Subhedral pyrite grains with pyrite cements in Sample 3. (**N, O**) "Fe-oxide coronas" with pyrite cores and pyrite rims. Py: pyrite; Fe-ox: Fe oxide. Small black spots in **L, M** and **O** showing SIMS pits. **(P, Q)** "Pyrite flowers" in Sample 4 showing framboidal pyrite cores and zoned pyrite overgrowth. Abbreviations: BSE = backscattered electron; SE = secondary electron. For more detailed SEM images of the studied samples, see online Appendices 2–5.

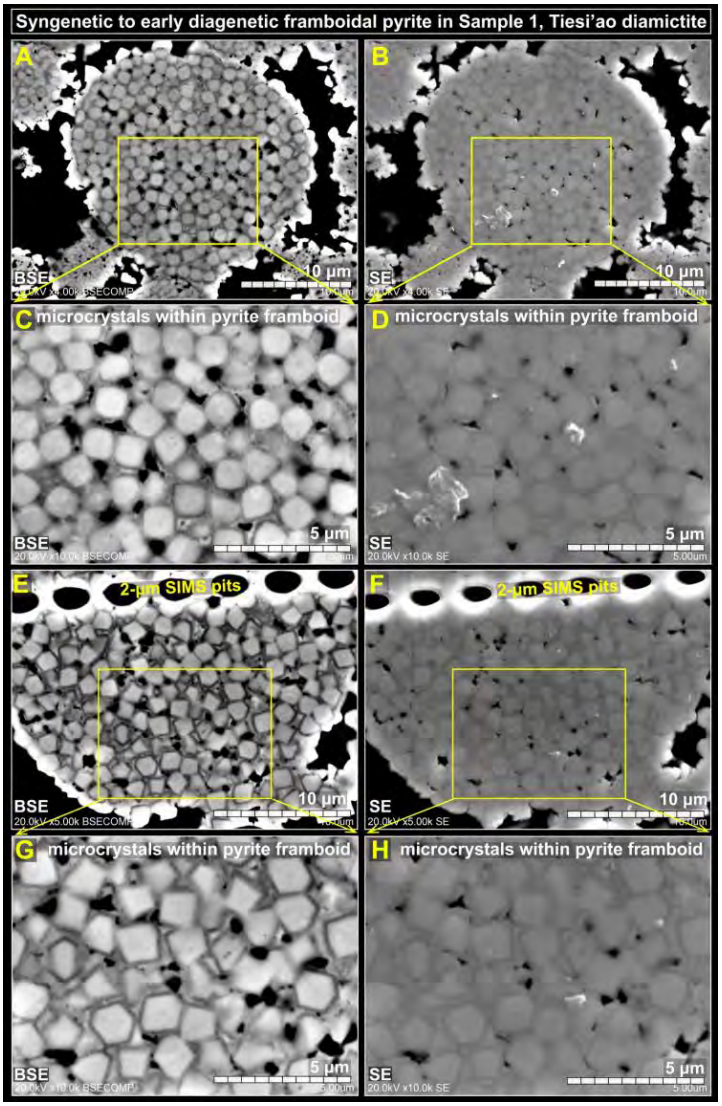


Figure 5. SEM petrography of the pyrite framboids in Sample 1. Images **C–D** and **G–H** showing magnified views of marked areas in **A–B** and **E–F**, respectively. Note that the pyrite microcrystals within the framboids are typically surrounded by darker rims (possibly rich in inclusion or porosity) and pyrite cements. Abbreviations: BSE = backscattered electron; SE = secondary electron. For more detailed SEM images of the studied samples, see online Appendix 2.

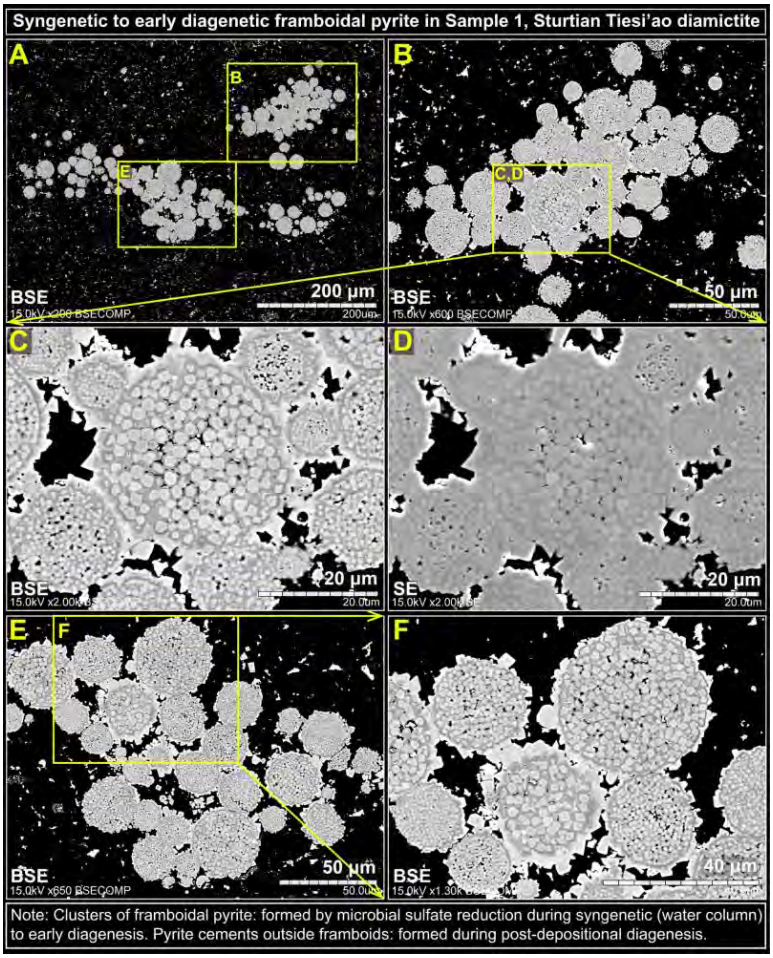


Figure 6. (A–F) SEM images showing clusters of framboidal pyrite in Sample 1. Magnified views are marked by yellow dash boxes. Note that many of the pyrite framboids are cemented by later-stage pyrite. Based on the petrography and $\delta^{34}S$ evidence, the framboidal pyrite in Sample 1 is interpreted to be syngenetic to early diagenetic in origin. See the main text for further discussion. Abbreviations: BSE = backscattered electron; SE = secondary electron. For more detailed SEM images, see online Appendix 2.

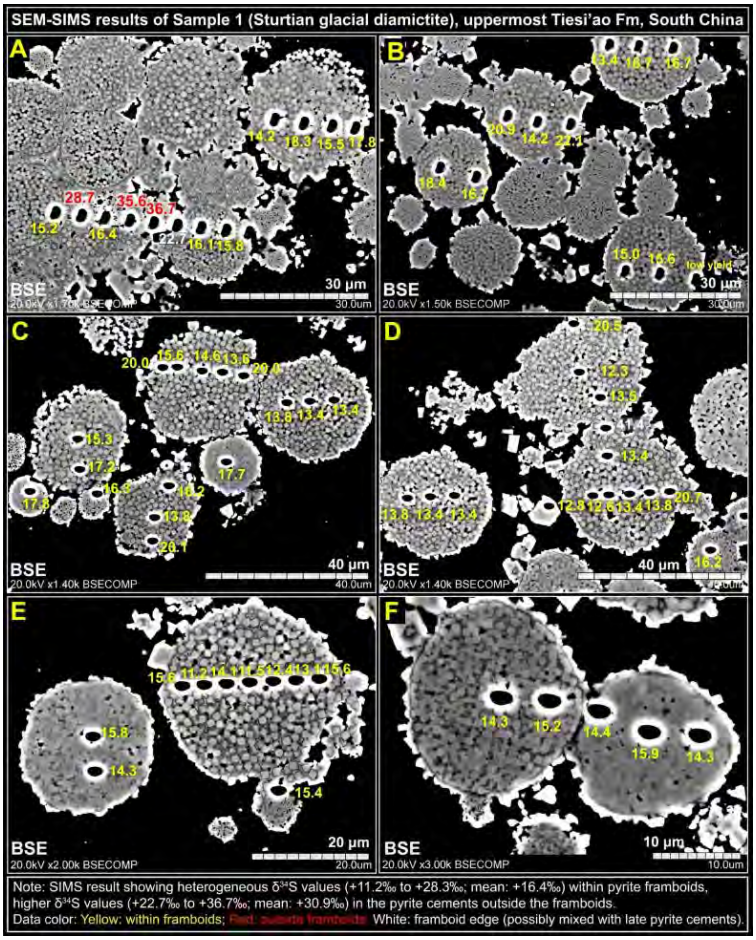


Figure 7. Backscattered electron (BSE) images and SIMS $\delta^{34}S$ results of framboidal pyrite in Sample 1. SIMS $\delta^{34}S$ data presented in different colors based on petrographic textures. Yellow: within framboids; Red, outside framboids; White: framboid edge. Detailed views of image A can be found in Slides 25–32 of the online Appendix 2. Note that the $\delta^{34}S$ data measured from the pyrite cements outside the framboids (red or white) are significantly higher than those measured within the pyrite framboids (yellow). For more detailed SEM-SIMS results of this sample, see online Appendix 2.

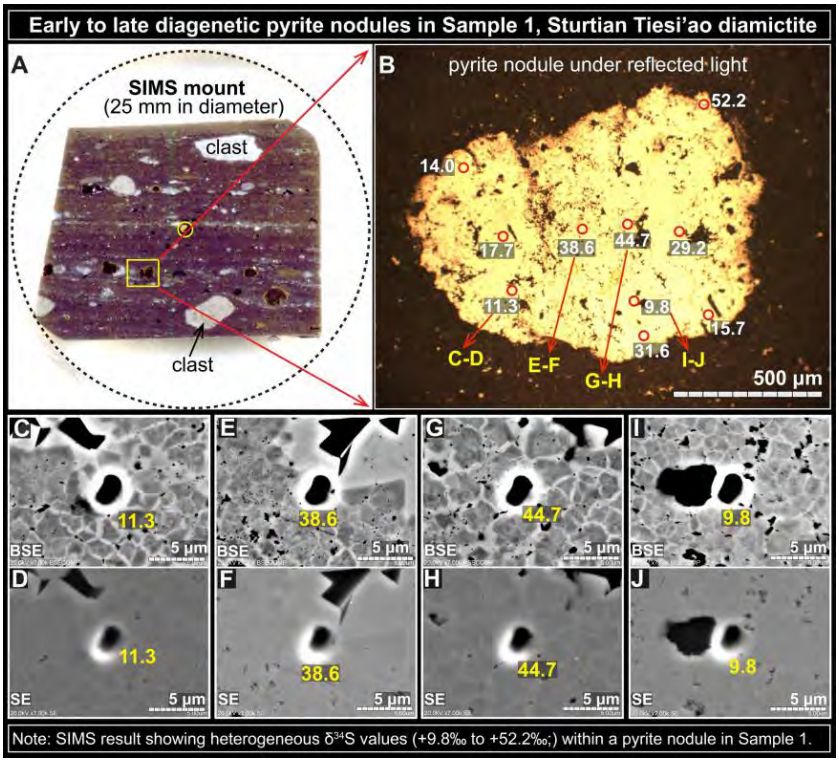


Figure 8. Pyrite nodules in Sample 1. (**A**) 25-mm-diameter SIMS mount of Sample 1 with in-house pyrite standard UWPy-1 (marked as yellow circle) mounted in the center. (**B**) A studied pyrite nodule under reflected light. SIMS $\delta^{34}S$ values showing heterogeneous values. Note that the symbols (red circles) are much larger than the actual SIMS spots (2 µm in diameter). (**C–D, E–F, G–H, I—J**) Coupled BSE–SE images of the analyzed spots. The spots are all shown in the center. Note that the pyrite nodule is very heterogeneous under BSE, representing progressive pyrite mineralization during a spectrum of diagenesis. Abbreviations: BSE = backscattered electron; SE = secondary electron. For more detailed SEM-SIMS results of this sample, see online Appendix 2.

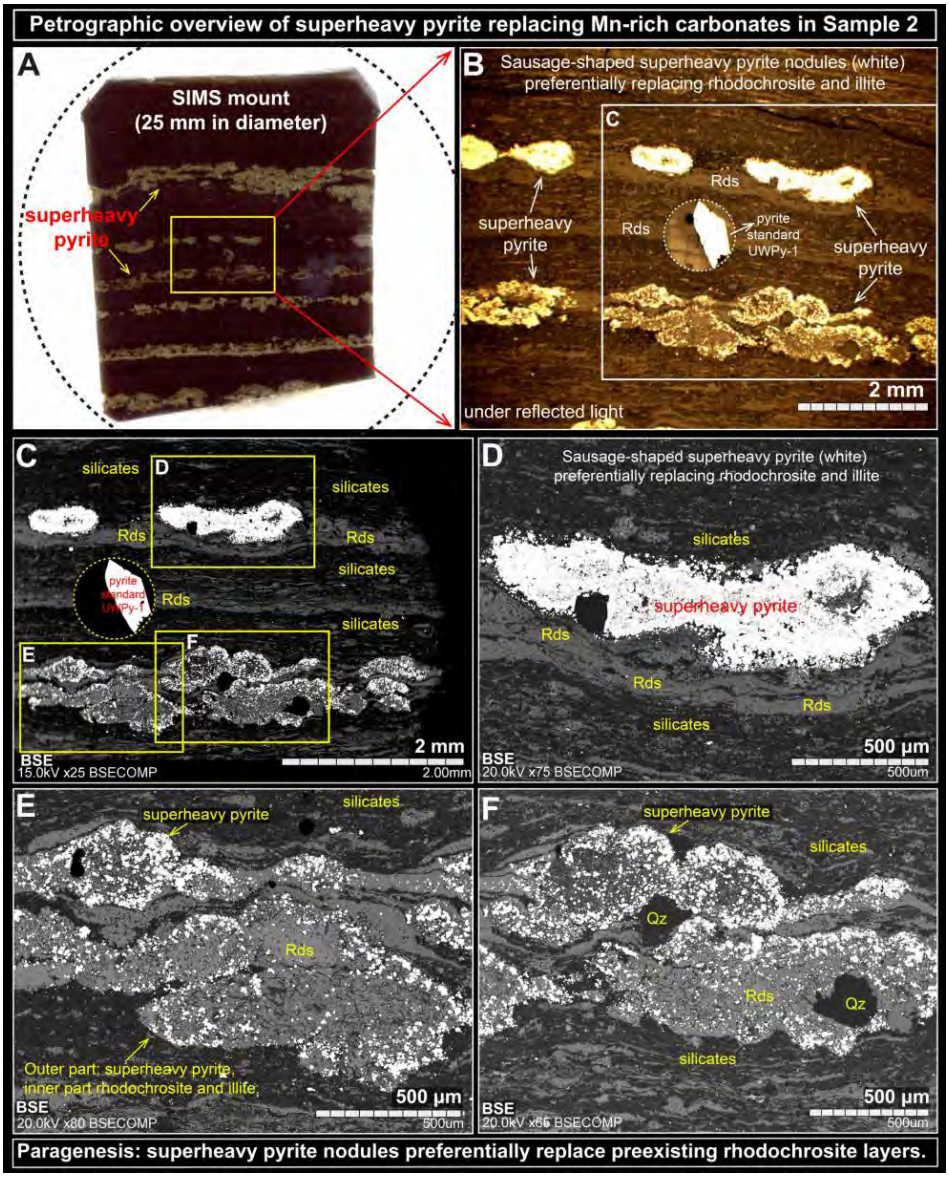


Figure 9. Petrographic observations of Sample 2. (**A**) SIMS mount of Sample 2 showing abundant sausage-shaped pyrite nodules within Mn-rich carbonates. (**B, C**) Sausage-shaped superheavy pyrite aggregates partially replacing rhodochrosite. Image **B** taken under reflected light; Image **C** taken with BSE. Note that some sausage-shaped textures have superheavy pyrite around margins and relict rhodochrosite in the center. (**D–F**) Magnified BSE views of the sausage-shaped textures. Note that superheavy pyrite in **E** and **F** is partially replacing the preexisting rhodochrosite (Rds) lamina, with superheavy pyrite concentrated at the margins and rhodochrosite in the core of the sausages. For more detailed petrographic images of this sample, see online Appendix 3.

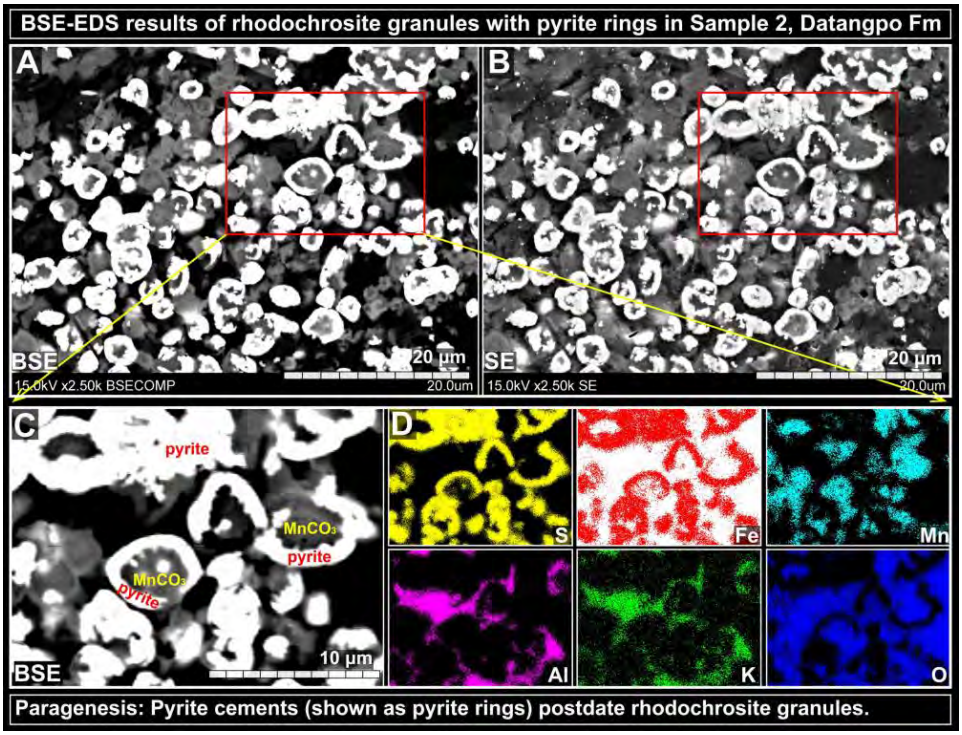


Figure 10. SEM-EDS results of rhodochrosite granules with pyrite rings in Sample 2. **(A, B)** Matched views under BSE and SE, respectively. (**C**) Magnified BSE view of marked zones in A and B. (**D**) ESD elemental mapping of the view in C. Black or white background colors in the EDS images represent zero detection. For more petrographic images of this sample, see online Appendix 3. Abbreviations: BSE = backscattered electron; SE = secondary electron; EDS = Energy-Dispersive X-ray Spectrometry. For more petrographic images of this sample, see online Appendix 3.

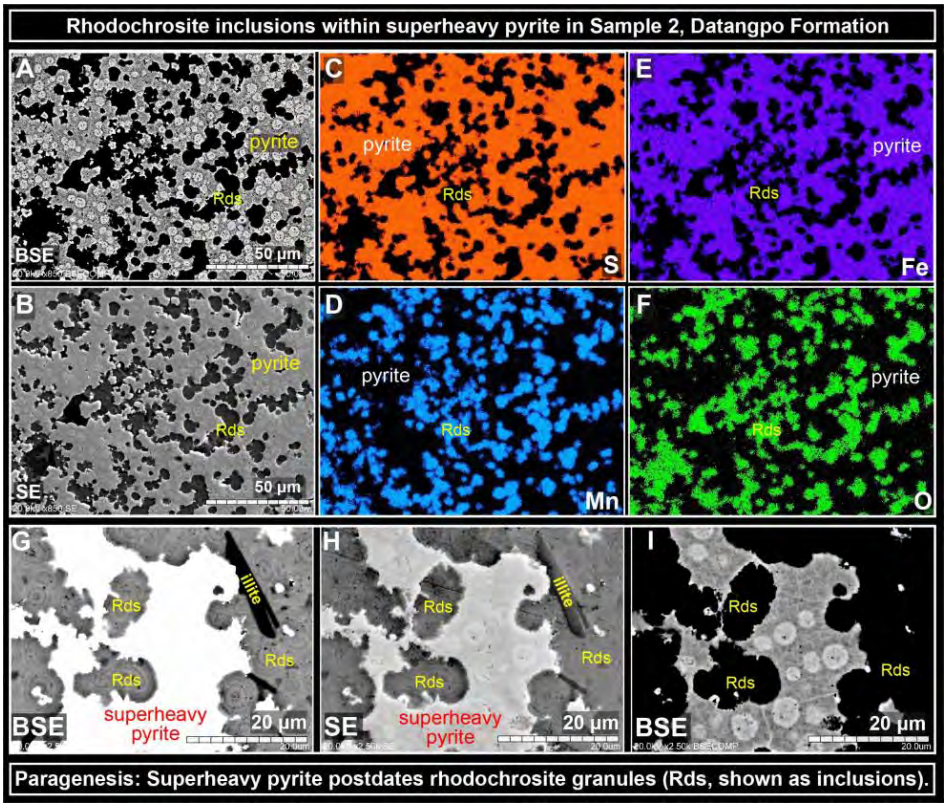
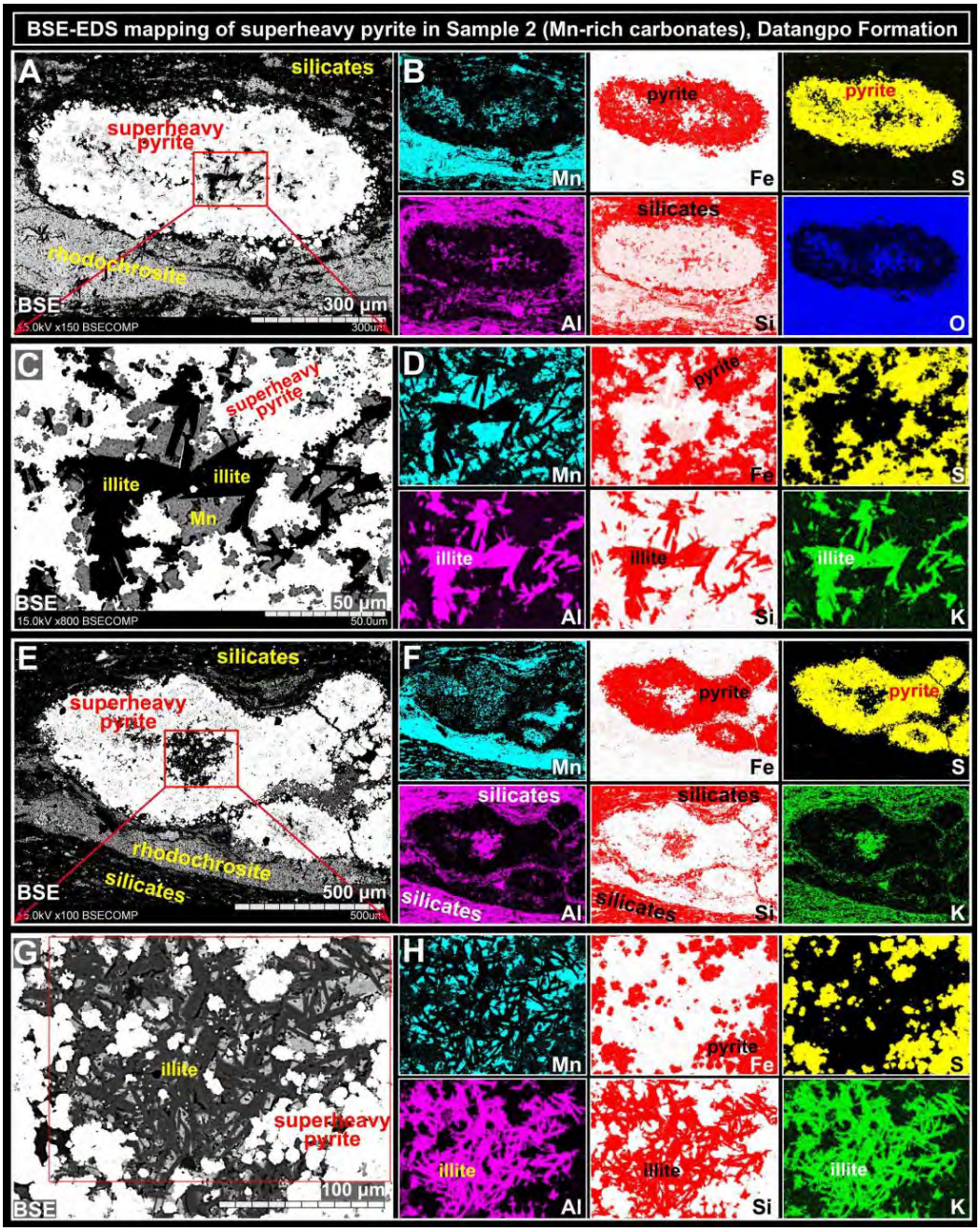


Figure 11. SEM-EDS views of rhodochrosite inclusions within the superheavy pyrite in Sample 2. **A–F** and **G–I** showing matched views of SEM and elemental maps by EDS. Black background in EDS element maps represents zero detection. The BSE images of superheavy pyrite are made with decreased color contrast (**A, I)** to show heterogeneous textures with pyrite framboids (brighter under BSE) and lacy pyrite overgrowths (darker under BSE). Note metasomatic corrosion textures and the massive rhodochrosite inclusions that are not yet replaced by superheavy pyrite, suggesting superheavy pyrite postdates rhodochrosite. Abbreviations: BSE = backscattered electron; SE = secondary electron. For more detailed SEM-EDS images of this sample, see online Appendix 3.



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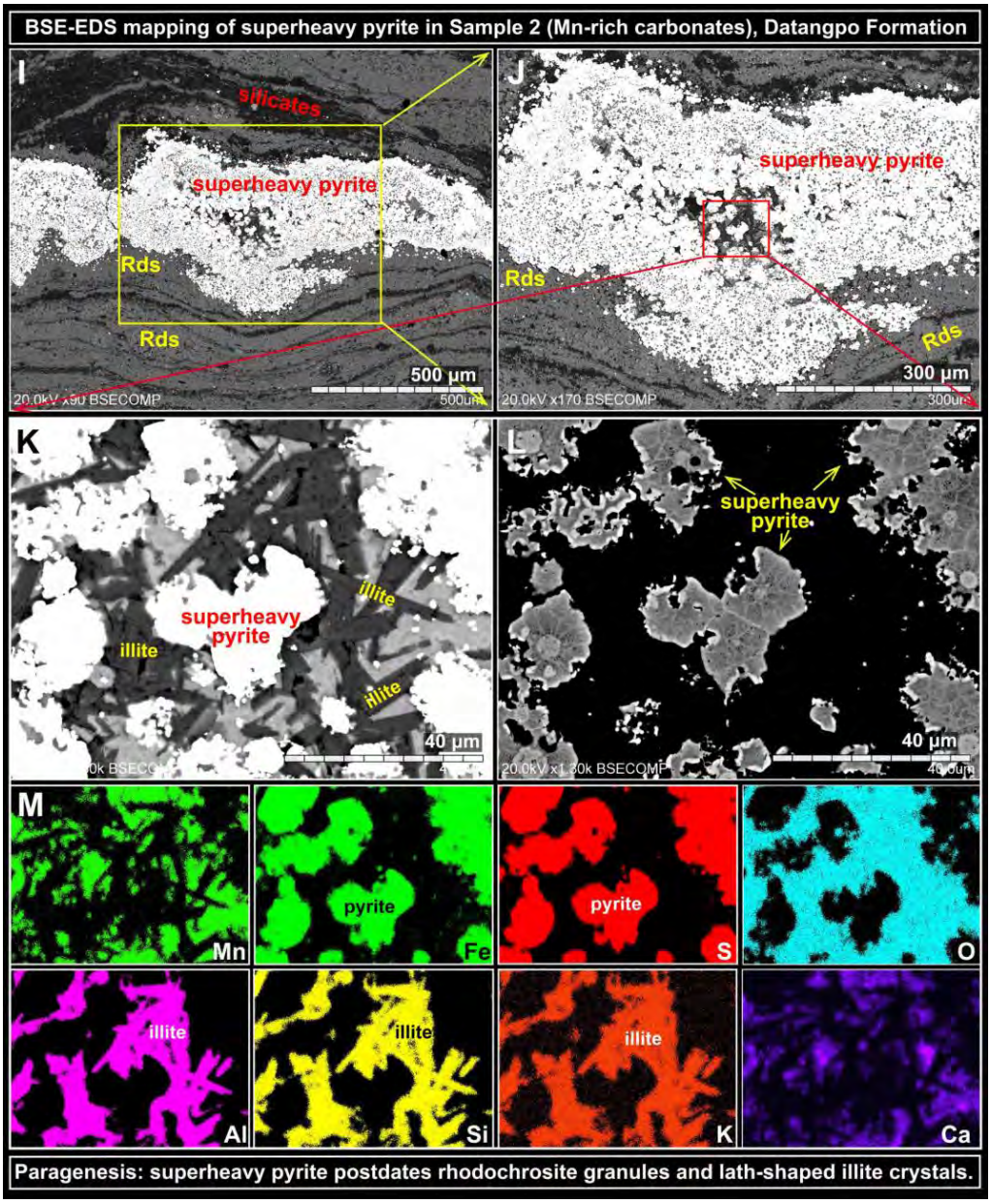

Figure 12. SEM-EDS results of superheavy pyrite in Sample 2. Images A–B, C–D, E–F, G–H, K/L–M showing pairs of matched views of BSE and EDS, respectively. Black or white background colors in EDS images represent zero detection. Abbreviations: BSE = backscattered electron; EDS = Energy-Dispersive X-ray Spectrometry. Note that superheavy pyrite in Sample 2 showing the replacement of preexisting rhodochrosite (Rds) and lath-shaped illite crystals. For more detailed SEM-EDS images of this sample, see online Appendix 3.

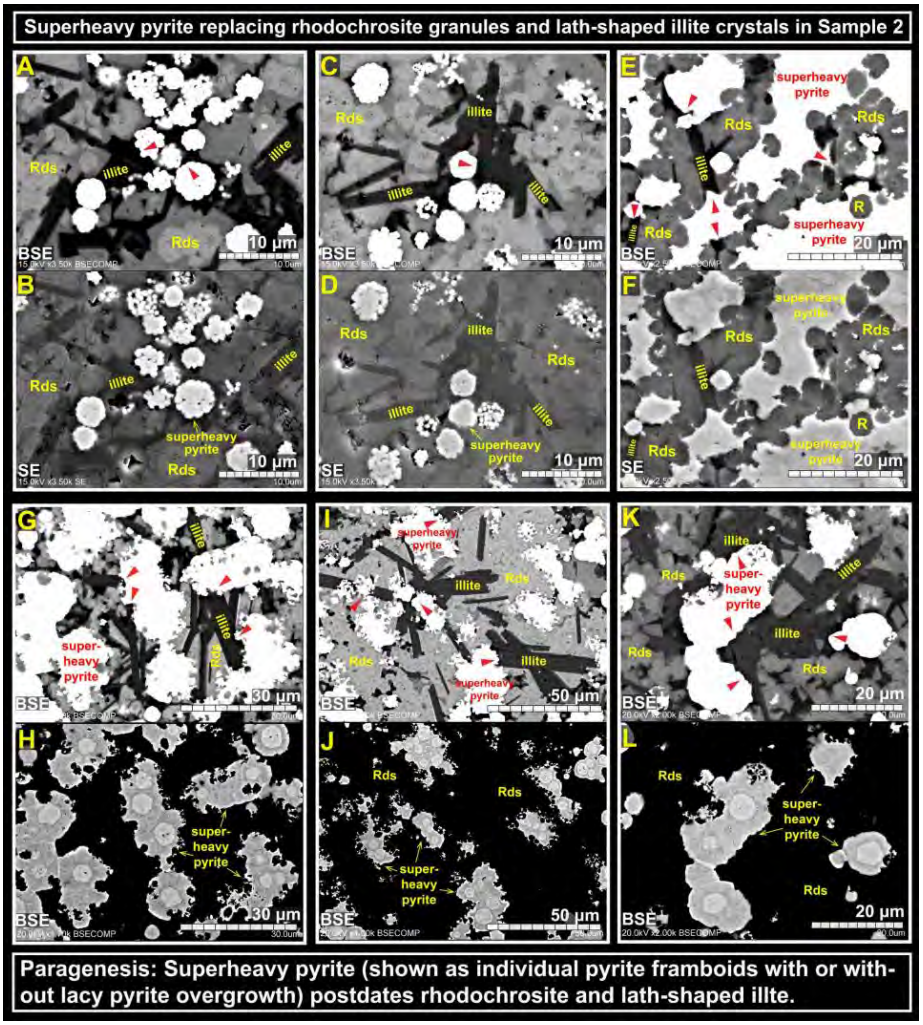

Figure 13. Backscattered electron (BSE) images of Sample 2 showing the replacement (marked by red arrows) of preexisting rhodochrosite granules and lath-shaped illite crystals by superheavy pyrite. **A–B, C–D, E–F** showing individual pairs of BSE and SE images of the matched views, respectively. **G–H, I–J, K–L** showing BSE images of the same view but in different color contrast. (**A–D**) Individual pyrite framboids (without lacy pyrite overgrowth) replacing rhodochrosite and illite. (**E–L**) Pyrite framboids with lacy pyrite overgrowth replacing rhodochrosite and illite. Note the irregular pyrite boundary showing metasomatic corrosion textures. Rhodochrosite (Rds or R) inclusions in E and F also suggest that superheavy pyrite postdate rhodochrosite. Abbreviations used: BSE = backscattered electron; SE = secondary electron. For more detailed SEM descriptions of this sample, see online Appendix 3.

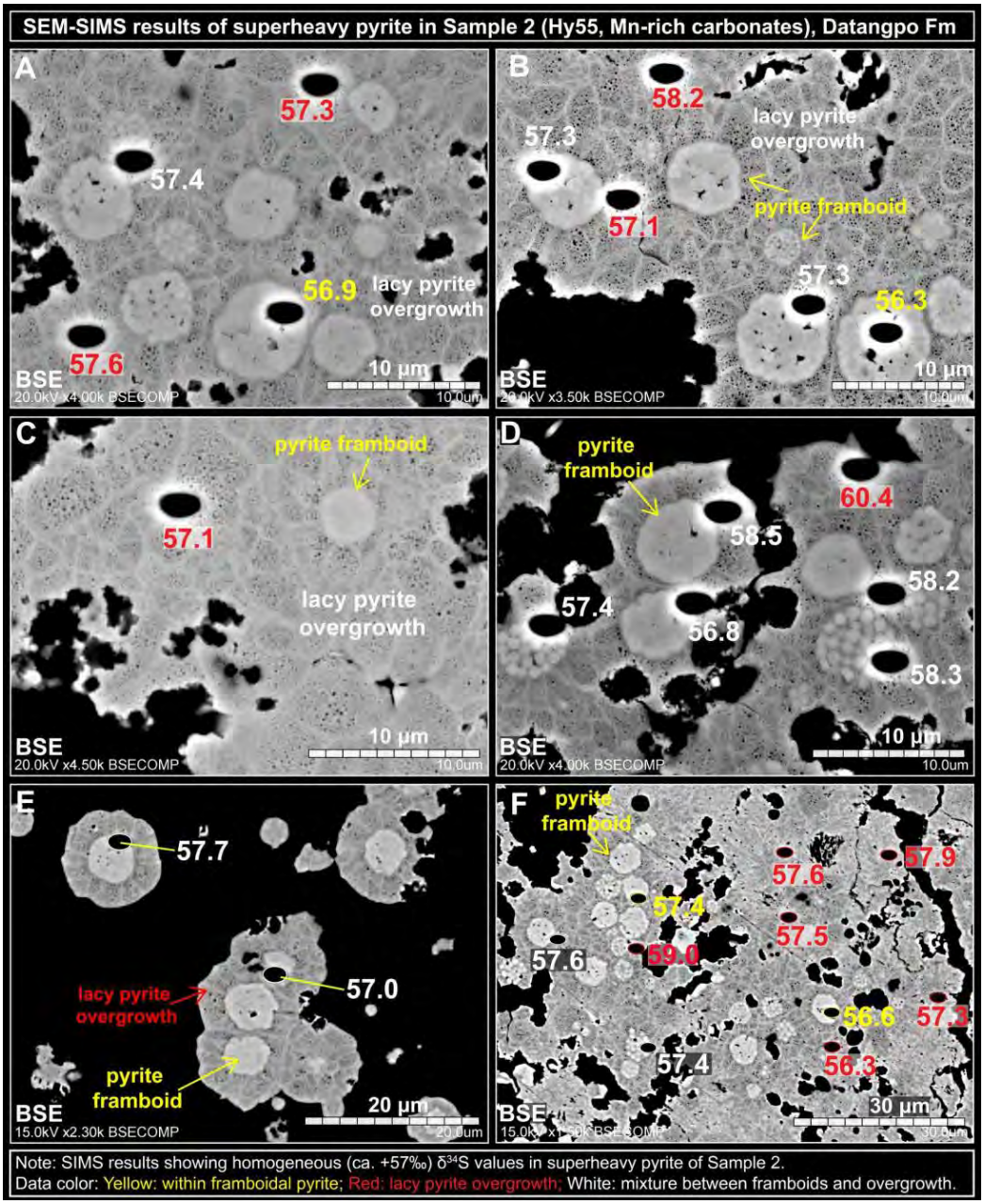

Figure 14. Backscattered electron (BSE) images with 2-µm SIMS pits in superheavy pyrite in Sample 2. SIMS $\delta^{34}S$ data (‰ V-CDT) presented in different colors based on different textures. Yellow: within framboids; Red, lacy pyrite overgrowth; White: mixture between pyrite framboids and pyrite overgrowth. Superheavy pyrite in this sample shows heterogeneous textures with pyrite framboids (brighter under BSE) and lacy pyrite overgrowth (darker under BSE) and metasomatic corrosion textures. Note the remarkably homogeneous $\delta^{34}S$ data regardless of heterogeneous petrographic textures. For more detailed SEM-SIMS data of this sample, see online Appendix 3.

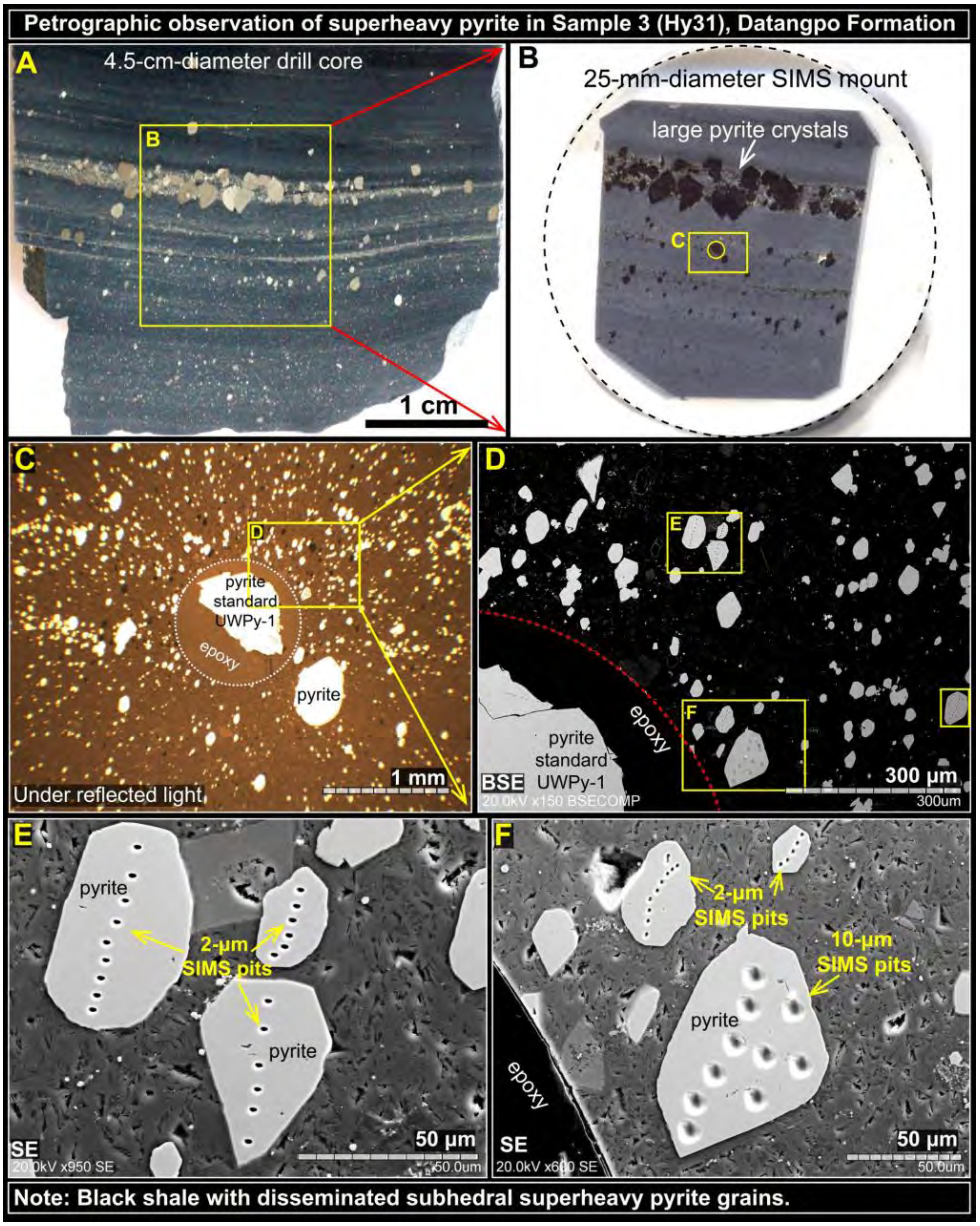

Figure 15. Petrographic observations of Sample 3. (**A**) A drill core section of Sample 3 showing abundant subhedral pyrite. (**B**) SIMS mount of Sample 3. (**C**) A magnified view of Sample 3 under reflection light (RL) showing disseminated subhedral pyrite grains in shale. (**D**) BSE image of the marked area in **C**. Analyzed pyrite grains in this study are marked by yellow dash boxes. Magnified views of these marked pyrite grains can be found in Figure 16 and the online Appendix 4. (**E, F**) SE images of the analyzed domains in **D**. SIMS pits of either 2 µm or 10 µm in diameter are shown on the analyzed pyrite grains. Abbreviations: BSE = backscattered electron; SE = secondary electron. For more detailed SEM descriptions of this sample, see online Appendix 4.

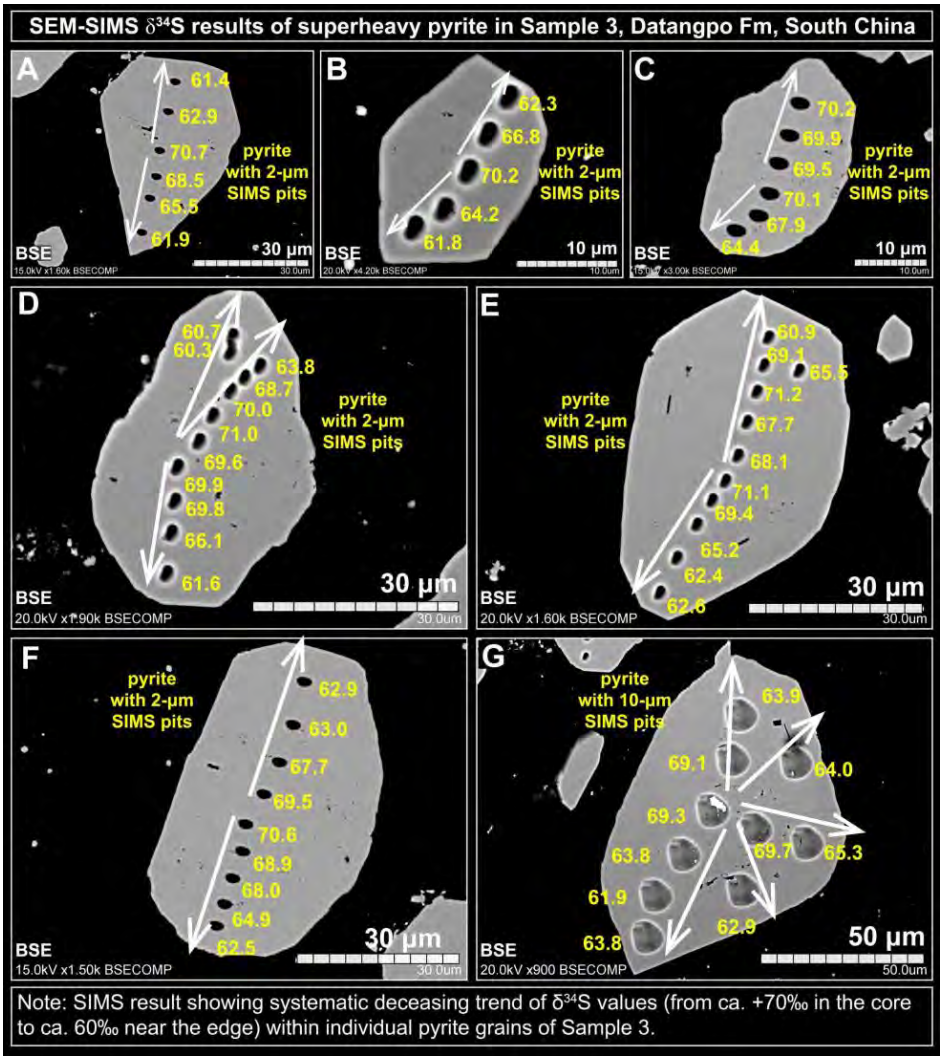

Figure 16. SEM-SIMS results of Sample 3. Note the consistent decreasing trend (white arrows) of $\delta^{34}S$ values from the core (ca. +70‰) to the edge (ca. +61‰) of the individual pyrite grains. For more detailed SEM-SIMS results of this sample, see online Appendix 4.

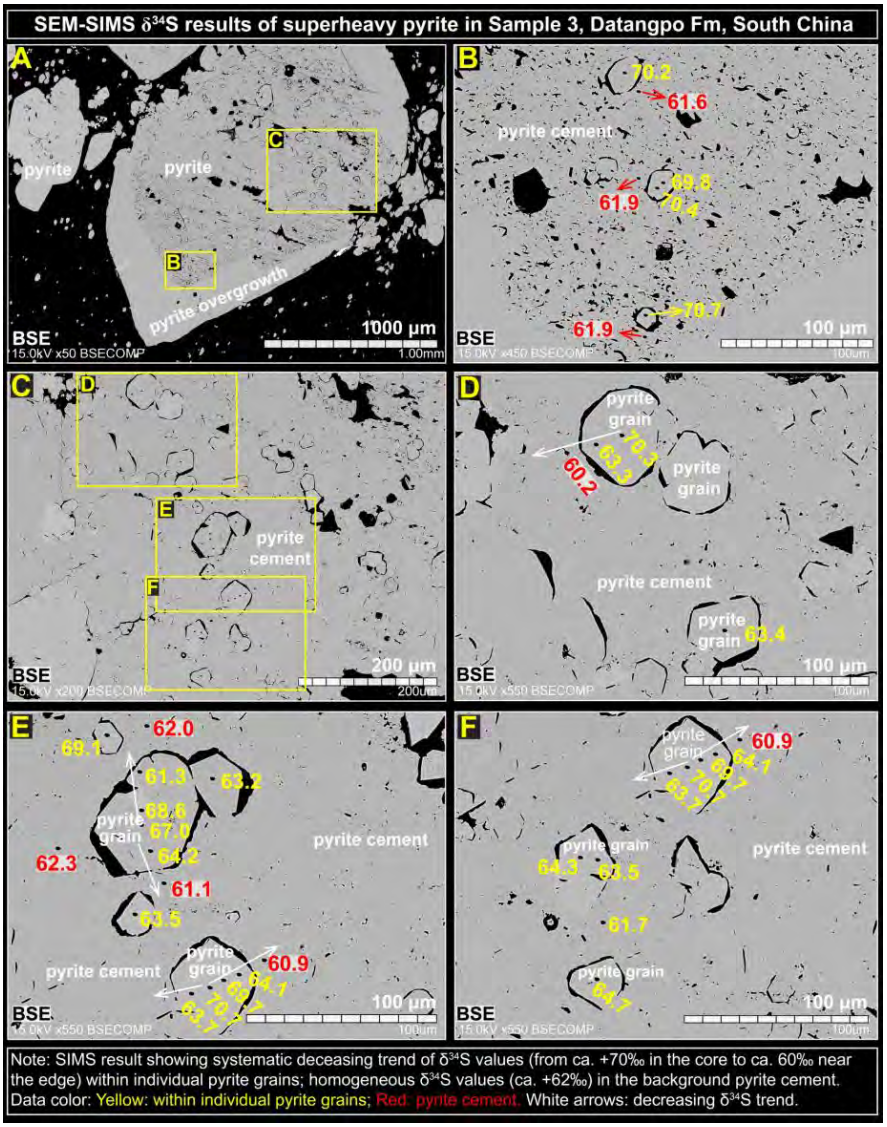

Figure 17. SEM-SIMS results of domains in Sample 3. (**A**) Large pyrite grains with multiple smaller pyrite grains cemented inside. (**B–F**) Magnified views of marked areas in **A** and **C** showing individual pyrite grains cemented by later-stage pyrite. SIMS $\delta^{34}S$ data (‰ V-CDT) presented in different colors based on different textures. Yellow: within individual pyrite grains; Red, later-stage pyrite cements. White arrows showing consistent deceasing $\delta^{34}S$ trends (ca. +70‰ to +60‰) from the core to the edge of individual pyrite grains. For more detailed SEM-SIMS data of this sample, see online Appendix 4.

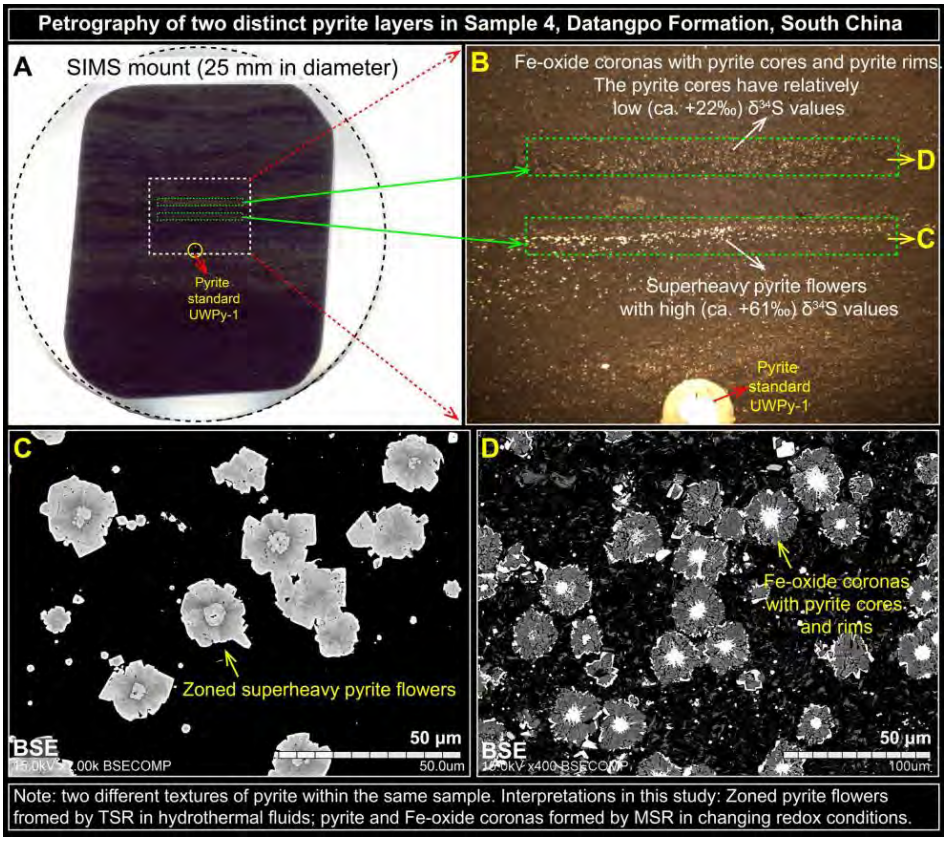

Figure 18. Petrographic observations of Sample 4. (**A**) SIMS mount of Sample 4. (**B**) A magnified view of the marked area in **A** showing two distinct layers of pyrite. The SIMS $\delta^{34}S$ data are also shown for convenience. (**C**) A magnified view of pyrite in the lower layer. This layer is characterized by "zoned pyrite flowers" with homogeneous and superheavy $\delta^{34}S$ values. (**D**) A magnified view of pyrite in the upper layer. This layer is characterized by "Fe-oxide coronas" with pyrite cores and pyrite rims. For more detailed SEM-SIMS data from this sample, see online Appendix 5.

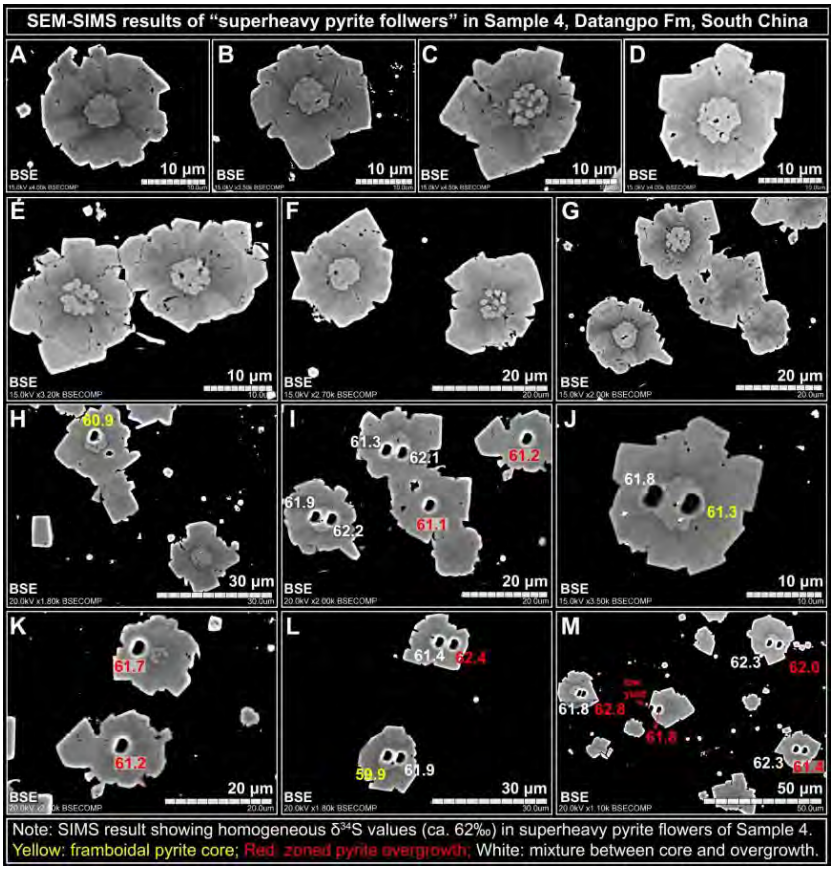

Figure 19. Backscattered electron (BSE) images showing SIMS $\delta^{34}S$ pits in "superheavy pyrite flowers" in Sample 4 (Hy1). The "superheavy pyrite flower" is characterized by a small framboidal pyrite core and a zoned pyrite overgrowth. SIMS $\delta^{34}S_{pyrite}$ values (‰ V-CDT) are presented in different colors based on the textures. Yellow: within framboids; Red, zoned pyrite overgrowth; White: mixture between pyrite framboids and pyrite overgrowth. Note that the $\delta^{34}S$ data measured from zoned "superheavy pyrite flowers" are remarkably homogeneous. For more detailed SEM-SIMS data from this sample, see online Appendix 5.

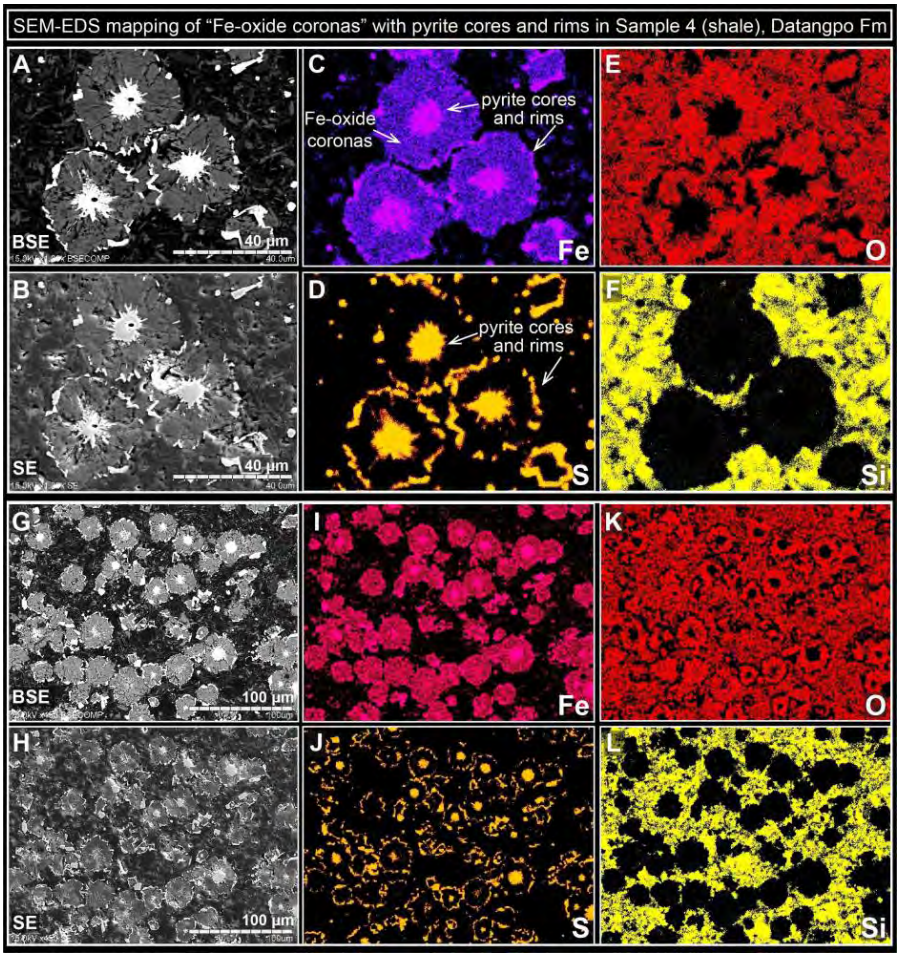

Figure 20. A–F and **G–L** showing SEM-EDS images and chemical maps of Fe, O, S and Si of matched views in Sample 4. Black background in EDS images represent zero detection. Abbreviations: BSE = backscattered electron; EDS = Energy-Dispersive X-ray Spectrometry. For more detailed SEM-EDS images from this sample, see online Appendix 5.

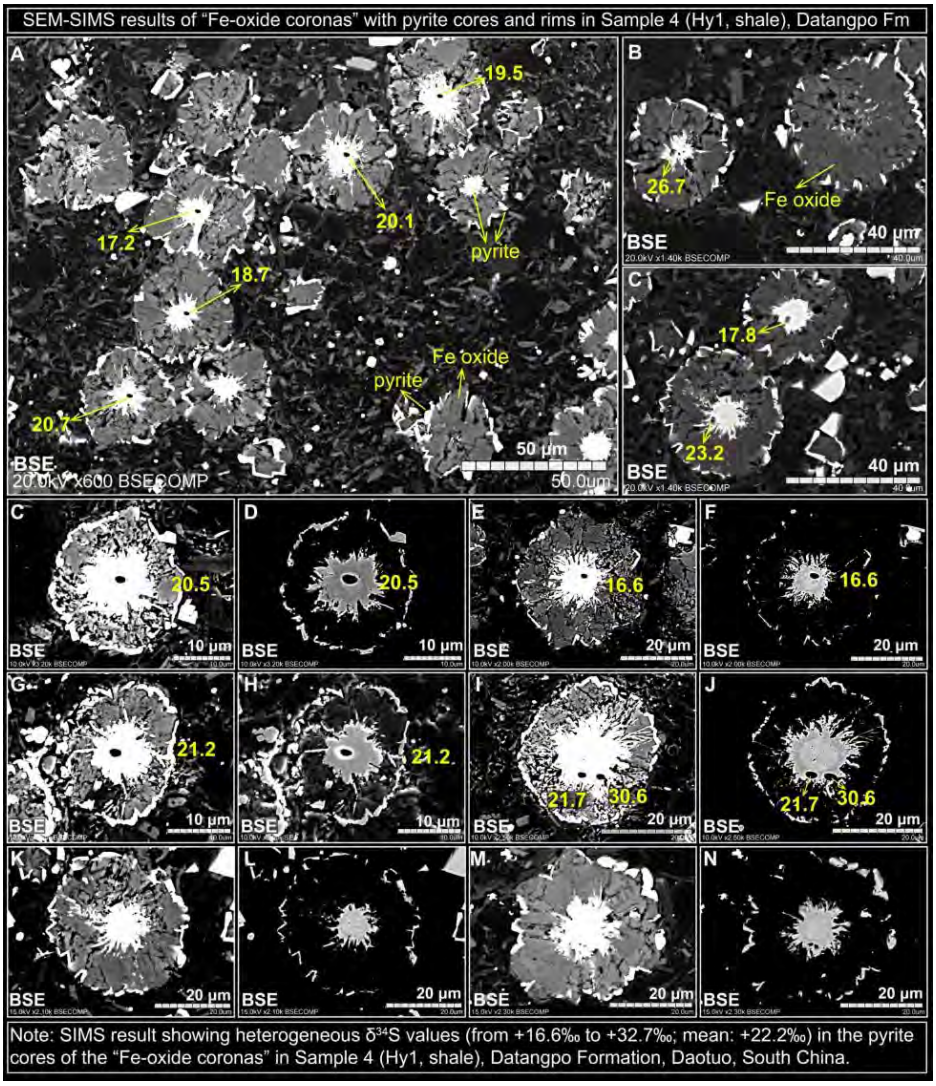

Figure 21. Backscattered electron (BSE) images showing SIMS $\delta^{34}S$ pits in pyrite cores inside the Fe-oxide coronas in Sample 4 (Hy1). The Fe-oxide corona surrounds a framboidal pyrite core with a fibrous surface (likely marcasite initially) and a thin pyrite rim. SIMS $\delta^{34}S$ values measured from the pyrite cores range from ca. +16 to +33‰. For more detailed SEM-SIMS data of this sample, see online Appendix 5.

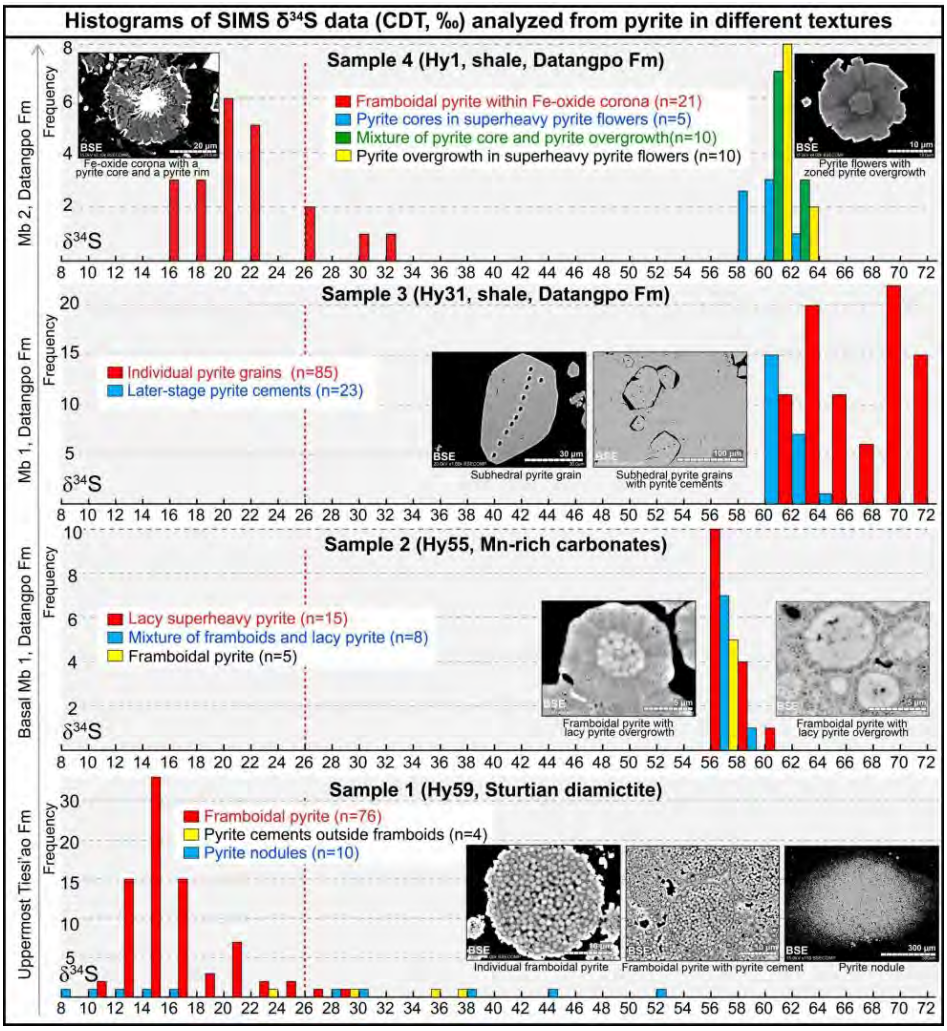

Figure 22. Histograms of the SIMS $\delta^{34}S$ values measured in this study. Different pyrite textures showing distinct ranges of $\delta^{34}S$. Red dash line representing the Cryogenian seawater $\delta^{34}S_{sulfate}$ value based on anhydrite analysis (Gorjan et al., 2000). Note the relatively large range of SIMS $\delta^{34}S$ data measured from Sample 1, homogeneous $\delta^{34}S$ values measured from Sample 2, remarkably high $\delta^{34}S$ values measured from Sample 3, a notable bimodal distribution of the $\delta^{34}S$ values measured from Sample 4. See the main text for detailed discussion of these patterns and their interpreted origins. For corresponding petrographic context of all the plotted data, see online Appendices 2–5.

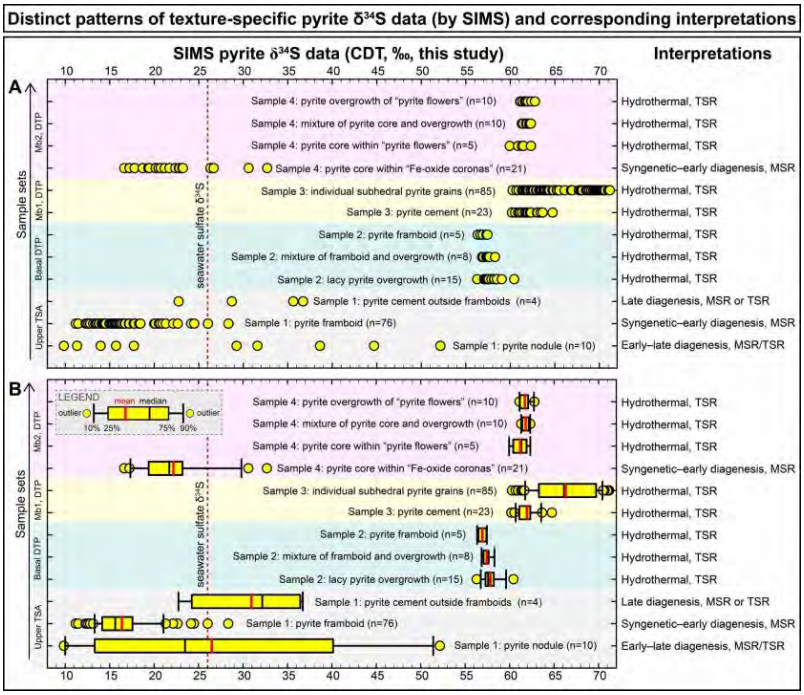

Figure 23. (**A**) Individual data points and (**B**) box plots of the SIMS $\delta^{34}S$ values measured in this study. Numbers in parentheses representing the amount of data analyzed by SIMS in this study. Red dash line representing the Cryogenian seawater $\delta^{34}S_{sulfate}$ value based on anhydrite analysis (Gorjan et al., 2000). Interpretations of the $\delta^{34}S$ values of each data set listed on the right-hand side. Abbreviations: MSR: microbial sulfate reduction; TSR: thermochemical sulfate reduction. TSA: Tiesi'ao Formation; DTP: Datangpo Formation. For corresponding petrographic context of all the plotted data, see online Appendices 2–6.

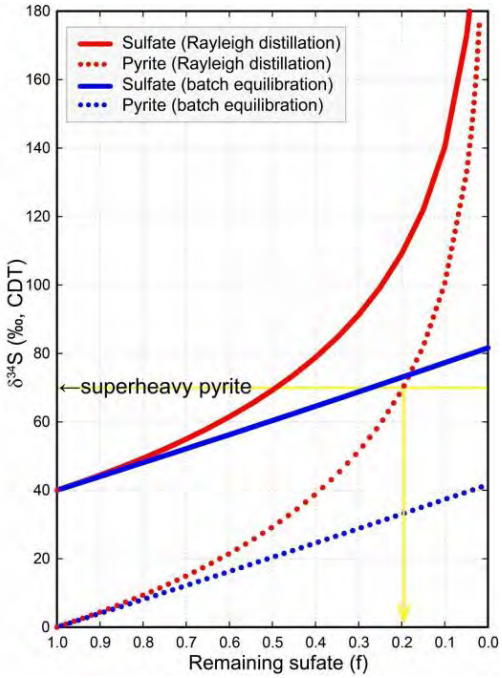

Figure 24. Models of $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{sulfide}$ evolution during Rayleigh distillation (red) and batch equilibration (blue) for precipitation of pyrite from sulfate (initial $\delta^{34}S$ = 40‰) in a system closed to externally-derived fluids or other sources of sulfur. Equations used in calculation are from: (Canfield, 2001a; Canfield, 2001b). Yellow arrow shows the condition when $\delta^{34}S_{sulfide}$ value achieves +70‰. See the main text for detailed discussion.

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