Abstract: The formation mechanisms of sedimentary pyrite nodules determined by trace element and sulfur isotope microanalysis

Redox sensitive trace elements in pyrite, including nodules, are increasingly used to infer the chemical conditions of ancient oceans—but considerable uncertainty remains regarding the mechanism and timing of nodule formation. Resolving these uncertainties is important because pyrite nodules must form in connection with the overlying water column, rather than during late diagenesis, to reflect the composition of the global ocean. Existing models for pyrite nodule formation have been specific to pyrite textures from individual sites, and we lack a unified model that can explain the compositional and textural diversity observed in nodules from different localities. In this study we examine ten pyrite nodules from several geological periods (Neoarchean to Carboniferous) using in situ LA-ICP-MS and SHRIMP-SI analyses. We present transects of spot analyses of trace elements (As, Ag, Cu, Co, Ni, Sb and Se) and S isotope ratios for each nodule. The pyrite nodules can be classified according to three main categories: those with (1) little to no trace element or isotopic zonation of the nodule from core to margin, (2) strong zonation from core to margin, and (3) minor zonation near the core but more significant zonation near the margin of the nodule. We further illustrate this zonation with a NanoSIMS element map from an additional pyrite nodule. These results are interpreted to indicate nodule formation along a spectrum between two end-member mechanisms. We suggest that the absence of trace element or isotopic zonation reflects nodule growth by a pathway that is analogous to the pervasive growth mechanism for carbonate nodules. This model involves the production of many nucleation sites that are evenly distributed within the volume that the nodule eventually occupies. Consequently, this mechanism results in a chemically homogenous nodule. Pyrites formed this way are suitable for paleoceanographic reconstruction. The other end-member mechanism is analogous to the concentric growth model for carbonate concretions. In this scenario, the core of the nodule forms first and is followed by the addition of concentric layers—each with a progressively different trace element content and $\delta^{34}S$ signature as diagenesis progresses. Despite having limited utility for reconstructing ancient seawater, these late forming nodules may track the evolving availability of bioessential trace elements for the subsurface biosphere with important implications for global biogeochemical cycles. Spatial trends in trace elements and S isotopes thus speak to the mechanisms of pyrite nodule formation and provide a framework for evaluating nodule suitability for a range of paleoenvironmental studies.

1. INTRODUCTION

Pyrite (FeS_2) nodules are ovoid to spherical, occasionally irregular masses of pyrite (±matrix) that are common in many carbonaceous siltstones and shales. Bioessential and redox sensitive trace metals are incorporated into pyrite, either by direct substitution into the pyrite crystal lattice (e.g., Ni^{2+}) or as metal sulfide inclusions (e.g., ZnS), and thus pyrite nodules may reflect local abundance of these metals during formation; which, with other data could help reconstruct the evolution of life and the environment on Earth. For example, in-situ pyrite compositions, focusing on non-nodular pyrite, are now used as proxies for trace element abundance in the oceans through geological time, which has been argued to ultimately be a reflection of atmospheric O_2 levels (Large et al., 2014, 2015; Gregory et al., 2015a, b; Gregory et al., 2017). Critically, however, we lack a detailed understanding of the timing and mechanism of pyrite nodule formation—limiting their utility in reconstruction of seawater composition. Given the potential for subsequent diagenetic pyrite overgrowths, a lack of understanding of macro-pyrite formation and its connection to the water column restricts current paleo-ocean chemistry studies to fine grained pyrites that may have formed in the water column or very early during diagenesis.

Inferring paleoenvironmental conditions from the trace element content of pyrite nodules requires that the nodules formed in sediment pore waters that were open with respect to the overlying water column. This assumption is incompatible with a number of different conceptual models proposed for the formation of pyrite nodules at individual sample sites. These models include replacement of early FeS mineral nodules formed during anaerobic oxidation of methane (van Dongen et al., 2007), remobilization of early pyrite or precursor Fe sulfide during later diagenesis (Kakegawa et al., 1998; Marin-Carbonne et al. 2014), remobilization or replacement of early Fe(hydr)oxide nodules (Peiffer et al., 2015), and formation of pyrite within an organic matrix (Schieber, 2002). However, none of these models examine the variability observed among nodules from different sites or attempts to define a comprehensive view of formation that accommodates the observed variability. Such variability should clarify the different formation mechanisms and their corresponding paleoenvironmental utility. In this study we have taken a step toward a more complete understanding of pyrite nodule formation by using sensitive high-resolution ion microprobe-stable isotopes (SHRIMP-SI) in combination with laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) to examine the in-situ S isotope signatures and trace element contents, respectively, from ten pyrite nodules that range in age from Neoarchean to Carboniferous. This work is supplemented with a NanoSIMS trace element map of an additional small nodule. These data will enable development of protocols to discriminate against analyses of pyrite that formed late during diagenesis or metamorphism and therefore are not representative of contemporaneous ocean chemistry and its early modification in shallow pore waters. At the same time, we can identify possible archives of later processes and conditions, such as trace element bioavailability in the subsurface biosphere.

2. BACKGROUND

The reaction pathway(s) involved in sedimentary pyrite formation have been investigated extensively. Herein, we provide a brief summary of the existing literature, but interested readers are referred to Rickard (2012) for a more exhaustive review.

There are two important aspects that must be investigated to understand the formation of sedimentary pyrite: the nucleation of pyrite and mineral growth (Rickard, 2012). Pyrite formation depends on three main mechanisms that are sensitive to the concentrations and sources of S and the pH of the solution:

1) $H_2S + FeS \rightarrow FeS_{2(pyrite)} + H_2$ (Rickard, 1997; Rickard and Luther, 1997)

2) $FeS + S_5^{2-} \rightarrow FeS_2 + S_4^{2-}$ (Rickard 1975; Rickard, 2012)

3) Sulfidation and replacement of Fe(hydr)oxides (Peiffer et al., 2015; mechanism is complex and potentially variable)

However, it should be noted that reaction one is probably somewhat different than written and slight oxidation of the FeS is needed for reaction at the following rates and may follow a different pathway (Benning et al., 2000; Swanner et al., *in press*). With that caveat some form of all reactions represented by here are likely to occur to some extent in natural systems. Which reaction predominates and the rate of reaction depends on pH, with higher reaction rates progressing through reaction 1 at lower pH (<8). When reaction 1 predominates, pH levels that favor more H_2S (relative to HS^- and S^{2-}) increase the rate of reaction, with calculated reaction rates of 3×10^{-4} to 3×10^{1} µmol $FeS_{2(pyrite)}$ per gram dry weight per year ($gdw^{-1}a^{-1}$) at pH 8 compared to 1.5×10^{-3} to 1.5×10^{2} µmol $FeS_{2(pyrite)}$ $gdw^{-1}a^{-1}$ at pH 7 (Rickard and Morse, 2005). As pH increases above 9, the H_2S concentration approaches 0 and the polysulfide pathway (reaction 2) predominates. However, reaction rates are still far below (10^{-2} to 10^{-11} µmol $FeS_{2(pyrite)}$ $gdw^{-1}a^{-1}$) those for the H_2S reaction mechanism unless an additional source of S(0) is available. It should be stressed that these are abiotic rates and Canfield et al., (1998) have presented isotopic evidence that both mechanisms proceed at similar rates when biologically mediated but much faster (10^4-10^5 times faster) than abiotic rates.

Direct nucleation of pyrite requires high levels of super saturation and/or the catalytic effects of trace components or the presence of active surfaces. However, in the presence of pyrite seed crystals, additional pyrite will precipitate more readily and at a lower concentration of reactants (Harmandas et al., 1998). The level of necessary super saturation of pyrite can similarly be decreased by the addition of trace elements, for instance, the presence of Ni has been shown to dramatically decrease the time taken for pyrite formation (Morin et al., 2017). However, this may be less due to the addition of the Ni and more due to the reaction mechanism chosen by Morin et al., (2017) (Fe^{3+} as a reactant) as Swanner et al., (*in press*) did not observe the same increased reaction rate using a Machinawite reactant. Additionally, other materials have been shown to act as nucleation sites for pyrite (e.g., Mackinawite, Rickard and Luther, 1997). Organic matter or cell material is also likely to act as nucleation sites for pyrite formation. While this has not been specifically tested for pyrite yet, live and dead sulfate-reducing bacteria have been found to aid nucleation and growth of mackinawite (FeS) (Picard et al., 2017), and it seems plausible that there will be a similar effect on the nucleation of pyrite.

Due to the occasional confusion in the literature, it is important to briefly discuss mackinawite and its role as a precursor to pyrite formation. Mackinawite is a popular reagent for forming pyrite in laboratory settings and is used commonly as an intermediate when writing balanced equations for pyrite formation. However, it is not necessarily formed and is often absent in modern marine environments (Rickard, 2012). It is not clear whether Fe is sufficiently high in most modern environments for mackinawite formation, in part because XRD tests for the presence of mackinawite are not common in sediment studies. Instead, acid volatile sulfur is analyzed, which yields the total amount of S that can be released during reaction of sediment with HCl (Berner, 1964). This extraction may include mackinawite but may also include a host of other species (Rickard, 2012), including dissolved FeS species. It should be noted that during other periods in Earth history, when Fe levels in the ocean were higher, mackinawite precipitation could have been more important. Importantly, however, even then pyrite does not replace mackinawite. Instead, the mackinawite dissolves to form $FeS_{(aq)}$ which reacts to form pyrite (Rickard, 2012).

Sulfidation and replacement of Fe (hydr)oxides (e.g. ferrihydrite, goethite, lepidocrocite) by pyrite is another, related, possible mechanism of pyrite formation (Peiffer et al., 2015). In this mechanism Fe(III) is reduced to Fe(II) and reacts with polysulfide complexes to form pyrite, sometimes via a FeS precursor (Peiffer et al., 2015). This mechanism could aid in nodule formation in two ways. First, polysufide species have been found to adsorb onto the surface of pre-existing Fe (hydr)oxide species and thus FeS precipitation can occur at or very near the location of the Fe (hydr)oxides species thus, though not replaced by solid phase transformation (Peiffer et al., 2015), a Fe (hydr)oxide nodule could be effectively replaced by pyrite. Alternatively, Peiffer et al., (2015) showed that diagenetic reactions related to reduction of Fe (hydr)oxides can produced $Fe(II)_{(aq)}$, this could then diffuse to areas with either seed crystals of pyrite or a higher concentration of H_2S or polysulfide complexes and react with them to form a pyrite nodule.

Although several models for pyrite nodule formation are described in the literature, there is not a single model that is consistent with all, or even most, of the nodules observed in nature. For example, Rickard (2012) described pyrite nodules that, upon etching, exhibit clear radiating, elongate crystals that formed by growth extending into regions that are supersaturated but not enough to initiate nucleation. As the crystal grows into the supersaturated fluids more pyrite nucleates onto the pyrite needle growing the needle. Alternatively, pyrite nodules commonly consist of numerous closely packed fine- to coarse-grained, equigranular, anhedral crystals. This pyrite texture cannot be explained by the model presented in Rickard (2012). Pyrite nodules in the Archean McRae Shale were interpreted to have formed by dissolution of early Fe sulfide generations in the surrounding shale (such as mackinawite or greigite) followed by migration of the Fe and S to the nodule site (Kakegawa et al., 1998). This mode of formation would have been favored by times when Fe in the ocean was sufficiently high to allow for mackinawite precipitation, such as during the Archean. However, this possibility implies that the sedimentary rock surrounding the nodule should be depleted in pyrite, and while this is sometimes the case, a pyrite poor halo around nodules is often not present (Gregory et al., 2015b, Chappaz et al., 2014; Gregory et al., 2016; Steadman et al., 2015), even in the Archean where Fe levels allow for the prolonged stability of metastable mackinawite. Furthermore, when this halo is present the degree and timing of mackinawite dissolution is not clear and the reaction of mackinawite can be very rapid (< 50 hrs for complete conversion of mackinawite to pyrite in the presence of Ni; Morin et al., 2017). As such, pyrite formed via this mechanism would still reflect the trace element content of the pore water early in the sediments.

Organic enrichments and secretions from organisms have been suggested as favoring pyrite nodule formation because organic enrichments provide a good medium for the growth of S-reducing bacteria (Schieber, 2002). However, if localized organic enrichments were the only requirement for pyrite nodule formation, we would expect to see pyrite layers rather than nodules in organic-rich horizons. Thus, fundamental questions regarding the formation mechanisms of the diverse pyrites observed in the rock record, including nodules, remain unanswered.

In this study we draw parallels with formation mechanisms for other types of nodules and concretions, specifically the calcareous variety. Morphological similarities exist between several types of calcareous concretions (spherical, lenticular, and bread loaf; Seilacher, 2001) and pyrite nodules. In this study only lenticular pyrite nodules are discussed, though similar growth models describe below will apply to spherical and bread loaf pyrite nodules as well. The pyrite disks, which form later, after compaction (Seilacher, 2001) will not be described here. Throughout the paper we will be referring to the models of carbonate nodule formation proposed by Raiswell and Fisher, (2000). These authors proposed two end member mechanisms of carbonate nodule formation: a pervasive growth mechanism and a concentric growth mechanism. The pervasive growth mechanism proposes that the entire volume of the eventual nodule has nucleation of carbonate throughout it and those grains grow together to form the nodule. The concentric growth mechanism has nucleation of carbonate first in the center of the eventual nodule with later carbonate nucleated around the margins of the growing nodule as it grows (Raiswell and Fisher, 2000). Here we discuss the possibility that pyrite nodules forming by one of these ends members or a combination of both of them.

3. METHODS

To address some of the many important unknowns surrounding pyrite nodule formation, we undertook microanalyses of diverse pyrite nodules that span the geologic timescale. Our ten representative pyrite nodules were selected from ten different carbonaceous shale units from diverse geographic areas and geologic ages, ranging from the Neoarchean to Carboniferous (see electronic Appendix I for samples details). A total of 95 new LA-ICPMS spot analyses and 62 SHRIMP-SI S isotope analyses were completed in the study. These analyses were combined with

31 published in-situ S isotope analyses (Gregory et al., 2015b; Gregory et al., 2016). An additional nodule from the Leicester pyrite member (Formolo and Lyons, 2007) was analyzed using NanoSIMS.

3.1. LA-ICPMS analyses

Trace element analysis of sedimentary pyrite was performed using LA-ICPMS at the Centre for Ore Deposits and Earth Sciences, University of Tasmania. Specifically, we used a 193 nm ArF Excimer ATL Atlex ILR laser coupled with an Agilent 7700 ICP-MS. The system is equipped with a custom-made constant-geometry Laurin Technic ablation chamber designed to hold up to 20 1-inch size mounts. Pyrite was sampled with a 30 µm spot size using a laser pulse rate of 5 Hz and laser beam fluence of ~ 2 J/cm^2 at the sample surface. Ablation occurred in an atmosphere of pure He flowing at a rate of 0.8 l/min. Immediately following the ablation point within the cell, the He carrier gas was mixed with Ar (0.85 l/min) for improved efficiency of aerosol transport. The ICP-MS instruments were optimized to maximize sensitivity on mid- to high-mass isotopes (in the range 80–240 amu). Further details on the LA-ICPMS method can be found in Large et al. (2014).

Pyrite nodules contained abundant inclusions of material that make up the host shale (matrix), challenging our ability to measure pure pyrite. Therefore, mixtures of pyrite and matrix were analyzed by LA-ICP-MS, and the composition of pyrite was estimated using an algorithm based on linear regression, similar to the method described in Gregory et al., (2017). The algorithm requires the following steps: segmentation of signal relative to time of ablation, preliminary calculation of pyrite and matrix composition and, recalculation of compositions to 100% sum of chalcophile elements and oxides for lithophile elements followed by plotting of the recalculated data versus S and using linear regression equations relative to S content to calculate the ideal, no inclusion, trace element concentrations of the pyrite. The preliminary composition was estimated using the stoichiometric Fe content of pyrite as an internal standard and calibration standards STDGL2b2 for chalcophile elements (^{65}Cu, ^{66}Zn, ^{75}As, ^{77}Se, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{195}Pt, ^{197}Au, ^{202}Hg, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{209}Bi; Danyushevsky et al., 2011), GSD-1G for lithophile elements (^{24}Mg, ^{27}Al, ^{29}Si, ^{43}Ca, ^{49}Ti, ^{51}V, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{90}Zr, ^{157}Gd, ^{178}Hf, ^{181}Ta, ^{182}W, ^{232}Th, ^{238}U; Guillong et al., 2005) and stoichiometric Peruvian pyrite for sulfur (^{34}S; Gilbert et al., 2014a,b). The final composition of pyrite was estimated by calculation of least squares regression through the data and the origin and projection to S values content estimated to produce a 100% sum of the chalcophile elements.

3.2. Scanning Electron Microscope

Backscattered scanning electron microscope (SEM) images were taken of the margins and centers of the three representative pyrite nodules (Fig. 1-3). The SEM backscatter images in Fig. 1 and 3 were taken at the University of California, Riverside using a NovaNanoSEM 450 in CFAMM while the SEM backscatter images in Fig. 2 were taken in the Department of Earth Sciences at the University of Toronto using a JEOL JSM-6610LV SEM.

3.3. SHRIMP-SI analyses

In-situ S isotope analyses were completed using the sensitive high resolution microprobe (SHRIMP SI) at the Australian National University. A spot size of ~20μm was used, and 5-13 analyses were conducted as a linear transect across the nodule. In the case of particularly large nodules, analyses were carried out from the center to the edge of the nodule to the extent that the sample holder size would allow. The exact spots of the S isotope analyses were then analyzed for trace element abundance using LA-ICPMS at the University of Tasmania. Arsenic, Sb, Ag, Ni, Se, Cu and Co were analyzed because these elements are among those commonly used in studies of paleo-ocean chemistry (Large et al., 2014, 2015; Gregory et al., 2015b), and they are also the elements most likely to be held predominantly within the crystal lattice of the pyrite (Gregory et al., 2015a). These data were generated using a 35μm beam size.

3.4. NanoSIMS mapping

NanoSIMS images were collected at the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory using a Cameca NanoSIMS 50L. Prior to the analyses, samples were coated with 10 nm of high purity Ir to improve conductivity. All images reported here were collected as two frames consisting of 256 × 256 pixels collected with a dwell time of 13.5 ms $pixel^{-1}$. NMR magnetic field regulation was employed in all cases. Analyses were conducted in two steps. Negative secondary ion images were collected prior to positive secondary polarity ion images using a 16 keV Cs^{+} primary ion beam. Secondary ions were accelerated to 8 keV and were collected using electron multipliers (EM)s. $^{75}As^{-}$, $^{78}Se^{-}$, and $^{80}Se^{-}$ peaks were m/z calibrated using GaAs and SeS suspensions that had been dried onto a Si wafer. Prior to image analysis, image areas were pre-sputtered with about 2×10^{16} ions cm^{-2} Cs^{+}. Ion images of $^{12}C_2^{-}$, $^{12}C^{14}N^{-}$, $^{28}Si^{-}$, $^{34}S^{-}$, $^{75}As^{-}$, $^{78}Se^{-}$, and $^{80}Se^{-}$ were collected using a 2pA, primary beam that had a diameter of approximately 120 nm. After imaging of negative-polarity secondary ions, instrument polarity was switched to acquire positive-secondary ions. EMs were used to simultaneously monitor $^{58}Ni^{+}$, $^{63}Cu^{+}$, $^{66}Zn^{+}$, $^{68}Zn^{+}$, and $^{133}Cs^{+}$ intensities. A ~ 10 pA, 16 keV O^{-} primary beam was employed with a diameter estimated to be about 300 nm. Previously imaged areas were pre-sputtered with about 2×10^{16} ions cm^{-2} O^{-}. A short-duration (5 ms $pixel^{-1}$) Cs^{+} image was acquired in order to more closely align images taken in opposite polarities prior to imaging. The Zn NanoSIMS data was judged to be unreliable as evidenced by an erroneous $^{66}Zn/^{68}Zn$ ratio and won't be considered further here. Analyses of the images were performed using OpenMIMS and ImageJ[43]. Images were deadtime corrected on a pixel × pixel basis and regions of interest (ROIs) areas were selected based on nodule morphology and counts per area for the isotope of interest were summed and expressed as isotope ratios with respect to ^{34}S or ^{56}Fe (Table 1). Uncertainties were estimated based on counting statistics.

4. RESULTS

4.1. LA-ICPMS and SHRIMP spot analyses

Three main trends in trace element abundance and $\delta^{34}S$ values were identified in the nodules analyzed in this study. The first shows minimal variation in trace element concentrations (usually < 0.5 of the log[concentration of the element in individual analysis/mean of the elements in the nodule] and $\delta^{34}S$ compositions (vary by less than 3‰) from center to the nodule margin (seen in three of the investigated nodules; Fig. 1 and supplementary materials), where margin refers to the outer zone of the nodule that is texturally and/or chemically different from the central part of the pyrite nodule. The second trend is characterized by a general zonation (systematic change from center of nodule to nodule margin) of trace elements (for several elements log[concentration of the element in individual analysis/mean of the elements in the nodule] is > 1.0) and variable $\delta^{34}S$ from center to margin, though usually higher on the margin (seen in three of the investigated nodules; Fig. 2 and supplementary materials) of the pyrite nodule. However, in the sample in Fig. 2 the trend is somewhat variable with the analysis closest to the center of the nodule having relatively low trace element compositions (similar to the nodule margins). The third trend has minor trace element zonation through most of the nodule but some variation in trace elements and/or $\delta^{34}S$ on the margin of the nodule (log[concentration of the element in individual analysis/mean of the elements in the nodule] is > 0 in center and < 0 on the margin of the nodule. Zonation of S isotopes from the center to margin of the nodule is more pronounced but variable, with a general trend of a few ‰ (seen in four of the investigated nodules; Fig. 3 and supplementary materials). Deviation of trace elements in each of these trends (e.g. S isotopes in Fig. 3) from the general trends is likely due to an underlying zonation in the microcrystals that make up each of the pyrite nodules, analogous to the variation of individual carbonate grains observed by Raiswell and Fisher, (2000). However, testing of this underlying zonation in the microcrystals is beyond the scope of the current study. Each of the nodules investigated here are ellipsoidal in shape, the images in Fig. 1 to 3 may appear irregular because they were taken after analysis, which required cutting and mounting in composite mount for SHRIMP analysis. Additionally, the sample shown in Fig. 1 was microdrilled for conventional S-isotope analysis.

Pyrite textures can give some indication of which of these three patterns is most likely. The non-zoned nodules and those zoned only on the margins of the nodule tend to be made up of fine-grained pyrite (< 20 μm diameter grains) and contain less matrix material, while the extensively zoned nodules tend to be composed of larger pyrite crystals (> 20 μm) and contain a higher matrix component. Representative examples of the three main varieties of pyrite nodule texture, trace element content and $\delta^{34}S$ pattern identified in this study are given in Figures 1, 2, and 3.

The pyrite nodule in Fig. 1 is from the 2629±6 million-year-old (Ma) Jeerinah Formation, Western Australia (Trendall et al., 2004). Trace element content (Co, Ni, Sb, As, Cu, Se and Ag) and $\delta^{34}S$ values change little across the nodule, although $\delta^{34}S$ increases slightly (<2 ‰) toward the nodule margin. The nodule is composed of many small (10-30 μm diameter), interlocked pyrite grains (Fig. 1).

The nodule in Fig. 2 is from the 1330±30 Ma Zigazino-Komarovo Formation, Yurmata Supergroup (Kuznetsov et al., 2008), Ural Mountains, Russia. In contrast to the nodule in Fig. 1, this nodule exhibits a clear decrease, from its center outward, in Ni (maximum 1875 ppm in the core, minimum 140 ppm in the nodule margin), Co (maximum 406 ppm in the core, minimum 3.5 ppm in the nodule margin), and Sb (maximum 9.5 ppm in the core, minimum 0.35 ppm in the nodule margin), and a radial increase in Cu (minimum 170 ppm, maximum 8047 ppm) and $\delta^{34}S$ values (-23.16 ‰ near center to -10.86 ‰ in the margin; the drop of $\delta^{34}S$ value at the edge of the nodule may reflect the presence of a later fluid).

Figure 3 shows a fine-grained pyrite nodule from the 499.3±0.9 Ma Que River Shale, Tasmania, Australia (Mortenson et al., 2015). Trace elements content of the nodule is relatively homogenous within the core of the nodule; however, there is a sharp decrease in Co, Sb, and As (averages of 285 ppm, 376 ppm and 500 ppm in the core for Co, Sb and As, respectively, versus averages of 116 ppm, 152 ppm and 237 ppm in the nodule margin for Co, Sb and As, respectively). These trends are accompanied by a slight, though erratic, general increase in $\delta^{34}S$ from the center of the nodule into the margin (35.33 ‰ in the center to 38.36 ‰ on the edge).

4.2. NanoSIMS map

NanoSIMS ion maps were acquired on a small nodule from the Leicester pyrite member (Baird, 1986; Formolo and Lyons, 2007) to provide a high-resolution example of the textures and trace element distributions across the transition of a pyrite nodule formed first via the pervasive growth and then via the concentric growth mechanisms (Fig. 4). Both early, overgrown framboids and later more euhedral pyrite can be identified on the left and right sides of the image respectively, for the CN^- and S^- maps (Fig. 5). Due to a lack of standard materials for the elements of interest the data is semi-quantitative and given in counts per pixel of the different parts of the nano-SIMS map. The earlier formed interior of the nodule also has higher Ni^{68}/Fe^{56}, Cu^{63}/Fe^{56}, $Se(Se^{78} + Se^{80})/S^{34}$, and As^{75}/S^{34}, ($5.78x10^{-3}$, $3.84x10^{-4}$, $1.11x10^{-4}$, and $5.58x10^{-3}$ average counts per pixel respectively) compared to the more euhedral margin of the nodule ($5.31x10^{-3}$, $3.17x10^{-4}$, $1.91x10^{-5}$, and $4.45x10^{-5}$ average counts per pixel respectively; Table 1).

5. DISCUSSION

The generally low amount of variation in both trace elements and $\delta^{34}S$ across the pyrite nodule in Fig. 1 are interpreted to reflect a relatively rapid rate of formation and high level of nucleation in pore waters highly supersaturated in Fe and H_2S. This observation, coupled with relatively low amounts of matrix inclusions, indicates that the nodule in Fig. 1 formed predominantly during early diagenesis, when the bottom muds still had very high porosity (>90% in some cases; Nafe and Drake, 1961) and the pore waters were strongly connected to the overlying water column.

Larger variations in trace element concentrations (see supplementary data) and S isotope compositions, evident in Fig. 2, are indicative of formation in an environment relatively isolated from the water column. As diagenesis progresses, pore fluid compositions evolve during diagenetic processing, including depletion of some trace elements through precipitation in earlier formed pyrite. Sulfate reducing bacteria preferentially select lighter S isotopes; therefore, in a closed or highly isolated system, the residual sulfate pool and corresponding later-formed sulfide are depleted in the light isotope, ^{32}S, yielding a progressively heavier isotopic signature in later formed pyrite (Ohmoto, 1992). This relatively coarse-grained nodule (Fig. 2) also has a relatively large number of inclusions, further suggesting that this nodule formed later than the example in Fig. 1. As pore space decreases due to compaction with deeper burial, the number of inclusions of host sediments is expected to increase (i.e. there is less pore space at deeper depths for the growing pyrite to fill). Moreover, the coarser grain size indicates a lower degree of super saturation that limits the number of nucleation sites (Rickard, 2012 and references therein) for pyrite formation and lowers the rate of growth.

The generally low degree of trace element variation in the center of the pyrite nodule in Fig. 3 (sample 79990) and the fine grain size (10-20 μm diameter) are indicative of a high degree of super saturation and the presence of many nucleation points. The decrease in trace element content and increase of $\delta^{34}S$ towards the nodule margins suggests that the nucleation sites were clustered at the center of the nodule due to a higher degree of super saturation. Thus the nodule center better captures more of the early trace element and S isotope signature. During later diagenesis, the empty space between the nucleation sites was filled by pyrite, resulting in slightly lower trace element contents and higher $\delta^{34}S$ values in the margin.

5.1. Pathways of pyrite nodule formation

Two main mechanisms have been proposed for the formation of *carbonate* nodules (Raiswell and Fisher, 2000): (1) the concentric growth model in which carbonate is added to an earlier core in an outward succession of layers and (2) the pervasive growth model in which carbonate precipitates at a large number of nucleation sites dispersed throughout the nodule and eventually grow together. Based on our data, we propose that similar mechanisms are involved with the formation of pyrite nodules (Fig. 4). We further suggest that the method of nodule formation at a particular site can be diagnosed by the in-situ trace element and S isotope analyses described here.

If our analogy is correct, there are three different ways in which pyrite nodules can form. The first is a rapid precipitation of the entire nodule building from a number of nucleation sites. In this scenario, we would expect an absence of significant $\delta^{34}S$ (>3 ‰ to account for minor local zonation) or trace element zoning of the nodule. The lack of zonation and a relatively low amount (e.g. Fig. 1 compared to Fig 2) of matrix inclusions suggest that the nodule formed early during sedimentation when the pore waters were still connected with the overlying water column and there was a large amount of pore space to accommodate the growing nodule (Fig. 1). Alternatively, nodules may form progressively deeper in the sediments where the pore waters are not well connected to the overlying water column and result in pyrite with diagnostic trace element and S isotope signatures. Specifically, this scenario results in a clear zoning of $\delta^{34}S$ and trace element compositions (Fig. 2). Nodules formed in this fashion also have relatively more shale matrix inclusions as they formed when there was less pore space to accommodate the growing nodule. The nodules tend to be made up of larger crystals (up to hundreds of µms, Fig. 2 compared to tens of µms, Fig. 1) and have more erratic trace element and S isotope chemistry. The erratic nature of the trace element and $\delta^{34}S$ trends are likely due to local chemical variations within the individual crystals and are dependent upon where in the crystal the analytical spots were put; however, confirmation of this will require further analyses. The third mode of formation is a combination of the first two (though in our samples they are more similar to the pervasive growth mechanism). These nodules initiated with rapid formation, as indicated by an initial lack of clear trace element and $\delta^{34}S$ zonation, followed by additional pyrite growth that exhibits zonation in the margins of the nodule (Fig. 3), note in these samples trace element and $\delta^{34}S$ zonation do not necessarily occur at the same time. Extreme examples of this third mechanism can be found in Archean sediments due to the mixing of different sulfur sources (seawater sulfate and elemental S) with markedly different mass independent S isotope properties (Gregory et al., 2015b). Other studies have similarly shown that this combined process yields S-isotope, Fe-isotope and trace element signatures for the nodule centers that differ significantly from those of the nodule margins (Marin-Carbonne et al. 2014). There are still other relatively rare forms of pyrite that are not explained by these three main mechanisms, such as those with reversed S isotope zonation (i.e., lighter S isotopes on the outside of the nodule; Prosser et al., 1994), which may require late addition of S.

In this study, an additional question arises from the pervasive growth method: how are the super saturation requirements for pyrite formation met within these highly localized areas? The answer is not simple and is likely the product of a number of different factors. Pyrite precipitation has been linked to the presence and abundance of S-reducing bacteria (Raiswell et al., 1993; Schoonen, 2004) both to effectively generate the required H_2S and as a potential substrate for sulfide nucleation (Picard et al., 2017). Therefore, it is reasonable that localized conditions that are optimal for S-reducing bacteria are needed for the formation of pyrite nodules. This proposition is similar to the mechanism involving organic secretions proposed by Schieber (2002); however, it allows for other possibilities. For example, higher populations of sulfate-reducing bacteria could simply reflect conditions more amenable to their growth. The degree to which these conditions are present then dictate whether the nodule forms predominantly via the concentric growth model or the pervasive growth model. In other words, if a large volume (i.e. the full volume of the final nodule) is populated by sulfate reducing bacteria this would result in both substrates for nucleation of pyrite throughout the nodule and high local production of H_2S throughout the future volume of the nodule. This results in the area immediately around the localized points of high H_2S production being where pyrite will form and then once those cores are formed later pyrite can be continuously added to the previously formed pyrite.

The trigger for nucleation may also be independent of localized sources of S and Fe. For example, Rickard and Luther (2007) showed that $FeS_{(aq)}$ complexes can simultaneously maintain micromolar concentrations of Fe and S in solution. Local changes in fluid chemistry (pH, microbial activity) could destabilize these complexes, resulting in nucleation of pyrite. Additionally, in abiotic pyrite formation (via Reaction 1), a decrease in pH from 8 to 7 enhances the reaction rate of pyrite precipitation through an increase in the concentration of H_2S. Unfortunately, the roles of pH and localized microbial populations are difficult to fingerprint independently in the rock record.

In some cases, there may be a sedimentalogical basis for initial nodule formation. Pyrite framboids form in the water column in euxinic environments (Rickard, 2012 and references therein), upon which they settle to the bottom. If they are concentrated into groups via bottom currents this could allow for the concentration of the initial framboids without the need for an anomalously concentrated area of pyrite nucleation sites. The later overgrowth of water column derived pyrite framboids has been observed in Green Lake (Suits and Wilkin, 1998) so it is conceivable that this is a pathway for pyrite nodule formation. Importantly, this mechanism would better preserve a direct water column trace element signature as the pyrite formed in the water column.

Recent work has suggested that trace elements may be important factors in rates of pyrite formation. Morin et al. (2017) showed, using reactions of $Fe(III)_{(aq)}$, that the presence of Ni in abiotic pyrite formation experiments accelerated the nucleation rate of pyrite by a factor of five and Ni concentration in solution decreased by a factor of 2000 from the start to end of the experiment. While the exact reaction mechanism used by Morin et al., (2017) is not likely to have been prevalent for pyrite formation in the samples in this study (from organic rich shales) our data suggest that there may be some correlation between type of nodule formation and Ni concentration. The lowest median Ni content (18.4 ppm, sample HP8-319.8, electronic appendix) is found in a nodule that presumably formed via the concentric growth mechanism. Additionally, the nodule in Fig. 2 that also formed via the concentric growth mechanism exhibits a significant decrease across the nodule (a high of 1875 ppm near center to a low of 140 ppm in the nodule margin). However, Ni concentration alone is not sufficient to explain which mechanism will be favored. Even though it decreases across the nodule, Ni concentration in the nodule in Fig. 2 is still among the highest of the pyrite nodules investigated. Therefore, it is likely a combination of trace element content, population of sulfate reducing bacteria, and availability of reactive Fe that dictates which pyrite nodule formation mechanism dominates.

The pyrite in Fig. 6, a sample not analyzed here, is interpreted to be a nodule that formed via the pervasive growth mechanism but without the availability of H_2S and/or Fe needed to completely infill the nodule with pyrite. Note that most of the pyrite is framboidal, which is typical for pyrite precipitating from highly saturated solutions. We suggest that most nodules that formed via the pervasive growth mechanism start as a cluster of framboids that then grow together (Wacey et al., 2014; Fig.5). Chemical conditions that result in pyrite nucleation tend to favor a localized 'cloud' of framboids or microcrystals. This localization, as discussed above, may be due to a higher concentration of organic matter or the presence of conditions that are more favorable for sulfate reducing bacteria, local pH variation, or pore water enrichments in trace elements that favor pyrite formation (such as Ni). Once nucleation has commenced (marked by early framboids), either the concentric growth or pervasive growth mechanisms can follow. If the pore waters are still in strong exchange with the water column, no significant zonation will be observed; however, with deeper burial and slower formation, stronger zonation patterns will be evident on each successive layer of pyrite on the nodule due to the changing composition of the pore fluids.

The transition from an early, "framboid cloud" to pyrite growth in the nodule margin, as proposed for the nodules that form by the pervasive growth mechanism followed by the concentric growth mechanism, is further demonstrated by the NanoSIMS map of the small nodule from the Leicester pyrite member (Fig. 5). Initial pyrite framboids can be identified in the CN panels of Fig. 5 as dark round objects (left side of image) followed by more euhedral crystal growth on the margin (right side of image). The CN panel also shows that organic matter was present between the pyrite framboids and later more euhedral crystals in similar amounts, suggesting that the two parts of the eventual nodule were finally cemented at a similar time even though the framboids and euhedral crystals presumably formed at different times. This is consistent with nanoSIMS data presented by Wacey et al., (2015) that showed early pyrite framboids within pyrite nodules. It is not clear when exactly the latest pyrite phase precipitated but because it appears to be after the slow growth of the more euhederal pyrite and the Leicester pyrite member has not experienced high grade metamorphism, thus it is expected that the late pyrite formed during diagenesis. Furthermore, Se, Cu, As, and Ni show enrichments in the center, early part of the nodule which is analogous with the trace element variation for the larger nodule shown in Fig. 2 and in the electronic appendix 2.

The presence of Fe(hydr)oxides in the host sediments may affect pyrite nodule formation. If pyrite replaces pre-existing Fe(hydr)oxide nodules (as described in the introduction) it could be an additional nodule formation mechanism. If this were the case it is expected that the margins of the Fe(hydr)oxide nodule would react first, with progressive transformation to pyrite towards the center. This does not appear to have occurred in the nodules investigated in this study because if this were the case we would expect an increase in $\delta^{34}S$ from the margin to the center. However, it is possible that this mechanism is present in other samples. If this mechanism were to occur, it is expected that the trace element chemistry of the resultant pyrite nodule would be dominated by elements that adsorb or are incorporated into Fe(hydr)oxides. Another way the presence of Fe(hydr)oxides in the sediments could affect pyrite nodule formation is that they could be a source for Fe(II) to infill later pyrite between early pyrite and build upon the early phases of the nodule. If this were the case it is expected that trace elements related to Fe(hydr)oxides would remain high in the growing pyrite through the nodule margin.

5.2. Implications for paleoceanographic reconstruction

The trace element content of pyrite is now widely used in reconstructions of ancient ocean chemistry (Large et al., 2014; Large et al., 2015a; Large et al., 2015b; Gregory et al., 2015b; Gregory et al., 2017). That the fidelity of the approach seems to extend beyond low metamorphic-grade sedimentary rocks to mid greenschist facies archives (Large et al., 2007) may elevate its value relative to whole-rock trace element approaches. Larger pyrite nodules are more likely to preserve their original trace element signature through metamorphism because recrystallization of the outer part of the nodule can occur while the inner pyrite preserves its initial trace element composition (Large et al., 2007). However, smaller pyrite (framboidal or other finer grained textures) that experience the same metamorphic conditions will be entirely recrystallized or have a large component recrystallized making the analysis of the preserved pyrite difficult. However, the largest pyrite nodules are most likely to grow over more time with unclear implications for seawater connectivity. Thus if we hope to use pyrite chemistry to see through metamorphic overprint, we must first assess how well large sedimentary pyrite nodules reflect early pore water trace element concentrations by completing trace element and S-isotope analyses similar to those discussed here to ensure the pyrite in question formed via the pervasive growth mechanism.

As shown above, some pyrite nodules are likely to have formed early via pervasive growth, as diagnosed via textural and compositional relationships, and thus their trace element content can be considered to reflect the trace element content of early sedimentary pore waters—perhaps only weakly modified from the overlying seawater. We recognize, however, that even early pore fluids can deviate markedly from the overlying water and this should be taken into account when interpreting the data. Moreover, pyrite nodules that formed fully via this mechanism compared with those with an aspect of the concentric growth can be difficult to distinguish using only textural observation, even with pyrite etching or staining, thus demanding the inclusion of multiple trace element and S-isotope measurements to identify the full history—such as purely pervasive growth mechanism with little variation from center to nodule margin.

5.3. Insights to the subsurface biosphere

Whereas early formed, pervasive-growth pyrite nodules may provide a reliable reflection of ocean bottom water and have utility for paleoceanographic reconstruction, late-forming pyrite nodules, via concentric growth could possibly track the evolution of pore waters that have become partly or completely isolated from seawater. These environments host diverse populations of microorganisms (Parkes et al., 1994), collectively known as the deep biosphere (Gold, 1992; Edwards et al., 2012; Colman et al., 2017). This deep, dark, and often hot biosphere is ubiquitous at depth in marine sediments and may represent a substantial fraction of the surficial biosphere (Whitman et al., 1998; LaRowe et al., 2017). These communities are inherently challenging to study, and the significance of subsurface life for global biogeochemical cycles remains poorly quantified. Nevertheless, the deep biosphere is thought to play a particularly important role in the cycling of H_2, CH_4 and CO_2 through the Earth system today (Colman et al., 2017, and references therein). The role of the deep biosphere in the long-term evolution of the Earth is even less constrained, yet an understanding is essential to any exploration of the emergence of life on Earth and the potential for life elsewhere in the Universe (Gold, 1992).

We argue that diagenetic pyrite nodules forming via concentric growth, which span the geologic timescale and are uniquely robust against moderate levels of metamorphism (up to mid-greenschist facies, Large et al., 2007), may provide a rich archive for probing the environmental conditions for subsurface communities throughout Earth history. Like the surficial biosphere, life in the subsurface is subject to energetic and substrate limitation. Chemical zoning within late-forming nodules may provide insight by tracking the evolution of electron acceptor and micronutrient availability in the subsurface. Biological reduction and subsequent drawdown of porewater SO_4^{2-}—the dominant electron acceptor available for the deep biosphere today (D'Hondt et al., 2002; Bowles et al., 2014)—manifests as $\delta^{34}S$ zonation through reservoir limitations, including Rayleigh distillation processes under closed-system conditions in the extreme. Similar zoning in trace metal abundance arises from trace metal drawdown as it is incorporated into the pyrite lattice and other sinks under reducing conditions, potentially resulting in biologically limiting levels of bioessential metals in pore waters.

This interplay between SO_4^{2-} drawdown and the sequestration of bioessential metals in pyrite in the subsurface may have wide-reaching impacts—and these dynamics can be reconstructed via microanalyses of pyrite nodules. As an example, Ni is a key enzymatic co-factor involved in both methanogenesis and anaerobic methane oxidation (AOM) coupled to SO_4^{2-} reduction (Scheller et al., 2010). Nickel also readily substitutes into the pyrite lattice (Huston et al., 1993). In addition to modulating net biogenic CH_4 production through inhibition of methanogenesis and anaerobic methanotrophy (e.g., Olson et al., 2016), SO_4^{2-} may also indirectly impact CH_4 cycling by promoting Ni sequestration in diagenetic pyrite—potentially inhibiting CH_4 production even upon the depletion of porewater SO_4^{2-} (see Konhauser et al., 2009). Coupled examination of $\delta^{34}S$ and Ni zonation in pyrite nodules, therefore, may provide insight to ancient CH_4 production—potentially with global climatic implications.

6. CONCLUSIONS AND RECOMMENDATIONS

The trace element and $\delta^{34}S$ signatures generated by in-situ pyrite analyses across nodules suggest that both pervasive and concentric growth models are valid. Indeed, it is more common that a given nodule will reflect both pathways, and one will dominate over the other depending on a number of factors, including depth of formation and connectivity to the overlying water column. Because the pervasive growth method appears to dominate when pore waters are in strong exchange with the overlying water column, pyrite nodules that form via this mechanism are preferred for studies of ancient ocean chemistry. To ensure that only pyrite nodules that formed in pore waters connected with the overlying water column are sampled for paleoceanographic reconstruction, transects of LA-ICPMS and SHRIMP-SI analyses should be conducted. If these techniques are not available, micro-drill sampling of the center and margin of the nodule can be sufficient to identify signature S isotope and trace element trends. Pyrites forming by concentric growth in isolation from seawater may provide different but equally important insight, particularly into the enigmatic deep biosphere.

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Figure 1: This pyrite nodule was taken from the 681 m depth of drill hole DD86WRL1. This sample was from the Jeerinah formation, Fortescue Basin, Western Australia and is approximately 2629 ±6 Ma (Trendall et al., 2004) old. The trace element content of pyrite varies very little across the nodule. The center of the nodule also has very minor $\delta^{34}S$ variation. The margins of the nodule have slightly higher $\delta^{34}S$. This suggests the nodule formed predominantly via the pervasive growth mechanism with minor additional pyrite production later during diagenesis on the nodule margins resulting in a slight positive $\delta^{34}S$ on the nodule margin. Approximate margin zones are shown in the shaded area. B) Reflected light image of acid etched pyrite nodule, the dark spots correspond to the LA-ICPMS spots that were placed directly on top of the SHRIMP-SI S-isotope spots. Each analytical spot corresponds directly with the data point immediately above it in section A. The red outlines refer to that areas where SEM images are given in C and D. C) and D) are backscattered SEM images where the pyrite is the brighter part of the image. C) is of pyrite on the margin of the nodule and D) is of pyrite from the center of the nodule.

Figure 2: Coarse-grained pyrite nodule (PETR14) from the 1330 ±30 Ma Zigazino-Komarovo Formation, Yurmata Supergroup, Russia (Kuznetsov et al., 2008). The trace element concentrations are erratic and tend to decrease in Ag, Cu and $\delta^{34}S$ towards the center and increase in Co, Ni, and Sb towards the center. This is interpreted to be due to the nodule forming predominantly via the concentric growth mechanism which resulted in clear variation in trace element content and $\delta^{34}S$ across the nodule. Approximate margin zones are shown in the shaded area. B) Reflected light image of acid etched pyrite nodule, the dark spots correspond to LA-ICPMS spots that were place directly on top of the SHRIMP-SI S-isotope spots. Each analytical spot corresponds directly with the data point immediately above it in section A. The red outlines refer to that areas where SEM images are given in C and D. C) and D) are backscattered SEM images where the pyrite is the brighter part of the image. C) is of pyrite on the margin of the nodule and D) is of pyrite from the center of the nodule.

Figure 3: Nodule (79990) from the 499.3 ±0.85 Ma Que River Shale, Mount Read Volcanics, Australia (Mortenson et al., 2015). A) The majority of the trace element data is generally constant in the middle of the nodule and some trace element concentrations decrease slightly in the 3 analyses on the nodule margin. This is interpreted to represent the inner part of the nodule forming predominantly via the pervasive growth mechanism and the margin forming more from the concentric growth mechanism when the pore waters were no longer connected to the overlying water column. The $\delta^{34}S$ signatures are generally heavier on the margin of the nodule; however, they are too erratic to be used for definitive interpretation. Approximate margin zones are shown in the shaded area. B) Reflected light image of acid etched pyrite nodule, the dark spots correspond to LA-ICPMS spots that were place directly on top of the SHRIMP-SI S-isotope spots. Each analytical spot corresponds directly with the data point immediately above it in section A. The red outlines refer to that areas where SEM images are given in C and D. C) and D) are backscattered SEM images where the pyrite is the brighter part of the image. C) is of pyrite on the margin of the nodule and D) is of pyrite from the center of the nodule.

Figure 4: The pervasive growth and concentric growth models for pyrite nodule formation. In the pervasive growth mechanism there are several places in which pyrite nucleates and those pyrites grow together to form the nodule. In the concentric growth mechanism, the pyrite first nucleates near a central point and additional layers are added by continuously nucleating pyrite on the edges of the growing nodule, possibly by nucleation on earlier pyrite.

Figure 5: NanoSIMS map (50 µm x 50 µm) of the interface between where a pyrite nodule stops forming via the pervasive growth mechanism (Left, A) and begins to grow via the concentric growth mechanism (Right, B). The former has distinct framboidal shapes with the area between the framboids filled with later pyrite. In the margin area, the crystals are distinctly euhedral with generally lower trace element content.

Figure 6: Dense cluster of framboidal and microcrystalline pyrite. This is interpreted to be a nodule that was forming via the pervasive growth mechanism with many nucleation points. However, there was not the requisite later pyrite to infill the void space between the pyrite grains. During compaction the void space was eliminated and a relatively flat disk of densely packed pyrite framboids was produced instead.