The Three-Dimensional Morphology of *Zoophycos* and its Influence on Sediment Biogeochemistry

by

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Abstract

The three-dimensional reconstruction and detailed biogeochemical analysis of *Zoophycos* presented in this thesis help to fully characterize the three-dimensional morphology, ethology, and biogeochemical impact of *Zoophycos.* The three-dimensional reconstruction revealed that this sample of Rosario Formation *Zoophycos* is composed of two morphotypes of *Zoophycos*, produced by a range of behaviors. One *Zoophycos* demonstrated selective detritus feeding from a clay-rich layer above the burrow environment. A later *Zoophycos* displayed opportunistic behavior in exploiting earlier spreite through infaunal deposit feeding. This data provides evidence that the *Zoophycos* trace-maker can adapt to changing sediment characteristics during the construction of its burrow. The biogeochemical analysis of *Zoophycos* revealed that the trace-maker has a measureable influence on sediment biogeochemistry. The trace maker influenced paleoredox proxies and mineralogy through sediment ingestion and digestion. The combination of a three-dimensional reconstruction and detailed biogeochemical analysis has revealed a means to systematically analyze trace fossil morphology and trace-maker ethology. The data in this study also has further implications on how bioturbating organisms influence paleoredox reconstructions.

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Co-authorship Statement

This master's thesis is composed of four chapters. The first chapter is an introductory chapter that contains a literature review and outlines the objectives of the thesis. I wrote this chapter, receiving editorial assistance from Dr. Duncan McIlroy. Chapters two and three are presented in manuscript form to be submitted to scientific journals. Dr. Duncan McIlroy and I wrote these chapters as co-authors. The final chapter is a summary of the thesis and ties together the objectives from each chapter. I wrote the contents of this chapter, receiving editorial assistance from Dr. Duncan McIlroy. Chapter two entitled "A Three-dimensional Reconstruction of the Trace Fossil *Zoophycos*" is to be submitted to the scientific journal Ichnos. Dr. McIlroy specified the field location. Dr. Richard Callow and myself completed sample collection, and though they are not authors, the University of Aberdeen Research Group also assisted in sample collection. I completed the sample preparation and processing with the assistance of Edgars Rudzitis and Dr. Dario Harazim. I was responsible for data analysis and interpretation. Dr. McIlroy provided expert knowledge, major editorial comments, and supervisory assistance during preparation of the manuscript. Chapter three entitled "The Influence of *Zoophycos* on Sediment Biogeochemistry" is to be submitted to the scientific journal Palaios. Dr. McIlroy specified the field location and samples. Dr. Richard Callow, and myself completed sample collection and though they are not authors, the University of Aberdeen Research Group also assisted in sample collection. I completed the sample preparation and processing with the assistance of Edgars Rudzitis and Dr. Dario Harazim. I was responsible for analyzing and interpreting the data. I prepared the manuscript with major editorial comments and supervisory assistance provided by Dr. McIlroy.

Chapter 1

Introduction and Overview

1.1 Introduction

The focus of this thesis-based Master's project is the three-dimensional (3D) morphology and biogeochemical significance of the trace fossil *Zoophycos*. This trace fossil is one of the most widespread, easily recognizable, and morphologically diverse trace fossils. *Zoophycos* has been described in a variety of sedimentary environments in Cambrian and younger sediments and sedimentary rocks. Although all authors agree that *Zoophycos* is a spreiten-bearing trace fossil, there is much contention surrounding the proposed ethological interpretations. The taxonomic confusion associated with *Zoophycos* has led to much debate concerning the morphological and ethological characterization of the trace fossil.

This study was derived from the need for further understanding of the three-dimensional morphology of *Zoophycos,* and a means to systematically document the biogeochemistry of the trace in to provide insights into the behaviour(s) that it results from. The outcomes of this research will be relevant to assigning an appropriate ethological model to the *Zoophycos* morphotype considered herein. I deal with this problem in two ways: 1) through a detailed three-dimensional morphologic reconstruction and description of a *Zoophycos* specimen, using the methods of Bednarz et al. (2015); and 2) using quantitative, targeted, biogeochemical analysis (cf. Harazim et al., 2015) to test the established ethological models for *Zoophycos.* This approach will be used to link the morphological and biogeochemical analysis of trace fossils to the behaviour of the trace maker (Harazim et al., 2015), and provides objective evidence to test ethological hypotheses.

1.2 Methods

This thesis involved two separate but related studies of the trace fossil *Zoophycos*, collected from the fine-grained Late Cretaceous (Maastrichtian) Canyon San Fernando channel-levee system of the Rosario Formation, Baja California, Mexico (Fig. 1.1). Through a three-dimensional reconstruction of serially ground surfaces we were able to study the complex morphology of the trace fossil and inform consideration of the ethology of the trace maker. Outcrop samples of *Zoophycos* were collected from the Rosario Formation, Baja California, Mexico (Fig. 1.1). For the three-dimensional morphological investigations, one sample of *Zoophycos* was subjected to precision serial grinding, high-resolution digital photography, and tomographic reconstruction (see Bednarz et al., 2015 for full methodology). The hand-sample was encased in plaster, squared off, and serially ground, at precise increments, using a computer guided CNC milling machine. Each ground surface was consecutively labeled, wetted with oil to enhance contrast, and photographed under identical lighting conditions. This process allowed for the collection of precisely spaced, high-resolution images of consecutive ground surfaces through the trace fossil. Each photograph was studied in detail to aid in understanding the subtle details of organism-sediment interactions and allowed a closer examination of the composition and structure of burrow linings and sediment infill.

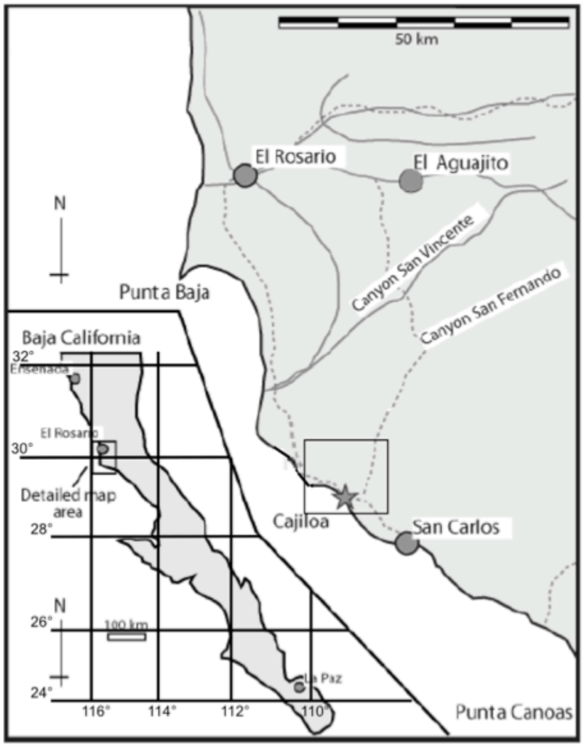

Fig. 1.1. Location of study area near Cajiloa, Canyon San Fernando, Baja California (modified from Bednarz and McIlroy, 2009).

The second study in this project focused on the biogeochemical analysis of burrowed and host sediment. The biogeochemical mapping undertaken in this study is designed to identify biogeochemical differences between *Zoophycos* burrows and the surrounding sediment as a means whereby aspects of the pre-established behavioral models for the *Zoophycos* trace-maker can be tested (Fig. 1.2). The geochemistry of the sediment was determined using three types of analysis: 1) Trace element analysis was performed using ICPMS (Appendix A); 2) mineral analysis was performed using X-Ray Diffraction (XRD) technology (See Appendix B); and 3) the isotopic composition and abundance of organic matter in the sediment was determined using carbon and sulfur isotopic analysis (Appendix C).

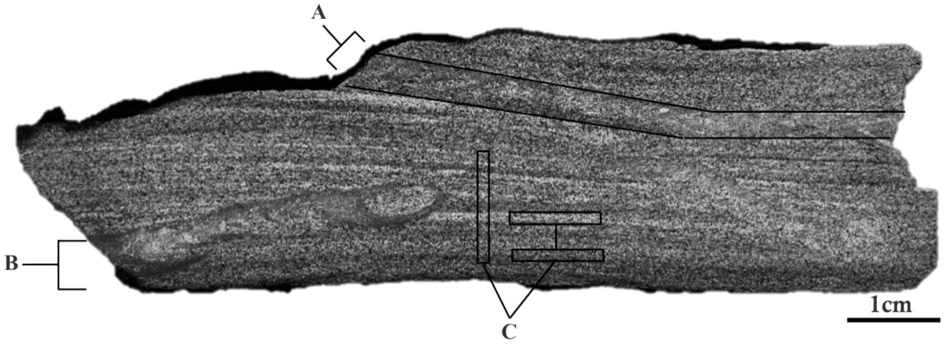

Fig. 1.2. Location of sampling areas for both the *Zoophycos* burrows and the surrounding host sediment. A: Clay-rich burrow. B: sand-rich burrow. C: Host sediment.

1.3 Literature Review

1.3.1 The Ethology and Morphology of *Zoophycos*

The trace fossil *Zoophycos* has been discovered in sediments ranging in age from the Cambrian (Alpert, 1977) to the Holocene (Seilacher, 1967; Wetzel and Werner, 1981) and from sub-littoral to bathyl environments (Ekdale and Lewis, 1991). *Zoophycos* occurs in a range of rock types, including: sandstones (Miller, 1991), limestones and marls (Ekdale and Lewis, 1991), and carbonate muds (Wetzel and Werner, 1991). The paleoenvironmental range of *Zoophycos* has changed through the Phanerozoic. *Zoophycos* are predominantly found in shallow marine facies in the Paleozoic and changing from offshore shelf to deep marine in the post-Paleozoic (Wetzel and Werner, 1981; Bottjer et al., 1988; Miller, 1991; Ekdale and Lewis, 1991; Olivero, 2003). The genus *Zoophycos* therefore can be seen to encompass a wide range of diverse morphologies that have the commonality of spreiten rich lobes typically centered round a vertical burrow (Fig. 1.3; Häntzschel, 1975).

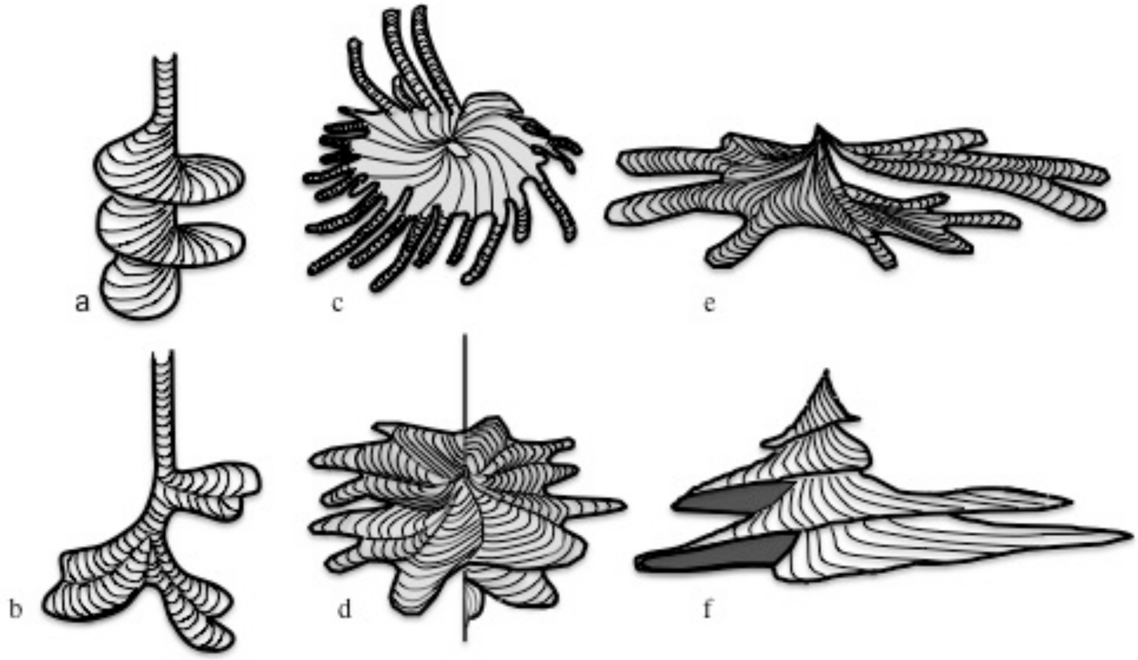

Fig 1.3. The morphological variability between existing morphotypes of *Zoophycos*: a) U-Shaped, continuous, helically coiled *Zoophycos* (Wetzel and Werner, 1981); b) J-shaped, discontinuous, tongue like *Zoophycos* (Wetzel and Werner, 1981); c) large, lobed Pliocene *Zoophycos* with skirt like zone and long extending marginal lobes (Bromley and Hanken, 2003); d) late Quaternary *Zoophycos* model reconstructed from X-Ray radiographs (Löwemark and Schäfer, 2003); e) late Cretaceous slope-deep basin *Zoophycos* (from Olivero, 2003); f) late Jurassic slope *Zoophycos* (re-drafted from Olivero, 2003). *Zoophycos* can be up to 1m in diameter.

The spreiten lobes are often helically coiled and are typically oblique with a shape that varies from helical to lobate. It is understood that the spreite are formed as the *Zoophycos* trace maker shifts its burrow laterally through the sediment, creating a succession of curved structures that are typically lunate (Seilacher, 1967). *Zoophycos* spreite are easily recognizable in cross section as crescentic alternations of clay and silt/sand grade material (Fig. 1.4). Many types of *Zoophycos* have lobes that are bordered by a marginal tube, which can be filled by both passive and active means (Häntzschel, 1975; Bromley and Hanken, 2003). The cylindrical marginal tube borders an area of spreite that in cross section are convex away from the marginal burrow (Fig. 1.4). The marginal burrow is generally considered to be the causative burrow, the original burrow where the organism inhabited and performed it's feeding strategies, and is typically unlined (Bromley, 1996; Olivero, 2003).

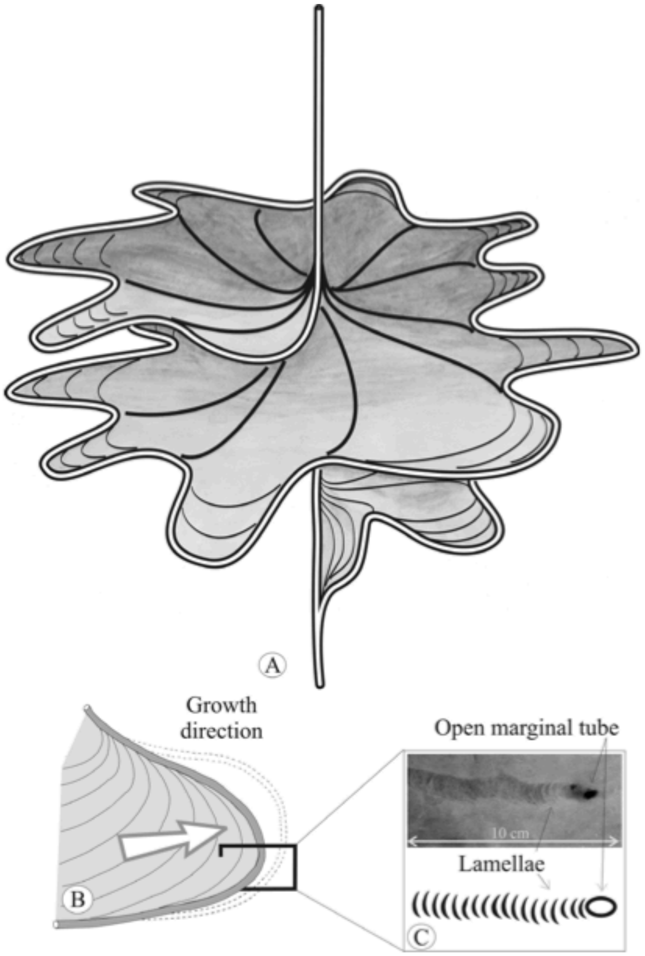

Fig. 1.4. A conceptual model of the basic morphological components of *Zoophycos* as modeled by Löwemark and Schäfer, 2003. A: Continuous, helically coiled spreite lobes centered round a vertical tube. A marginal tube borders the spreite and a vertical tube connects the trace fossil to the sediment surface. B: Spreite are shown as near-horizontal, sheet-like structures between limbs of the marginal tube that are formed by successive lateral shifting of the tube. C: Alternating dark and light crescent shaped spreite showing the previous positions of the marginal tube's inner wall (Löwemark et al., 2004).

While modern *Zoophycos* are seen in shallow sediment cores, the trace-maker remains unknown. Any attempt to understand the biological function of such a complex structure must therefore rely upon careful description of the structure itself in the absence of direct observation of the burrowing activity of a known trace maker. *Zoophycos* was initially described as an alga (Massalango, 1855) and is traditionally accepted as the burrow of a wormlike organism (Seilacher, 1967; Wetzel and Werner, 1981; Ekdale and Lewis, 1991; Kotake, 1992; Olivero, 2003). There is no known modern trace maker, nor can one be inferred from paleobiological or biomechanical evidence, and as such it is most appropriate to consider the trace maker unknown (cf. Leaman et al. 2015). The ethology of the *Zoophycos* trace maker has been long discussed (Seilacher, 1967, Simpson, 1970; Ekdale, 1977; Wetzel and Werner, 1981; Kotake, 1989, 1991, 1994; Ekdale and Lewis, 1991; Bromley, 1991; Fu and Werner, 1995; Löwemark and Schäfer, 2003; Olivero and Gaillard, 2007) as recently summarized by Löwemark (2015). The *Zoophycos* tracemaker was originally considered to be a deep-tier deposit-feeding organism that exploited nutrient rich sediment (Seilacher, 1967; Simpson, 1970). This model was based on its elaborate and highly regularly structured spreite system where sediment is consumed and deposited in the active front of the spreite. The oxygenation of these deep tiering burrows is facilitated by their permanent U- or J-tube, which provided an open connection to the seafloor (Wetzel and Werner, 1981). Some types of *Zoophycos* can be demonstrated to transfer organic-rich surficial sediment deep into the sediment profile as fecal matter (Kotake, 1989, 1991, 1992). The discovery of this detritus-feeding style behavior generated three additional models to account for the introduction of surface material into the burrow (Bromley, 1991). These models include: 1) the refuse dump model, which suggests surface material is introduced to the burrow to fill the cavity formed by deposit feeding; 2) the cache model, where surface material is collected as a food source and stored at depth within the burrow for nutrient poor times; and 3) the gardening model, where refractory carbon is stored and used to cultivate microorganisms as a food source. A specialized form of gardening of chemolithoautotrophic bacteria includes the introduction of organic material to create optimal conditions for chemolithotrophic bacteria living in proximity to the trace maker (Bromley, 1991; Bromley and Hanken, 2003; Löwemark and Schäfer, 2003; Löwemark et al., 2004; Dubilier et al., 2008). It is noted that few of these hypotheses have been independently tested or verified by observational or geochemical means. Due to the abundant diversity among the many morphological types of *Zoophycos* and the wide range of palaeoenvironments in which they are found, it is thought that not all of these traces signify the same type of behaviour (Löwemark and Schäfer, 2003; Olivero, 2003). The morphological diversity within the ichnogenus *Zoophycos* is so great that there have been repeated calls for taxonomic revision (e.g. Olivero and Gaillard, 2007), with some authors considering that current species be placed within a supra-generic taxon *Zoophycos* (Uchman, 1995, 1999). In the absence of a full taxonomic revision of all *Zoophycos*-like trace fossils, which is beyond the scope of this study, the loose concept of the ichnogenus *Zoophycos* that has been adopted by most ichnologists is also applied herein.

As one of the sub-disciplines within the field of ichnology, the study of biogenic structures as a preservation of trace maker behaviour has hitherto been a useful tool in paleoecologic and paleoenvironmental analysis (cf. Tribovillard et al., 2006). These structures provide information on the paleobiology of the trace maker and facilitate the connection between trace fossil behaviour and the paleoecological importance of ichnofauna. Trace maker behaviour may be derived from the detailed analysis of ichnofossils, which is aided by the *in situ* nature of trace fossils, allowing for their use in paleoecological and paleoenvironmental studies (Aller, 1982). The genus *Zoophycos* is particularly complex due to the wide variety of proposed behaviours and paleoenvironments assigned to the ichnofossil (Ekdale and Lewis, 1991; Olivero and Gaillard, 2007; Bromley and Hanken, 2003; Löwemark et al., 2006; Löwemark, 2015).

1.3.2 Biogeochemistry

Bioturbation is a first order control on all microbially- mediated biogeochemical reactions below the sediment-water interface (Dapples, 1942; Rhoads, 1974; Aller, 1978, 1982; Fisher, 1982; Berner, 1976; Aller and Yingst, 1978; Robbins et al., 1979; Robbins, 1985; Grossmann and Reichardt, 1991; Seilacher and Pfluger, 1994; McIlroy and Logan, 1999; Zhu et al., 2006; Cao et al., 2010; Volkenborn et al., 2012; Herringshaw and McIlroy, 2013). Infaunal macrobenthos and meiofauna (microbiota and meiobenthos respectively) strongly influence fluid and particle transport processes in marine sediment through displacement during burrowing, feeding, and the construction and irrigation of tubes and burrows (Aller, 1982). These processes significantly affect the composition of sediment and the concentration of dissolved solutes within surrounding and overlying waters (Aller, 1982). The effect of macrobenthos on the physical characteristics of sediment has been extensively reviewed (Dapples, 1942; Rhoads, 1974; Lee and Schwartz, 1980; Rhoads and Boyer, 1982). The present review focuses on the impact of bioturbating organisms on the biogeochemical characteristics of marine sediment. Emphasis will be placed on the influence of macrobenthos on the biogeochemical properties of sediment, including the distribution and transfer of particles, fluids, organic material, reaction rates, and the exchange of material across the sediment water interface

(Davis et al., 1975; Petr, 1977; Aller, 1978a,b, 1982; Aller and Yingst, 1978; Fisher, 1982; Karickhoff and Morris, 1985; Robbins, 1985).

1.3.3 Particle and solute transfer, redox gradients, and diffusion reactions

The physical and biological activity of bioturbating organisms controls the transport of solutes by diffusion, advection, and mixing processes in sediments (Aller, 1982). The construction and irrigation of permanent burrows by bioturbating macrofaunal animals (e.g., bivalves, crustaceans and polychaete) increases the downward diffusion of oxygen below the sediment-water interface, skewing the geometry and the dynamics of vertically stratified microbial zonation (Aller, 1982; Grossmann and Reichardt, 1991; McIlroy and Logan 1999; Zhu et al., 2006; Stockdale et al., 2010; Fig. 1.5). The distributions of redox sensitive elements around burrow microenvironments are influenced by these newly constructed redox and diffusion gradient geometries (Aller, 1977, 1978, 1980; Hines et al., 1982; Hines and Jones, 1984). Diagenetic decomposition reactions of surficial sedimentary deposits were initially considered to be profiles of one-dimensional, vertical distributions (Froelich et al., 1979; Berner, 1980; Aller, 1982; Aller, 1988). Through feeding, burrow construction, and irrigation, macrobenthos influence the arrangement of these reactions around burrow and fecal pellet microenvironments, transforming surficial sedimentary deposits into dynamic, three dimensional arrangements of biogenic microenvironments (Rhoads, 1974; Aller, 1980; Fisher, 1982; Fig. 1.5). Burrowing organisms significantly influence the bulk geochemical composition of sediment, including factors such as sedimentary solute profiles, reaction rate distributions, pathways, rates, the extent of organic matter remineralization (Aller and Aller, 1998), and *in-situ* weathering (McIlroy et al., 2003; Harazim et al., 2015).

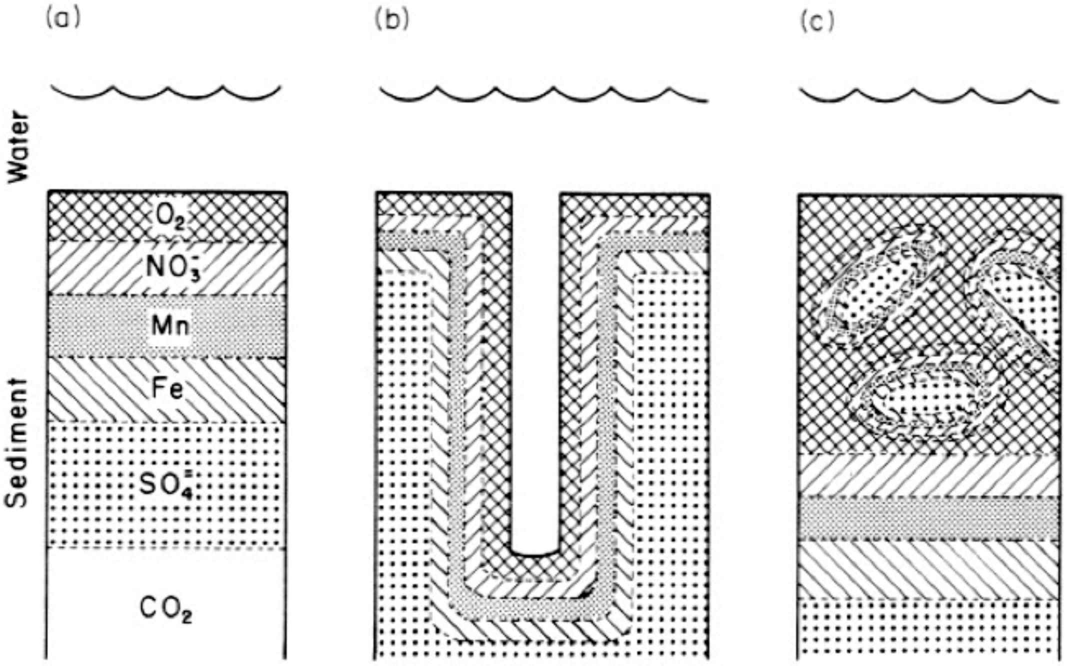

Fig. 1.5. (A) The traditional, one-dimensional vertically stratified distribution of major electron acceptors involved in heterotrophic metabolism and diagenetic reactions of marine sediment organic matter below the sediment water interface. (B) The zonation of diagenetic reactions around a cylindrical burrow microenvironment. (C) The spatial distribution of reaction geometries around fecal pellet microenvironments (After Aller 1982, 1988)

The distribution of these reaction profiles is directly influenced by macrobenthos in a number of ways: 1) material is constantly transferred through different oxidation and reduction reaction zones due to burrow construction and feeding activities (Rhoads, 1974; Fischer, 1982; Aller, 1982, 1988; 2) burrows and their fill distort the distribution of the vertically-stratified reaction and solute diffusion geometry (Hargrave, 1976; Aller and Yingst, 1978; Aller, 1988); 3) burrowing animals secrete mucus during burrow construction, which delivers a new organic and reactive substrate to the sediment (Herringshaw et al. 2010); and 4) macrobenthos directly alter and release sedimentary minerals through digestive processes and biological weathering (McIlroy et al., 2003;

Needham et al., 2006; Harazim et al. 2015).

In addition to altering the geochemical profiles in sediments, animals also modify the rates of microbially mediated organic matter decomposition (Fenchel, 1970; Hargrave, 1970; Fenchel and Harrison, 1976; Aller, 1978; Yingst and Rhoads, 1980). Burrow irrigation is an important process in transporting solutes, stimulating microbial activity, and influencing net remineralization of organic material in areas within and surrounding the bioturbated zone (Aller and Aller, 1998; Herringshaw et al., 2013). The net remineralization rates of organic matter in euxinic sediments increase with increasing intensity of irrigation and diffusive exchange between neighboring burrows (Aller and Aller, 1988). These remineralization reactions affect a number of important geochemical characteristics such as the pH, oxidation-reduction potential, and the buildup or depletion of both fluid and solid phase reactants and products (Aller, 1982). This is achieved through: 1) mechanically increasing the surface area of organic detritus during feeding through maceration (Canfield et al., 2005); 2) control of microbial populations through macrofaunal cropping, particularly by bulk sediment deposit feeders (McIlroy & Logan 1999); 3) increasing electron acceptor supply and decreasing metabolites during irrigation, particle reworking, and diffusion (Aller, 1988; McIlroy and Logan 1999); 4) sediment reworking and organic material capture (Aller, 1982). Biogeochemical activity is enhanced by organic enrichment, which is common along burrow walls and is influenced by the proximity of the oxic-anoxic boundary in the surrounding sediment (Aller, 1988). Bioturbating animals can transport newly deposited organic matter from the seafloor or from suspension to various depths in the sediment, increasing its availability to decomposers (Aller and Yingst, 1980, Hines and Jones, 1984). The reverse transfer of already reduced organic material back to the surface thus increases the oxidation potential of the organic material (Fenchel and Reidl, 1970; Rhoads, 1974). Particle transport processes during feeding often involve the separation of particles based on grain size (cf. Bednarz and McIlroy, 2012; Izumi, 2014; Harazim et al. 2015). Various chemical properties of sediments often co-vary with particle size; therefore, these processes often also lead to new distributions of microenvironments and reaction rates (Aller, 1982). In terms of organic remineralization reactions, fine-grained sediments are more reactive than coarser-grained sediments, thus the selective feeding and particle organization of burrowing animals can significantly influence reaction rate distributions (Hargrave, 1972; Aller, 1982; Bednarz and McIlroy, 2012).

Macrofauna can thus influence diagenetic reactions involving solute transport through the geometric and spatial patterns of their burrows (Aller, 1980, 1982, 1988; Aller and Aller, 1988). Burrow wall permeability may influence burrow biogeochemistry by modification of solute transport and diffusion from surrounding sediment pore waters (Aller, 1980, 1988). The resultant variations in sediment chemistry are controlled by the number, species, and size of organisms present in a given benthic community (Rhoads et al., 1977; Aller, 1980, 1982). To fully understand and quantify the effects of macrofauna on sediment chemistry, we must consider the type of behaviors represented by the infauna, the characteristics of the sediment, and the depositional environment (Aller, 1982). In addition to changing the geometry of reaction rate distributions in marine sediments, the macrobenthos may also affect microbial growth rates by the addition of fecal pellets to the sediment, by consuming microbial bacteria, or by adding nutrients and removing metabolites (ZoBell, 1946; Hargrave, 1970; Fenchel, 1970; Aller, 1977; Yingst and Rhoads, 1980; Hines and Jones, 1984; McIlroy and Logan, 1999). Increased microbial activity within sediments is often found along burrow linings (Aller, 1977, 1980b; Aller and Yingst, 1978). These areas experience an increase in bioirrigation and development of complex burrow microenvironments that strongly influence the distribution of redox-sensitive elements along biologically-mediated redox and diffusion gradients (Aller, 1977, 1978, 1980; Hines et al., 1982; Hines and Jones, 1984; Fig. 1.5). Redox-sensitive metals such as Fe and Mn are solubilized under reducing conditions and precipitated under oxidizing conditions and can sometimes become enriched along the oxic-anoxic boundary near the burrow and surrounding porewater system (Aller, 1988).

1.3.4 Biologic weathering

There has long been recognition of the participation of biota in weathering reactions and macrobenthos have been shown to alter sedimentary minerals during digestion (McIlroy et al., 2003; Harazim et al., 2015). The guts of organisms are known to be hostile and chemically active microenvironments and studies have shown that in many deposit-feeding animals, the gut pH values are up to 2 orders of magnitude lower than that of seawater (Ahrens and Lopez, 2001). Biological weathering has been demonstrated, the inferred process perhaps being pH since some organisms have highly acidic guts (e.g. Ahrens and Lopez, 2001) but also enzymes and redox likely play their parts (McIlroy et al., 2003; Harazim et al., 2015). The harsh gut environment conditions of polychaetes accelerates the alteration of unstable crystalline grains producing neo-formed clay minerals at a much faster rate than many naturally occurring chemical weathering reactions (McIlroy et al., 2003). The gut microenvironment of macrobiotic organisms may have slightly reducing pH signatures, complicating paleoredox proxy data in heavily bioturbated formations, as seen in this study and in Harazim et al. (2015). Based on the significance of biologic influence on clay mineral authigenesis, organisms can also be shown to have an effect on siliciclastic reservoir quality since clay minerals lining the pores between sand grains can either destroy or preserve porosity, which ultimately affects the recoverable oil reserves of petroleum bearing formations (McIlroy et al., 2003).

1.3.5 Impact of organisms on stable isotope fractionation

The isotopic composition of an organism can reveal information about the carbon food source ingested by the organism, giving insight into the ancient ecosystem environment it inhabited (Hayes, 1993). Since $\delta^{13}C_{org}$ values are influenced by environmental conditions, they are seen as useful paleoenvironment indicators (Hayes, 1993). Some studies have shown a relationship between the $\delta^{13}C_{org}$ values of the body of a heterotrophic organism and that of both its ingested food source and its excrement (DeNiro and Epstein, 1979; McConnaughey and McRoy, 1979; Checkley and Entzeroth, 1985). Animals are generally enriched in $\delta\ ^{13}C_{org}$ in comparison to their food source. When organic matter is ingested and demineralized, the ^{12}C/ ^{13}C fractionation results in the isotopically lighter carbon (^{12}C) exhaled as CO_2, leaving a relative enrichment of $\delta^{13}C_{org}$ values in the residual organic matter (Hayes, 1993). There are also differences in kinetic fractionation and residual $\delta^{13}C_{org}$ values among different animals, which may be influenced by the selective digestion of compounds with varying $\delta^{13}C_{org}$ values (Hayes, 1993; Breteler et al., 2002). The expected metabolic effect for some animals, such as copepods and some small terrestrial animals, has demonstrated residual fecal matter with heavier $\delta^{13}C_{org}$ values of +1 to +2‰ (Checkley and Entzeroth, 1985; DeNiro and Epstein, 1979). Other studies that analyzed residual fecal organic matter showed values that were lighter by -0.5 to -2‰ than the ingested food source (Macko et al., 1982; Breteler et al., 2002; Landrum and Montoya, 2009). These authors suggest that some of the variability and complications in the interpretation of stable carbon isotopes can be related to the metabolic processes involved in isotopic fractionation (Breteler et al., 2002). They emphasize the need to differentiate between kinetic fractionation by isotopic discrimination of carbon atoms of a molecule, and processes related to the selective digestion of various food sources that have diverse isotopic compositions (Breteler et al., 2002). These studies demonstrate that it is common to have residual organic matter in ichnological materials with either isotopically lighter (Breteler et al., 2002) or heavier (Hayes, 1993) isotopic signatures, depending on the variety of kinetic fractionation and metabolic processes utilized by the animal.

1.4 Relevance of the Study

This research is relevant to the morphological and ethological interpretation of *Zoophycos*, one of the most enigmatic and poorly understood trace fossils. The three-dimensional reconstruction of *Zoophycos* created in this thesis allows for a more complete understanding of the organism-sediment interactions and the three-dimensional morphology. A greater understanding of the complex morphology of this trace fossil will aid in their identification in outcrop and core. The biogeochemical study of *Zoophycos* in this thesis allows for a detailed understanding of the organism-sediment interaction and the influence of the *Zoophycos* trace maker on sediment biogeochemical properties. A combination of the three-dimensional morphology study and the biogeochemical analysis in this thesis are used to develop a systematic means of assigning an evidence-based ethology to a given *Zoophycos* trace fossil. In addition this study also allows for an understanding of the effect of bioturbation on sediment redox proxies. The three-dimensional investigative approach in this study has been recently developed and utilized in a growing number of studies on a variety of different trace fossils (Bednarz and McIlroy 2009; Boyd et al., 2012; Bednarz et al., 2015; Leaman et al., 2015; Leaman and McIlroy 2015; Boyd and McIlroy, 2016 (in review). This approach is providing novel insights into our understanding of trace maker behavior and real world applications of ichnology (McIlroy 2004a, 2008). The biogeochemical analysis in this study adds to the newly documented effect of bioturbating organisms on the geochemical properties of sediment (Harazim et al., 2015). This work can help to interpret the influence of bioturbation on redox proxy data and geochemical analysis of bioturbated reservoirs, data that is often lost in bulk rock geochemical analysis.

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Chapter 2

A Three-dimensional Reconstruction of the Trace Fossil *Zoophycos*

ABSTRACT

Zoophycos is an easily recognizable and enigmatic trace fossil. There has been much discussion and contention surrounding the ethological model(s) used by the trace-maker responsible for the construction of this ichnofossil. *Zoophycos* is easily identified in outcrop and core by its spreite that typically form crescentic patterns of clay-rich and sand-rich material. To resolve the issue concerning assigning an ethological model among the wide variety of three-dimensional forms of this trace fossil, a high-resolution three-dimensional model was created using a sample of late Cretaceous Rosario Formation *Zoophycos*. Observation of the detailed morphological features in this sample reveals that the two *Zoophycos* herein were produced via a range of behaviors. A later *Zoophycos* trace maker selectively fed upon pelleted material derived from a younger bed and stored in the spreite of one Zoophycos. This opportunistic infaunal deposit-feeding style behavior is inferred using preservation of revisited spreite. The marginal tube for *Zoophycos* is not often described as a lined burrow. Our study demonstrates that the two *Zoophycos* ichnofossils in this study featured mud lined marginal tubes with a maximum thickness of 5 mm. The widely variable morphology of *Zoophycos* requires the direct three-dimensional observation of detailed structures within the trace fossil, such as those described herein, before an ethological model can be confidently assigned to an individual trace fossil.

Keywords: *Zoophycos*, 3D Morphology, Descriptive Ichnology, Ethology

1.0 INTRODUCTION

The trace fossil *Zoophycos* is known in rocks ranging in age from the Cambrian to the present (Seilacher, 1967; Alpert, 1977; Wetzel and Werner, 1981) and deposited in sub-littoral to bathyal environments (Ekdale and Lewis, 1991). The paleoenvironmental range of *Zoophycos* has changed through the Phanerozoic, mainly being associated with shallow marine environments in the Paleozoic and offshore shelf to deep marine in post-Paleozoic strata (Bottjer et al., 1988). The ichnogeneric diagnosis of *Zoophycos* encompasses a wide range of three-dimensional morphologies that all have spreiten-rich lobes that are typically centered round a vertical shaft (Fig. 1).

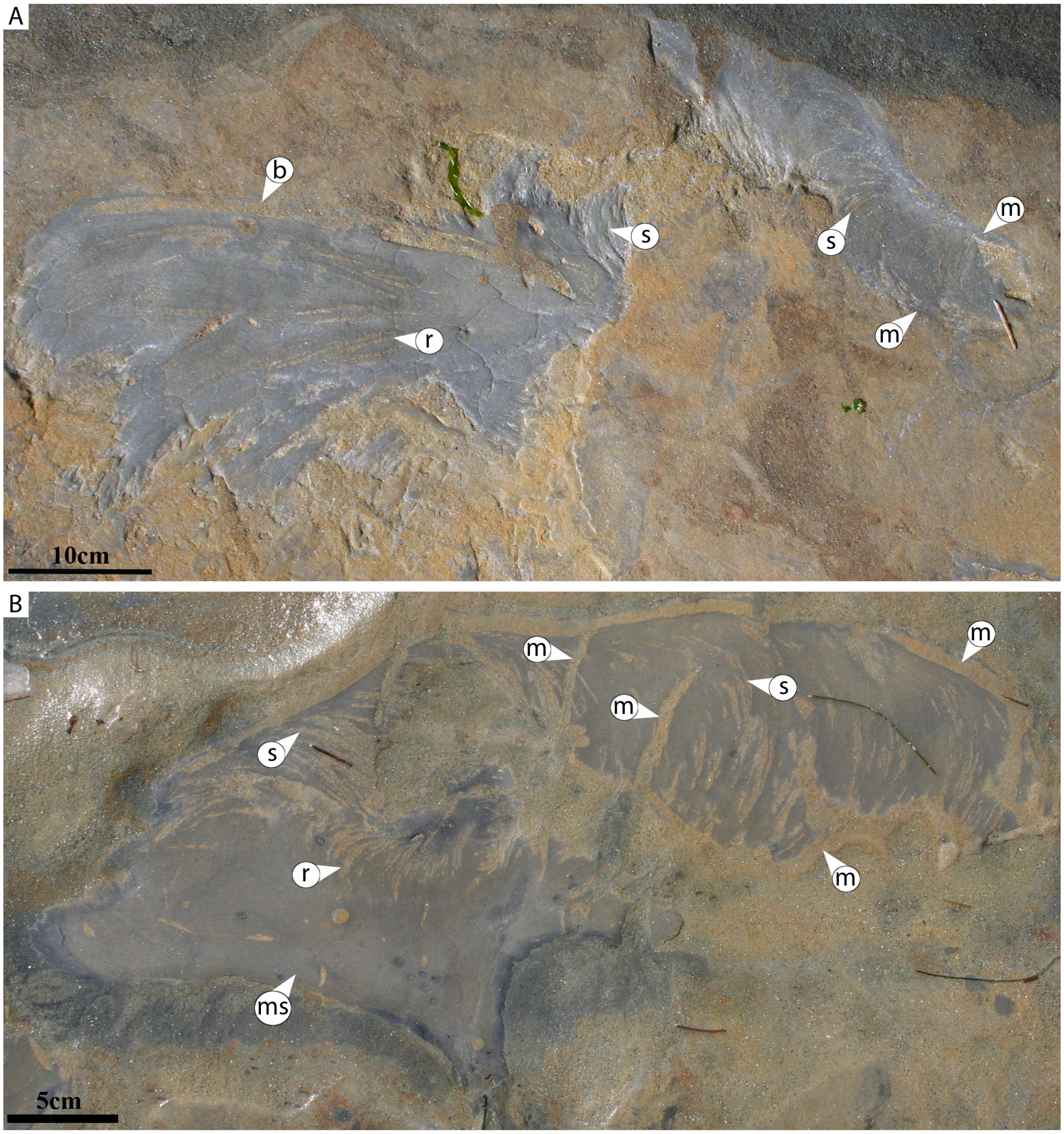

Fig. 1. Field photographs of *Zoophycos* in bedding plane view. A: Two individual *Zoophycos* are coincident in which one has narrow, tightly curved spreite (s) that are bordered by a mud-rich marginal tube (m). The second *Zoophycos* has long, radial spreite (r) that are terminated by a sand rich-causative burrow (b), B: A *Zoophycos* with a mud-rich sheet (ms) is cut by small, radial spreite (r) of a later *Zoophycos* which has a sand rich marginal tube (m) that cuts across the narrow, curved spreite (s) in its lobe in multiple locations. These samples were observed in the field and not used in this study.

There are several proposed behavioral models to explain the formation of *Zoophycos*, including: deposit feeding; food caching; surface detritus feeding; gardening; and chemosymbiosis (Seilacher, 1967; Lewis, 1970; Simpson, 1970; Ekdale, 1977; Wetzel and Werner, 1981; Bromley and Ekdale, 1984; Kotake, 1989, 1990; 1991; Ekdale and Lewis, 1991; Wetzel, 1991, 1992; Fu and Werner, 1995; Bromley and Hanken, 2003; Löwemark and Schäfer, 2003; Löwemark 2012, 2015). Few of these hypotheses have been independently tested or verified by observation or geochemistry. Due to the morphological diversity within *Zoophycos*, and the wide range of palaeoenvironments in which they are found, it is unlikely that all *Zoophycos* represent the same type of behaviour (Löwemark and Schäfer, 2003; Olivero, 2003). Some authors have suggested the need for *Zoophycos* to be considered supra-generic taxon (Uchman 1995, 1999). If a suprageneric classification of *Zoophycos*-like burrows was established, much of the constructional variability might then be expressed at the ichnogeneric level. As the taxonomic revision of all *Zoophycos*-like trace fossils is beyond the scope of this study, the loose concept of the ichnogenus *Zoophycos* adopted by most ichnologists is applied herein.

While modern *Zoophycos* are known from shallow cores (Kotake, 1989; Löwemark and Schäfer, 2003) the trace-maker remains unknown. Any attempt to understand the biological function of such a complex structure must therefore be based upon careful description of the structure itself rather than observations of a burrowing organism producing similar structures (cf. Leaman et al., 2015). The broad-scale architecture of lobes attributed to *Zoophycos* is highly variable, ranging from simple (planar) to complex (helically arranged) spreiten-bearing structures (Fig. 2). The outline of a *Zoophycos* lobe varies from semi-circular to lobate, with an outer marginal tube bordering each spreite lobe (Häntzschel, 1975). The internal arrangement of *Zoophycos* spreite varies less than the size and shape of the trace fossil as a whole (Wetzel and Werner, 1981).

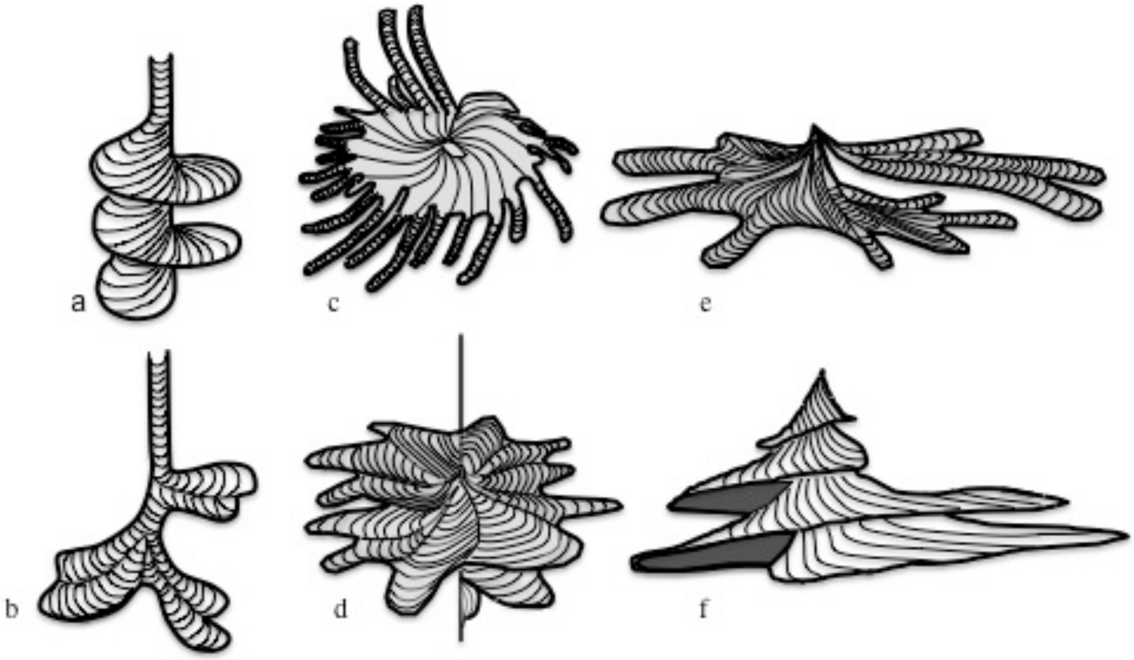

Fig. 2. The morphological variability between existing morphotypes of *Zoophycos*: a) U-Shaped, continuous, helically coiled *Zoophycos* (Wetzel and Werner, 1981); b) J-shaped, discontinuous, tongue like *Zoophycos* (Wetzel and Werner, 1981); c) large, lobed Pliocene *Zoophycos* with skirt like zone and long extending marginal lobes (Bromley and Hanken, 2003); d) late Quaternary *Zoophycos* model reconstructed from X-Ray radiographs (Löwemark and Schäfer, 2003); e) late Cretaceous slope-deep basin *Zoophycos* (from Olivero, 2003); f) late Jurassic slope *Zoophycos* (re-drafted from Olivero, 2003). *Zoophycos* can be up to 1m in diameter.

This study involves the serial grinding and three-dimensional reconstruction of a hand sample of *Zoophycos* using established lab protocols (Bednarz et al. 2015). The purpose of the reconstruction is to: 1) consider the distribution patterns of different sediment types in *Zoophycos* lobes; 2) determine the origin of the different sediment types present in the *Zoophycos* lobes; 3) describe *Zoophycos* spreiten morphology; and 4) incorporate these observations into an improved paleobiological/ethological understanding of *Zoophycos* by combining three-dimensional observations with the predictions of previously proposed ethological models (e.g. Seilacher, 1967; Wetzel and Werner, 1981; Kotake, 1989, 1991; Ekdale and Lewis, 1991; Bromley and Hanken, 2003; Löwemark and Schäfer, 2003).

The sample of *Zoophycos* in this study was collected from the Late Cretaceous, Canyon San Fernando channel-levee system of the Rosario Formation, Baja California, Mexico (Fig. 3). *Zoophycos* from this field location include specimens up to 30 cm in diameter, with an observed maximum tiering depth of 10 cm (Callow et al., 2013) (Fig. 1). The *Zoophycos* lobes, situated around a central shaft, are < 5 mm thick, and are composed of narrow arcuate spreite which are chevron shaped in vertical cross section (Callow et al., 2013). *Zoophycos* from the Rosario Formation are exclusively found as a component of *Nereites/ Phycosiphon*- ichnofabrics in slope turbidite facies (see Callow et al., 2013).

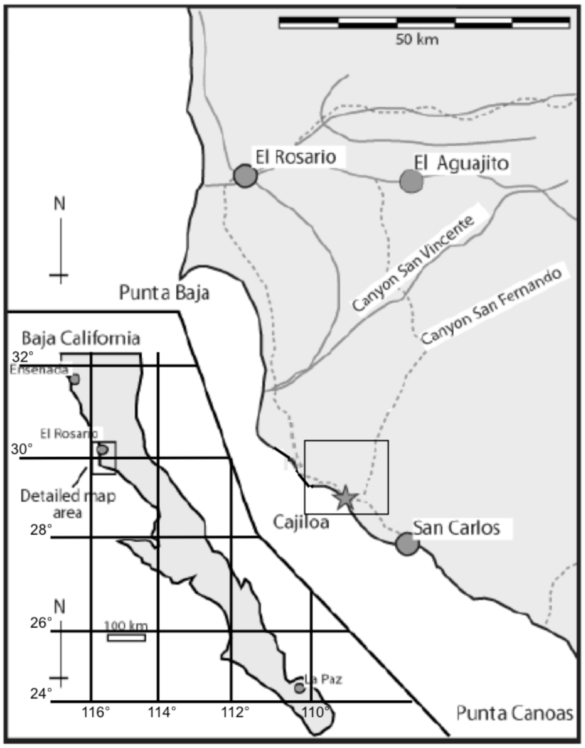

Fig. 3. Map of the sample collection site near Cajiloa, Canyon San Fernando, Baja California (modified from Bednarz and McIlroy, 2009).

Field photographs of *Zoophycos* from the Rosario Formation show multiple, coincident *Zoophycos* trace fossils that display a range of morphological variability (Fig. 1). One *Zoophycos* morphotype has broadly concentric arcuate spreite that are bordered distally by a marginal tube, which is found to, in some cases, be coincident with a separate *Zoophycos* morphotype with narrow, curved radiating probe-like spreite (Fig. 1).

2. METHODOLOGY

This study employs the methodology used in a growing number of works (cf. Bednarz and McIlroy, 2009, 2012; Boyd et al., 2012; Leaman et al., 2015; Evans and

McIlroy, 2016; Boyd and McIlroy, 2016a,b in review) and formally described in Bednarz et al. (2015). The collected sample was encased in a rectangular prism of plaster, which was used to align the sample through the serial grinding and photography process. The sample was serially ground using a HAAS VF3 VOP-C CNC milling machine at increments of 0.1 mm thickness (665 passes). Each surface was cleaned, wetted with oil to enhance contrast before being photographed. The corners of the sample block were used to position the sample in the same location for each photograph. Once the sample had been completely ground, the photographs were image processed to enhance the contrast between the trace fossil and host sediment. Photoshop pixel count enabled the approximation of mud and sand percentages in the burrow. The elements of interest for each *Zoophycos* consisted of clay-rich spreite; sand-rich spreite and a sand-filled, clay-lined marginal burrow. Each of these elements were selected separately, and exported as images set over a black background. These stacked images were then loaded into the tomographic reconstruction VG Studio Max. The resultant three-dimensional model can be manipulated and intersected in any plane, allowing for detailed study of the burrow elements (see supplementary materials).

3. DESCRIPTIVE ICHNOLOGY

The sample reconstructed in this study is composed of two separate *Zoophycos* trace fossils that have a crosscutting relationship in which a separate and earlier *Zoophycos* (herein referred to as lobe 1) is cut by a later *Zoophycos* (lobe 2) (Fig. 4). Rosario Formation *Zoophycos* are composed of alternating sand and clay spreite and are terminated distally by a sand-filled marginal tube (Fig. 4). These morphological components are discussed separately for both *Zoophycos* lobes in this sample.

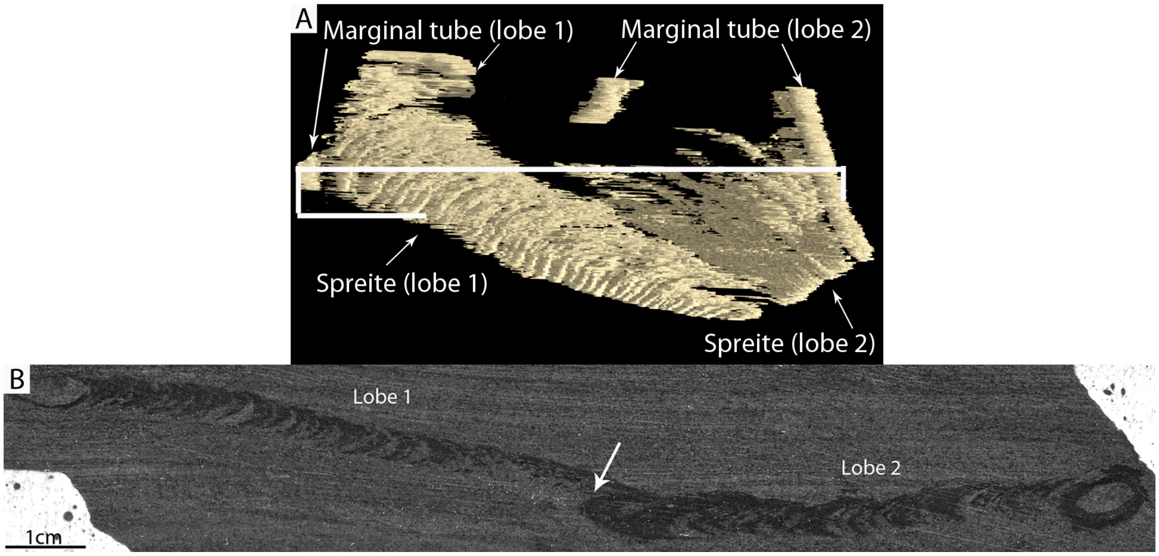

Fig. 4. A: Bedding parallel top-down view of the reconstructed three-dimensional model of the *Zoophycos* trace fossils in this sample labeled as lobe 1 and lobe 2. The sand spreite layer is shown individually to best demonstrate the morphology of each lobe, B: A photograph of the two *Zoophycos* in vertical cross section, taken along the white box in A. White arrows highlight where the two lobes intersect.

3.1 *Zoophycos* lobe 1

The orientation of lobe 1 is generally at a low angle to bedding. It is composed of adjacent spreite that are alternately sand-rich and clay-rich in composition (Fig. 5). Based on horizontal cross sections of the lobe, the approximate percentage of mud to sand in the lobe is 30% mud to 70% sand. The *Zoophycos* lobe is consistently 4-6 mm in vertical thickness (Fig. 5). The internal diameter of the marginal tube is between 8 mm to 2cm, with clay rich lining of variable thickness ranging from 0.5-2cm (Fig. 5). The marginal tube is separated from the alternating spreite by a portion of almost structureless, clay-rich material, such that very few sandy spreite are in direct connection with the marginal tube itself (Fig. 5).

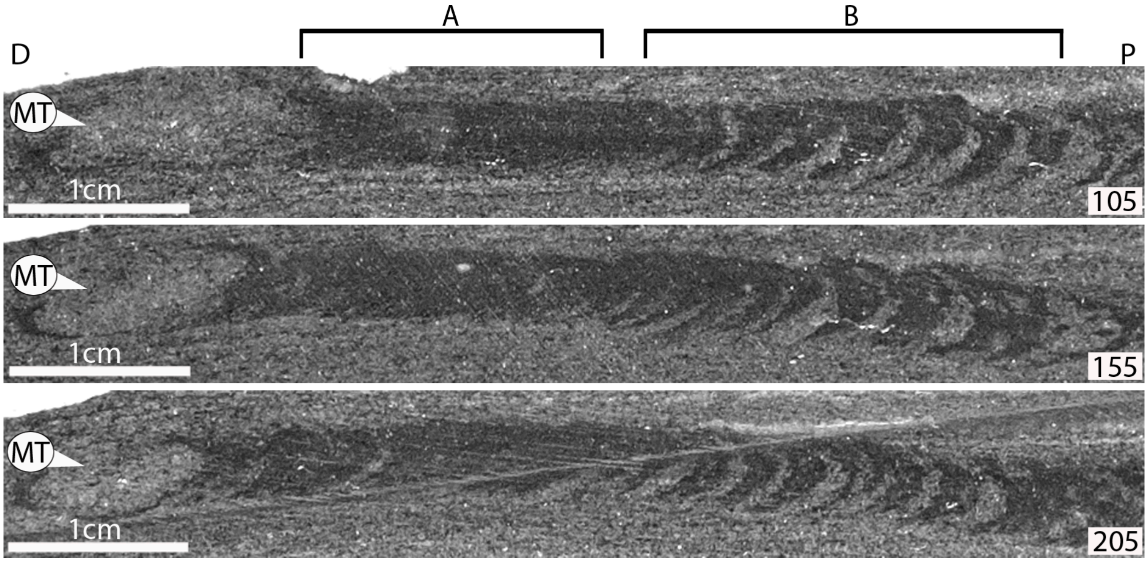

Fig. 5. Morphology of *Zoophycos* lobe 1. A series of vertical cross section images through lobe 1 separated by 0.50 mm. (A) A predominantly clay-rich segment of the lobe that separates the alternating, 1-2 mm spaced sand and clay, chevron to arcuate shaped spreite (B) from the marginal tube (MT). P= proximal, D=distal to the center of the trace.

3.1.1 Spreite

The spreite show large morphological variability from the proximal to distal area of the trace fossil (Fig. 5). The proximal portion along the inclined plane of *Zoophycos* 1 is characterized by chevron-shaped to crescentic-shaped, alternating clay-rich and sand-rich spreite (Fig. 4). As the lobe changes in orientation from slightly inclined to nearly horizontal distally, spreiten morphology changes along the same cross section. The most distal spreite are characterized by alternations of clay rich, arcuate spreite, and comma-shaped sand-rich spreite when seen in vertical cross section (Fig. 6).

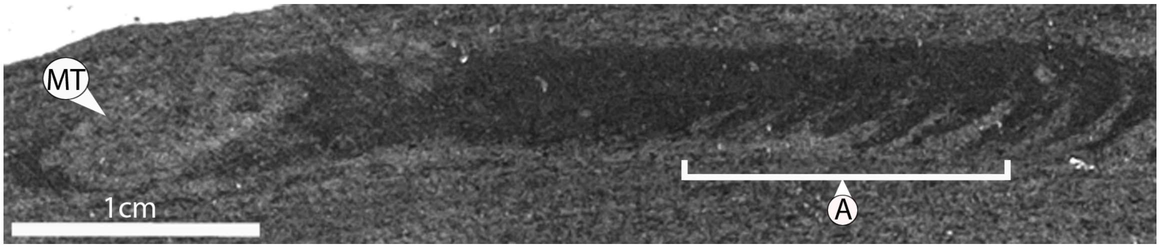

Fig. 6. Vertical cross section through the distal spreite of *Zoophycos* lobe 1 showing comma-shaped sand spreite (A); MT=marginal tube.

In vertical cross section, the spreite range in shape from chevrons to arcs, and consist of closely spaced, alternating sand-grade (light colored) and clay-grade (dark colored) sediment (Fig. 5). Spreite are normally between 1-2 mm in width but can be up to 4 mm in width and are 6 mm in height, and are convex away from the causative (marginal) burrow (Fig. 5). In distal portions of the *Zoophycos* lobes with comma shaped sand-rich spreite, some clay rich spreite occur in clusters that are closely spaced, and lack sand-rich spreite to emphasize their morphology (Fig. 6). Some of the clay-rich spreite contain scattered spherical pellets, though there is no observed systematic organization of pelleted clay spreite in lobe 1 (Fig. 7).

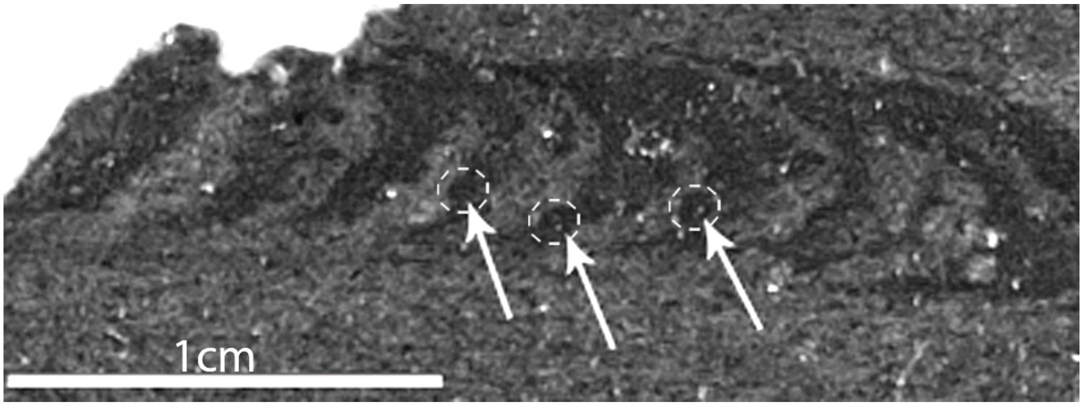

Fig. 7. Spreite of *Zoophycos* lobe 1 with pellets highlighted in the clay rich spreite.

A sequence of digital cross-sections taken from a plane in the bedding parallel orientation of the sample reveals that there are some differences in the distribution of sand- and clay-grade within spreite (Fig. 8). Most of the distal sand-rich spreite are laterally continuous within a single *Zoophycos* lobe (Fig. 8), but at least some of the sand-rich spreite are discontinuous (Fig. 8, 9). Analysis of vertical cross-section photographs and digitally created horizontal cross-sections reveal that the laterally discontinuous spreite are comma shaped in vertical cross section (Fig. 9).

Proximal spreite show more evenly spaced alternations of sand and clay spreite that are of similar width and vertical thickness (Fig. 8). In some cases, however, sand-rich spreite are found to bifurcate suggesting that they were not continuously formed (Fig. 9).

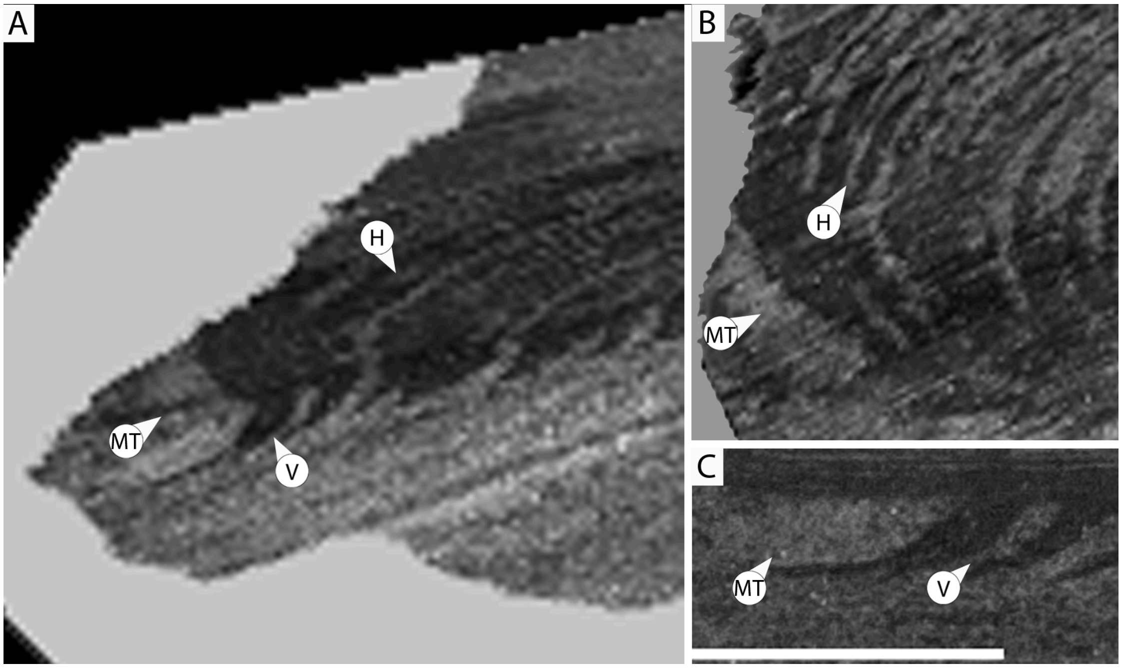

Fig. 8. A three-dimensional reconstruction of the distal spreite near the marginal tube (MT) in *Zoophycos* (1). (A) Three-dimensional view of the trace fossil showing the same spreite in vertical cross section profile (v) and in horizontal cross section profile (H) through Lobe 1, (B) A horizontal cross section of Lobe 1 showing the discontinuous nature of the distal spreite along across the lobe, (C) The vertical cross section of the

spreite showing the comma shape of distal spreite.

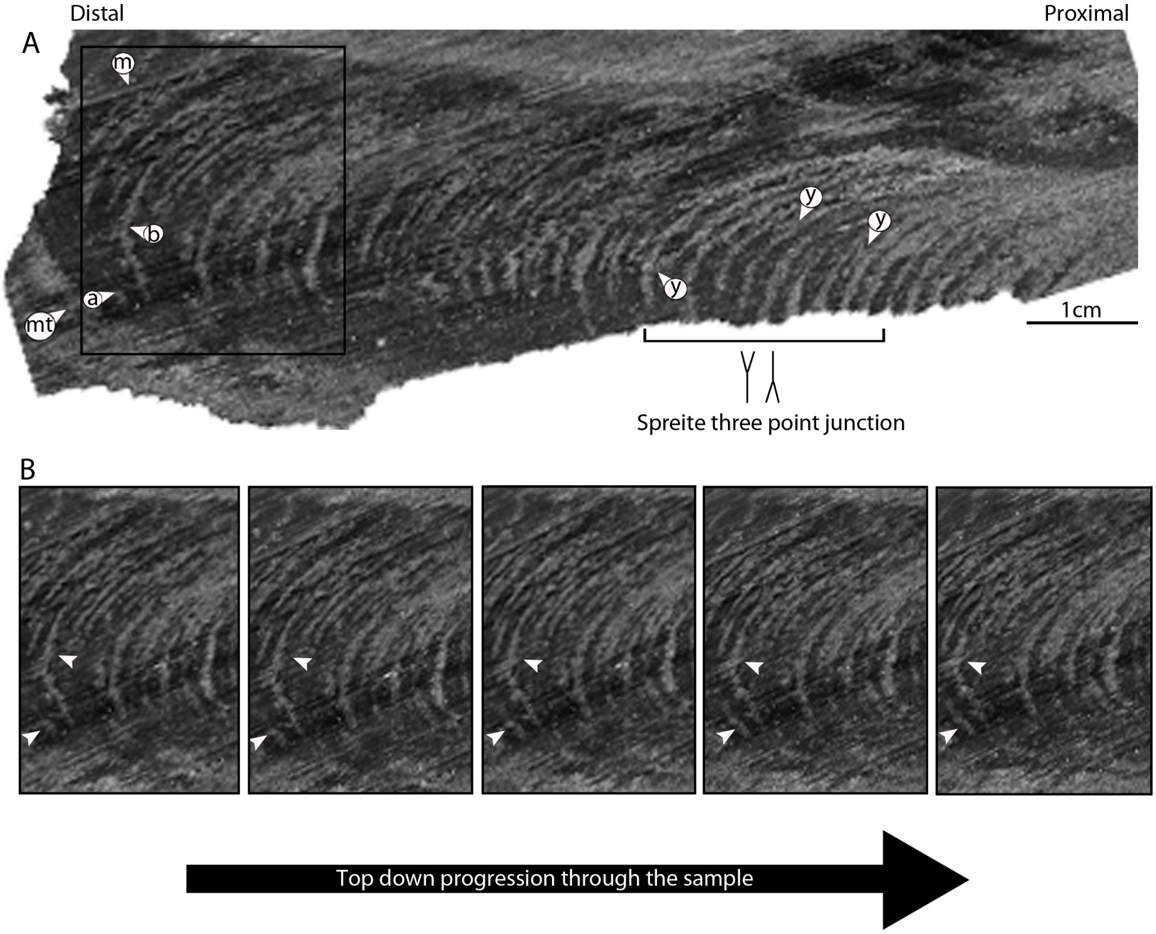

Fig. 9. A: Digitally generated bedding parallel view of *Zoophycos* lobe 1 from the proximal to distal end of the trace fossil. Black box highlights the area of distal spreite as observed in Fig. 8. White arrows highlight two sand spreite, of which one is composed of discontinuous sand packages (a) and the other is continuous across the lobe (b), B: A series of digital cross sections taken from the same plane as in A and separated by 0.5 mm intervals through the bedding parallel plane. White arrows highlight the morphology of the individual spreite in A.

3.1.2 Marginal burrow

The bedding-parallel u-shape marginal burrow of lobe 1 is sand-filled has a very thin (0.5 to 2 mm thick) clay-rich burrow lining (Fig. 10; cf. Wetzel and Werner, 1981).

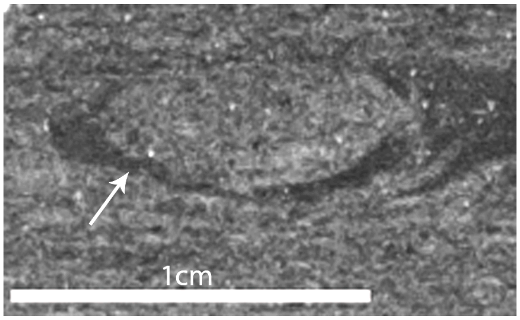

Fig. 10. A cross-section view of the marginal tube of *Zoophycos* lobe 1 showing the clay rich burrow lining and sand infill.

Cross sections of the burrow indicate that the burrow fill does not have meniscate backfill or any angle of repose laminae (Fig. 11). The marginal burrow extends beyond the margins of the hand sample and is thus incomplete (Fig. 4A).

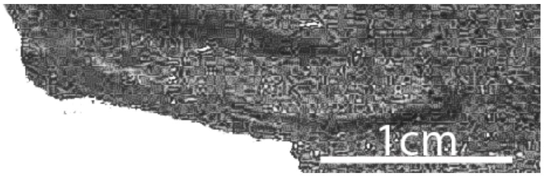

Fig. 11. Vertical cross section through the marginal tube of *Zoophycos* lobe 1.

3.2 *Zoophycos* lobe 2

Zoophycos lobe 2 is broadly bedding parallel, but is in part adjusted so that it becomes coincident with lobe 1 (Fig. 4). The percentage of sand to mud in lobe 2 is approximately 8:2. The thickness of lobe 2 decreases from the proximal to the distal portion (Fig. 12B) in contrast to the predominantly uniform thickness of spreite in lobe 1.

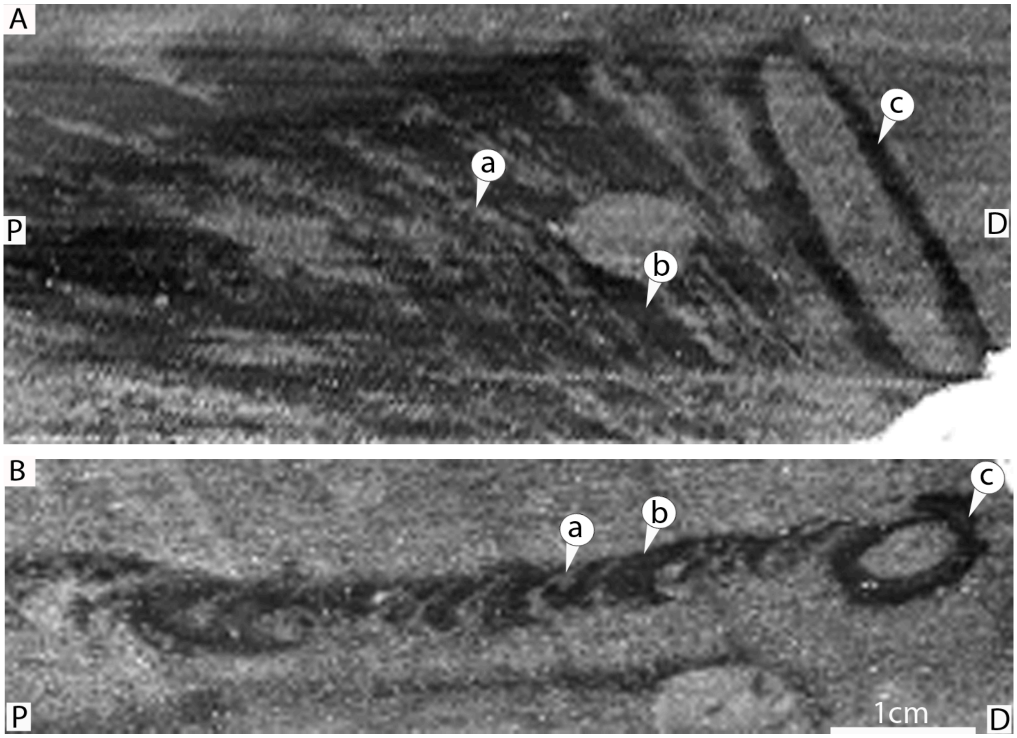

Fig. 12. A: Digital cross-section through the bedding parallel plane of the trace fossil showing the organization of sand (a) and clay (b) spreite and the marginal tube of lobe 2 (c). B: A digital vertical cross-section showing the variation of horizontal and vertical thickness of sand (a) and clay (b) spreite in lobe 2, and the clay lined marginal tube (c). P=proximal area of the trace fossil, D=distal area of the trace fossil.

3.2.1 Spreite

Zoophycos lobe 2 is composed of alternations of clay-rich and sand-rich chevron to arc shaped spreite (Fig. 12B, 13). The spreite in lobe 2 are highly variable in their cross-sectional shape and both vertical and horizontal thickness (Fig. 13). Individual spreite vary in width from 0.5 to 5 mm, and range from 3 to 5 mm in vertical height and width (Fig. 12B). The variability of spreite thickness in lobe 2 may be related to the plane of intersection with the lobe (Fig. 13). For example, in vertical cross-section the proximal end of the trace fossil is characterized by multiple, closely spaced clay rich spreite that form a composite spreiten structure that has a horizontal thickness of 6 mm and a vertical thickness of 7 mm (Fig. 13C). Investigation of the model through various different planes determined that this large spreiten structure had an exaggerated thickness based on the angle of intersection of the spreite and the vertical cross-section plane (Fig. 13). There were no pellets observed in spreite of lobe 1.

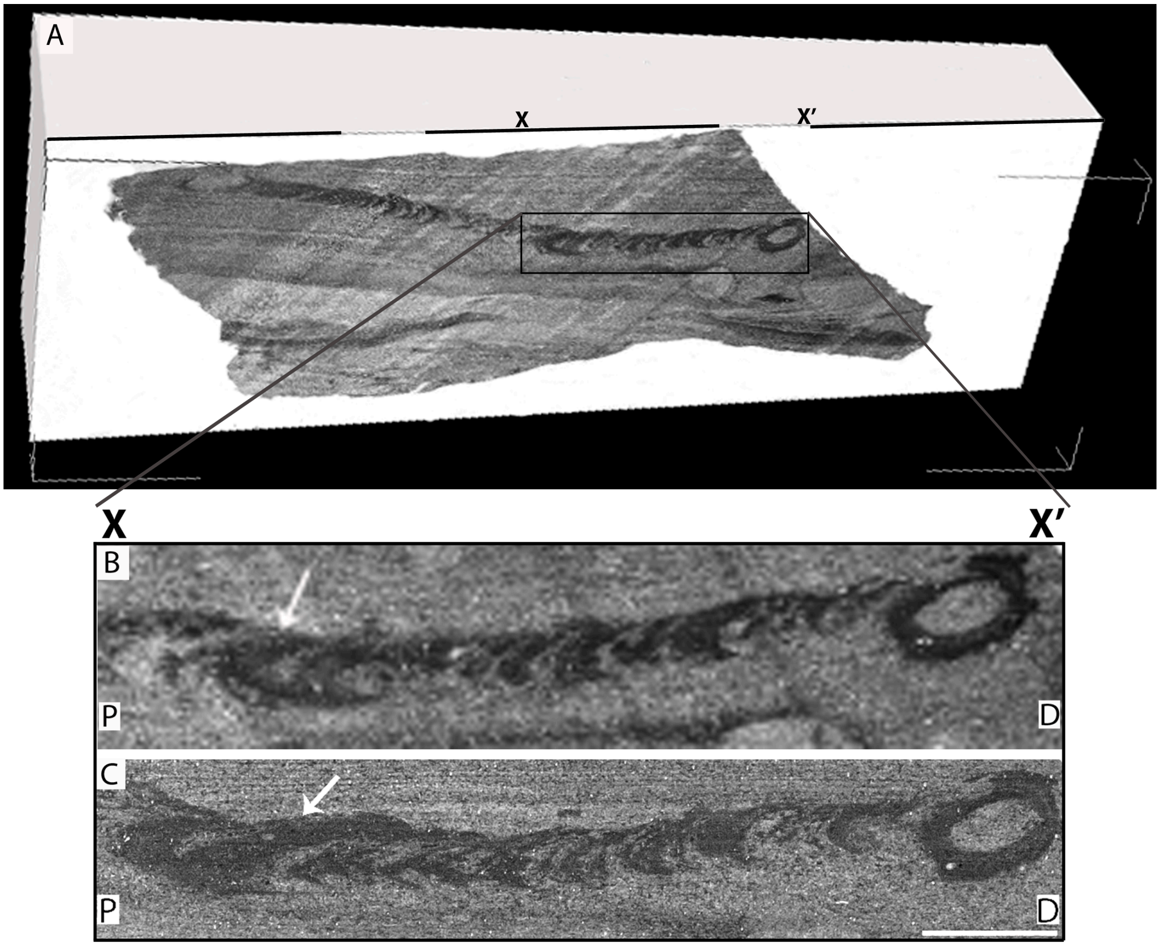

Fig. 13. A: Digital cross-section through the X-X' plane of the trace fossil showing the morphology of the spreite through an oblique plane. White lines show the original dimensions of the rectangular sample block, (B): A vertical digital cross section along X-X' that shows proximal spreite (P) as individual chevron shaped spreite of similar height and width in the lobe, C: Photograph of a vertical cross-section of the lobe from proximal (P) to distal (D) spreite. White arrow highlights a large proximal spreite of abnormal

height and width in the lobe. Investigation of the trace fossil through different planes as in (B) determined the large spreite to be an artifact with an exaggerated thickness due to the angle of intersection of the grinding plane and lobe 2.

3.2.2 Marginal Burrow

The marginal burrow of lobe 2 has a 3 to 5 mm thick clay-rich lining and an internal diameter of 6 to 8 mm, with a sandy inner fill that is similar to the composition of the host sediment (Fig. 14A). There is some irregularity in the outer margin of the clay-rich lining of the marginal tube due to re-burrowing by a different trace-maker (Fig. 14B)

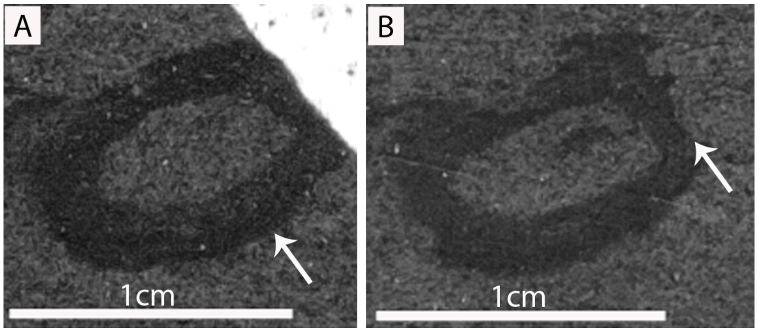

Fig. 14. Marginal burrow of *Zoophycos* 2. (A) Vertical cross-sectional photographs showing the concentric layer of clay around marginal lobe 2, (B) The concentric layer of clay appears to be modified by other burrowing organisms. White arrow highlights the irregularities in the burrow lining that are attributed to the feeding of other organisms and not a constructional process of the *Zoophycos* trace maker.

4.0 DISCUSSION

The appearance of alternating clay-rich and sand-rich spreite in a single *Zoophycos* burrow suggests that the spreite were constructed by successive periods of excavation of sand and deposition of clay, along the proximal side of the causative burrow (cf. Löwemark and Schäfer, 2003). Spreite are thus formed through the successive lateral displacement of the burrow (Häntzschel, 1975). Detailed examination of the *Zoophycos* lobes herein, reveals some of the complexity that is superimposed upon those well accepted models.

4.1 Morphology of Lobe 1 Spreite

The curvature of the spreite in lobe 1 demonstrate the constructional process of the lobe, since they represent the edge of a causative burrow, and are thus convex away from the direction of construction (Wetzel and Werner, 1981). When viewed in the bedding parallel plane, the spreite of lobe 1 are narrow and tightly curved, and are bordered by a marginal tube on both lateral margins (Fig. 4), formed by a U-tube shaped causative burrow (cf. Wetzel and Werner 1981). In the proximal, inclined area of *Zoophycos* lobe 1, the organism alternately lined the entire proximal side of its tube with clay and sand rich material. In the distal, bedding parallel, portion of the burrow, the proximal side of the tube is consistently lined with clay-rich material, while some the sand-rich spreite are comma shaped (Fig. 6). This comma shaped spreiten morphology has been previously described as geopetal indicators (Seilacher, 2007). The asymmetry between adjacent clay and sand meniscate backfill structures has been related to the less cohesive nature of sand grains, causing them to naturally slide to the bottom half of the burrow, leaving an asymmetrical space to be filled by the subsequent clay-rich spreite (Seilacher, 2007). These structures are created during the transport of material as backfill by a burrowing organism, while spreite created by the *Zoophycos* producing animal result from the lateral shifting of its burrow.

In the distal area of the lobe, there is a greater proportion of mud to sand on one side of the lobe, specifically in the area of the comma shaped spreite (Fig. 9). A lateral change in morphology between spreite within the same *Zoophycos* lobe has not been described hitherto in the literature, and is instructive in that it suggests that the process by which *Zoophycos* spreite are formed is not a simple packing of one lithology next to the other, but that there is a directionality to the behavior. The difference in grainsize along the margin of a causative burrow is strongly suggestive of grain-selective behavior by the trace maker, and most probably deposit feeding, which is consistent with the observation of fecal grains in the mud-rich spreite.

It is widely considered that the *Zoophycos* making organism introduced clay rich material from the seafloor, and deposited it on the margins of the causative burrow (Fu and Werner, 1995; Löwemark and Schäfer, 2003). The position of the tube during the excavating phase is then preserved by the packing of sand-rich material from the host sediment and preserved as the sand rich spreite. This general model is likely to hold true for the Rosario Formation *Zoophycos* since the spreite are significantly more mud-rich than the host sediment. It is possible that the trace-maker performed some grain-selective deposit feeding both at the sediment-water interface and by grain selective deposit feeding from surrounding sediment. The organism may also have stored the fine-grained sediment in the *Zoophycos* structure either to fill a void in the sediment left by deposit feeding (cf. Bromley, 1991), or it could be exclusively composed of fecal matter deposited by a surface deposit feeder (cf. Kotake 1989, 1990, 1991). Several studies have shown that in some *Zoophycos* spreite*,* the sediment was transported down from higher levels (cf. Ekdale and Bromley, 1983; Kotake, 1989, 1991; Miller, 1991; Fu and Werner, 1995). *Zoophycos* in the Plio-Pleistocene deposits of Japan consisted of tuffaceous spreite that were linked to an overlying tuff layer, demonstrating the downward transfer of material by a *Zoophycos* trace-making organism (Kotake, 1989). Subsequent studies used carbon dating analysis of carbonate tests in planktonic foraminifera found within the spreiten and adjacent host sediment to show age differences of about 2500 years between the spreiten and adjacent host sediment (Löwemark and Schäfer, 2003).

4.1.2 Fecal pellet distribution

Clay-rich spreite from *Zoophycos* lobe 1 consist of both pelleted and non-pelleted material (Fig. 7), but there is no systematic arrangement of pelleted spreite in this sample (cf., Bischoff, 1968; Chamberlain, 1975; Ekdale, 1977; Wetzel and Werner, 1981; Kotake 1989, 1990, 1991; Fu and Werner, 1995; Miller and D'Alberto, 2001). The Rosario Formation *Zoophycos* spreite contain small, 1 mm diameter, homogenous, spherical pellets composed of clay-grade material, comparable in lithology to the associated mudstones.

4.2 Morphology of Lobe 2 Spreite

The majority of the *Zoophycos* lobe 2 is composed of clay-rich spreite (~85%). Variability in the preserved vertical dimension of spreite in lobe 2 is reflected in the irregular shape of the burrow (Fig. 13). The spreite of this lobe are significantly more clay rich than the otherwise sand-rich host sediment. Since the proximal portion of *Zoophycos* lobe 2 is modified such that it corresponds to the plane of *Zoophycos* lobe 1 (that it post-dates based on their cross-cutting relationship; Fig. 4C). This is taken to indicate that the trace maker of lobe 2 preferentially exploited lobe 1, rather than the host sediment because of the local abundance of fine-grained sediment.

Since the spreite of lobe 1 are re-burrowed by lobe 2, and at least some spreite of *Zoophycos* lobe 1 are composed of pellets that are likely to be fecal (Fig. 7), we consider the reworking of lobe 1 by lobe 2 to possible evidence of allo-coprophagy (cf. Jumars, 1990, 2015). It is unclear whether *Zoophycos* lobe 1 would have been rich in undigested fecal matter, or wither more refractory organic matter in the fecal material would have stimulated a local microbial hotspot that would have been similarly attractive as a food-source for the organism that made *Zoophycos* lobe 2. The clay rich sediment within lobe 1 was bioturbated by another unknown organism, further supporting the inference that the fine-grained portion of *Zoophycos* lobes was an attractive nutrient source. It is not possible to unequivocally demonstrate that the pellets of lobe 1 are fecal or organic rich, and that the trace maker of lobe 2 burrowed the lobe in search of nutrition, though it seems likely. It is possible that the tracemaker preferentially sought to exploit the clay rich spreite of lobe 1 for other reasons, for example burrow stabilization in otherwise loose sediment (Fig. 14).

4.3 Marginal burrow of Lobe 1 and Lobe 2

Zoophycos causative burrows are commonly classified as being either U-shaped or J-shaped (Wetzel and Werner, 1981). A U-shaped burrow indicates that the spreite were completely bound by an open tube system that has been inferred to have been used for burrow ventilation (Wetzel and Werner, 1981). In J-shaped burrow model, an open burrow is present on only one side of the *Zoophycos* lobe (Wetzel and Werner, 1981). The different methods of construction for each type of burrow system have implications on the behaviour of the trace maker, and both types of burrow systems are present in this sample in direct association with one another. The method of construction of *Zoophycos* 1 has been used to suggest a surface detritus- feeding mode of life (downward conveyor), in which the trace-maker deposited fine-grained sediment, and/or fecal matter in the host sediment, whether on purpose as a food cache or not is equivocal at present. Since *Zoophycos* lobe 2 documents successive laterally shifting probing of the sediment and that it seems that it was targeting fine grained sediment it is most likely to have been formed by head-down deposit feeding (an upward conveyor).

The marginal tubes of the two lobes also differ with respect to their burrow linings (Figs. 10, 14). The marginal burrow in lobe 2 is thickly lined with a 3 to 5 mm concentric clay lining, whereas the marginal tube of lobe 1 is similarly clay-rich, and concentric but is only 0.5 to 2mm thick, which is normal for *Zoophycos* ispp. (Olivero and Gaillard, 2007). Organisms that maintain a burrow for long periods of time tend to pay more attention to the construction of their walls (Bromley, 1996). The presence of a thick mud lining to the causative burrow of lobe 2 is inconsistent with the long occupancy model, because the spreite lateral to the burrow suggests frequent systematic burrow shifting. The burrow lining could otherwise have been constructed to isolate the burrow environment from the surrounding, perhaps sulfidic, pore waters (Herringshaw and McIlroy, 2013). The marginal tubes of both *Zoophycos* lobes are oval in cross section, which we attribute to normal sedimentary compaction of a sand-filled burrow rather than collapse of an open burrow (cf. Ekdale and Bromley, 1984; Bromley and Hanken, 2003).

4.4 Ethological Implications of Rosario Formation *Zoophycos*

Examples of complex behavior have been described in *Zoophycos* where the spreite consisted of two main features which include spreite with marginal tubes, and straight to curved, radial tunnels that cross cut the spreite (cf. Miller and D'Alberto, 2001; Knaust, 2009). Galleries of straight to curved tunnels coincident with simple-to-planar spreite with marginal tubes have also been described, which signifies differing behaviours from the same producer in *Zoophycos* trace fossil (Ekdale and Bromley, 1991; Knaust, 2009). *Zoophycos* with radial tunnels that cross cut and preferentially align with spreite have been described as a series of recycling excavations within the burrow system (Miller and D'Alberto, 2001). The evidence of multiple styles of behaviour in a single *Zoophycos* have been linked to seasonal variation in food supply available to the *Zoophycos* producer (Löwemark, 2001; Miller and D'Alberto, 2001; Löwemark and Schäfer, 2003). The expression of this behavior is reflected by the revisitation and exploitation of previously constructed spreite by the *Zoophycos* tracemaker. Evidence of this behaviour has been demonstrated herein through the observation of field photographs, and the three-dimensional reconstruction of Rosario Formation *Zoophycos*.

5.0 CONCLUSIONS

Through serial grinding and three-dimensional reconstruction, the morphology of two *Zoophycos* trace fossils was examined in this study. Several new discoveries have been presented herein:

- The morphology of the two *Zoophycos* burrows present in this sample suggests that they were formed by two different types sets of behaviors.
- *Zoophycos* 1 displays evidence of selective detritus feeding from a layer above the burrow environment since the spreite are more clay-rich than the host sediment.
- *Zoophycos* 2 displays direct evidence of an opportunistic trace maker that sought

to exploit the spreite of another *Zoophycos* through infaunal deposit feeding.

- While the normal mode of life of the *Zoophycos* trace maker cannot be determined conclusively from this sample, this research provides evidence that *Zoophycos* trace-makers can opportunistically adapt to sediment characteristics such as deposit feeding on a previously constructed *Zoophycos* spreite burrow.
- Sand-rich *Zoophycos* spreite have been demonstrated to be laterally discontinuous, passing laterally into mud-rich spreite. This was found to be a systematic lateral trend that persists through many lateral spreite, causing one side of the *Zoophycos* lobe to be more sand-rich than the other.

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Chapter 3

The Influence of *Zoophycos* on Sediment Biogeochemistry

ABSTRACT

Zoophycos **is a widely studied trace fossil that can be found in a range of paleoenvironments. It encompasses a range of vertical burrows characterized by helically stacked sub-horizontal lobes that are composed of radial spreite arranged around a central shaft. A variety of ethological models have been proposed for** ***Zoophycos*****. Few of these ethologies have been verified by detailed biogeochemical analysis. A systematic evaluation of biogeochemical data is demonstrated herein to provide a means by which an ethological model may be tested. This study demonstrated that the** ***Zoophycos*** **trace maker affects the spatial distribution of organic matter, trace element geochemistry, mineralogy, and isotope geochemistry. Analysis of bioturbated and host sediment revealed a measureable difference between ratios of several redox sensitive trace elements commonly used in paleoenvironmental analysis. In-vivo weathering was inferred in this study by the presence of the authigenic clay mineral berthierine within the** ***Zoophycos*** **spreite. The detailed biogeochemical analysis employed in this study has provided a systematic method to analyze biogeochemical data and document the influence of the** ***Zoophycos*** **trace maker on sediment biogeochemistry. This study also has implications on the validity of detailed biogeochemical analysis in paleoenvironmental studies in heavily bioturbated sedimentary units. There is a documented spatial difference in redox sensitive trace elements between bioturbated sediment and host sediment. These results favor a detailed biogeochemical analysis over box-geochemical models in order to**

properly characterize the geochemical characteristics of bioturbated intervals.

1. INTRODUCTION

It has long been known that organisms modify the physical, chemical, and biogeochemical properties of sediments (e.g. Aller, 1982; Aller, 2004; McIlroy et al., 2003). The fossil record of the biogeochemical changes induced by burrowing organisms is, however, less well documented (cf. McIlroy and Logan, 1999; Löwemark et al., 2004, 2007; Harazim et al., 2013; Izumi, 2014; Harazim et al., 2015). Recent study of *Phycosiphon*-like trace fossils of the Rosario Formation documented complex spatial redistribution and fractionation of redox-sensitive trace elements in different portions of the burrow (Harazim et al., 2015). These *Phycosiphon*-like trace fossils have been found to change sediment mineralogy due to biological weathering (McIlroy et al., 2003), fractionate and redistribute redox-sensitive trace elements, and affect both the abundance and stable isotopic composition of organic matter (Harazim et al., 2015). The present study employs the same approach to investigate the fractionation and redistribution of elements and minerals in association with the common deep marine trace fossil *Zoophycos*. Despite over a century of research, there remains no unifying explanation for the construction of *Zoophycos* that accounts for its interactions with the host sediment (cf. Löwemark, 2015). The biogeochemical mapping undertaken herein is designed to identify biogeochemical differences between *Zoophycos* burrows and the surrounding sediment as a means whereby aspects of the pre-established behavioral models for the *Zoophycos* trace-maker can be tested.

The studied *Zoophycos* sample was collected from the fine-grained sandstones of the late-Cretaceous Rosario Formation, Baja California, Mexico (Fig. 1).

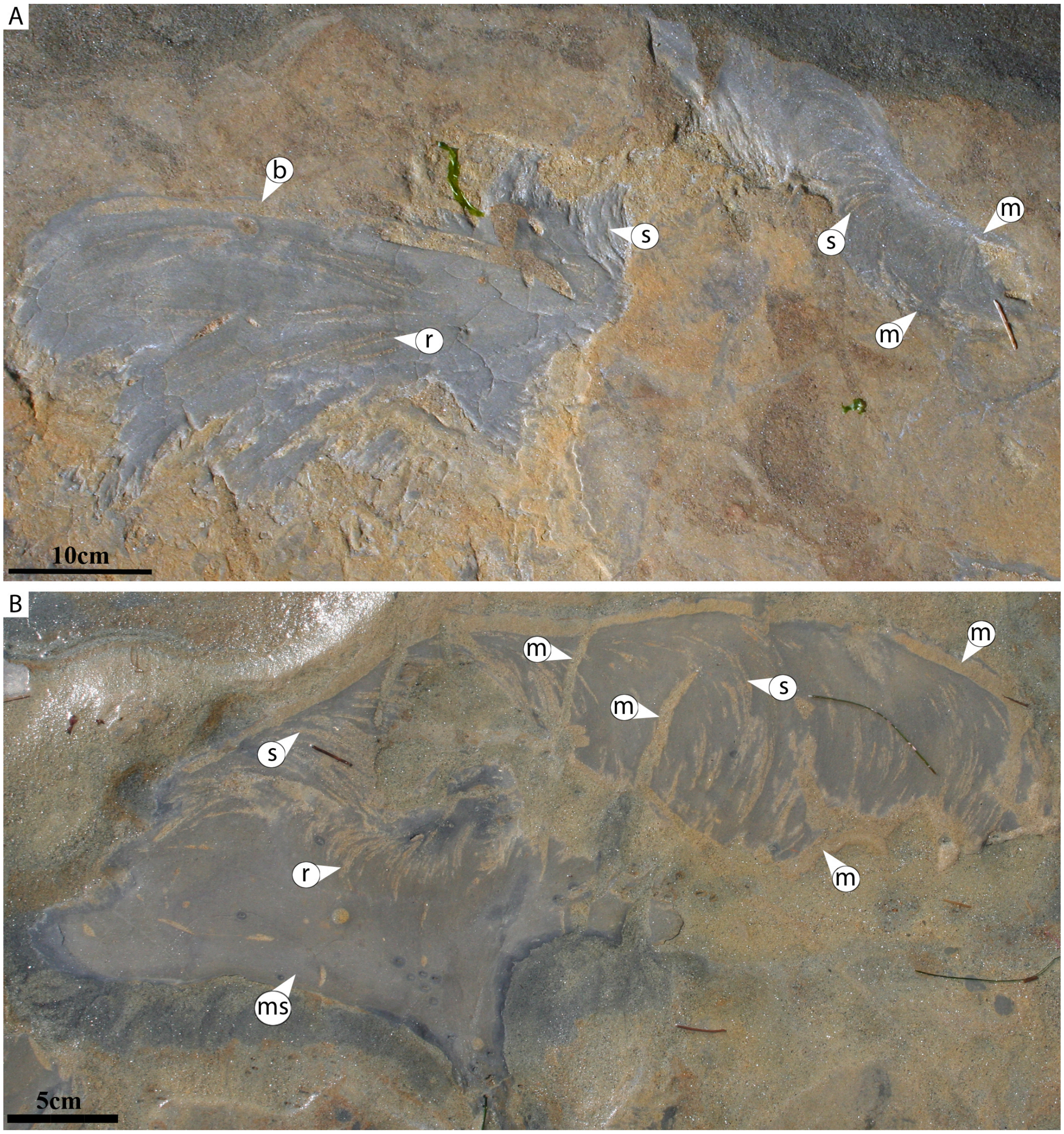


FIGURE 1— Field photographs of *Zoophycos* in bedding plane view. A: Two individual *Zoophycos* are coincident in which one has narrow, tightly curved spreite (s) that are bordered by a mud-rich marginal tube (m). The second *Zoophycos* has long, radial spreite (r) that are terminated by a sand rich-causative burrow (b), B: A *Zoophycos* with a mud-

rich sheet (ms) is cut by small, radial spreite (r) of a later *Zoophycos* which has a sand rich marginal tube (m) that cuts across the narrow, curved spreite (s) in its lobe in multiple locations. These samples were observed in the field and not used in this study.

Zoophycos is a highly heterogeneous taxon which encompasses a range of vertical burrows that are characterized by helically stacked sub-horizontal lobes composed of radial spreite arranged around a central shaft (Löwemark and Schäfer, 2003). In vertical cross-section, *Zoophycos* spreite are crescent-shaped to chevron-shaped alternations of light and dark material that are convex towards the burrow center and have at their distal margin a causative burrow with no internal lamination (Fig. 2).

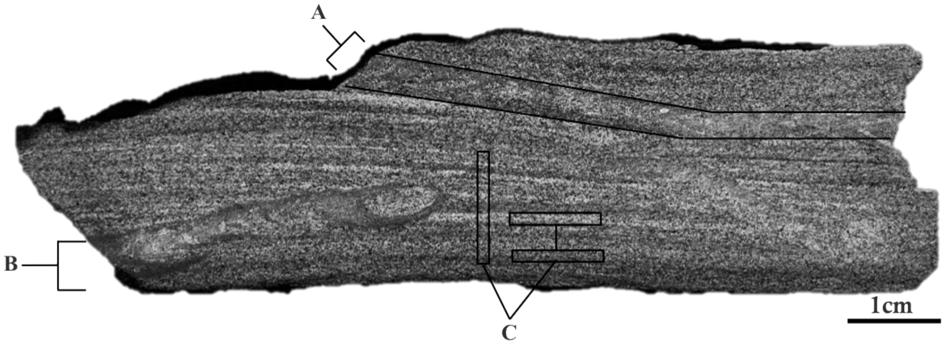


FIGURE 2— Location of sampling areas for the *Zoophycos* burrows and surrounding host sediment. A: Clay-rich burrow. B: sand-rich burrow. C: Host sediment.

The detailed analyses undertaken herein include the spatially constrained characterization of: 1) redox-sensitive trace element abundance and ratios; 2) mineralogy; and 3) stable isotopic composition and abundance of organic matter.

Studies have shown that trace-element abundances within sedimentary rocks can be used to reconstruct palaeoenvironmental conditions (cf. Forchielli et al., 2014 and papers therein: Werne et al., 2003; Lyons et al., 2003; Rimmer, 2004; Algeo, 2004; Tribovillard et al., 2004; Algeo and Lyons, 2006; Gains and Droser, 2010). Certain trace elements are known to vary predictably to changes in bottom water redox conditions (e.g. Algeo and Maynard, 2004; Tribovillard et al., 2004). Some studies have proposed that systematic trace element enrichments and depletions can be used to distinguish between sub-oxic and anoxic-euxinic environments (Tribovillard et al., 2004). Vanadium, chromium, nickel, copper, colbalt, molybdenum, and uranium are considered to be the common trace elements that are least vulnerable to burial diagenesis (Tribovillard et al., 2004). Any difference in abundance of trace elements in the *Zoophycos* spreite relative to the host sediment could potentially indicate that the sediment biogeochemistry was altered by the life activities of the trace maker and associated microbiota. If trace element distributions are indeed fractionated during creation of *Zoophycos* burrows, then the use of redox proxies for the reconstruction of paleo-oxygenation in *Zoophycos*-bearing facies is likely to reflect this biogenic signal rather than seafloor oxygenation (cf. Harazim et al., 2015). Trace element fractionation might be a product of the creation of authigenic minerals from detrital minerals by biological weathering (McIlroy et al., 2003; Harazim et al., 2015), which would also be reflected in changes in bulk mineralogy.

2.0 MATERIALS AND METHODS

This study is based on a sample of *Zoophycos* from the fine-grained Late Cretaceous (Maastrichtian) Canyon San Fernando channel-levee system of the Rosario Formation, Baja California, Mexico (Fig. 3). The hand sample was cut to expose a fresh surface from which sediment grains could be extracted for analysis. Bioturbated and non-bioturbated sediment was excavated with sub-millimeter precision using a stationary high-precision micro-mill sampling device. Powders were collected from three areas of the sample, including the host sediment, mud-rich spreite, and sand-rich spreite (Fig. 2). Analytical replicates were taken from a subsample of the initial sample. The geochemistry of the sediment was determined using three types of analysis: 1) Trace element analysis was performed using ICPMS (Appendix A); 2) mineral analysis was performed using X-Ray Diffraction (XRD) technology (See Appendix B); and 3) the isotopic composition and abundance of organic matter in the sediment was determined using carbon and sulfur isotopic analysis (Appendix C). See Appendix D for the collection of *Phycosiphon*-like trace fossil data used to compare similar biogeochemical data from another trace fossil in the Rosario Formation.

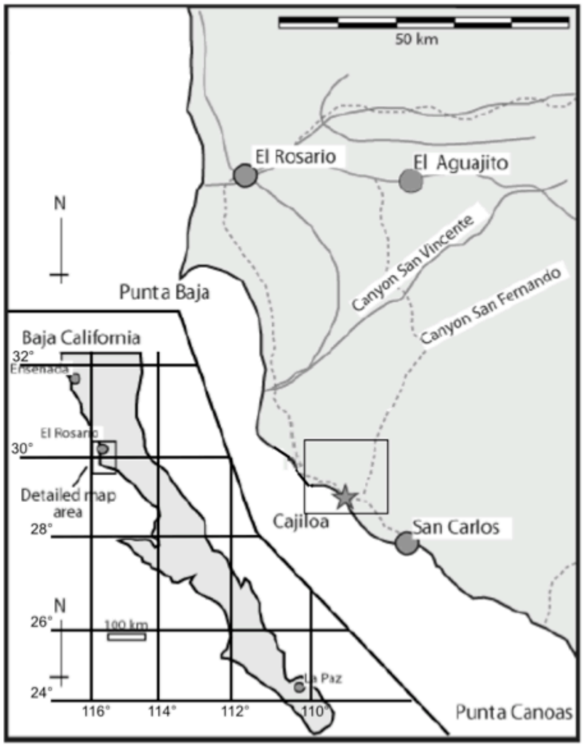


FIGURE 3— Location of study area near Cajiloa, Canyon San Fernando, Baja California (modified from Bednarz and McIlroy, 2009).

3.0 RESULTS: COMPARATIVE BIOGEOCHEMISTRY OF *ZOOPHYCOS* AND ITS HOST SEDIMENT.

To quantify biogeochemical differences between the trace fossil and the host sediment, three separate areas were precisely sampled using a micro-milling machine and a hand held micro-engraver. These areas include: 1) an area of host sediment; 2) a sand-rich *Zoophycos* burrow; and 3) a clay-rich *Zoophycos* burrow (Fig. 2).

3.1 Biogeochemical characteristics of *Zoophycos* spreite: ICPMS trace element data

ICP-MS trace element data are presented as ratios of relative enrichment or depletion for redox-sensitive trace elements between *Phycosiphon*-like and *Zoophycos* trace fossils, and their respective host sediment (Fig. 4). These trace elements are commonly used in paleoenvironmental reconstructions (Tribovillard et al., 1994; Robinson et al., 2002; Riboulleau et al., 2003; Cruse and Lyons, 2004; Algeo and Maynard, 2004; Tribovillard et al., 2004, 2005; Tribovillard et al., 2006).

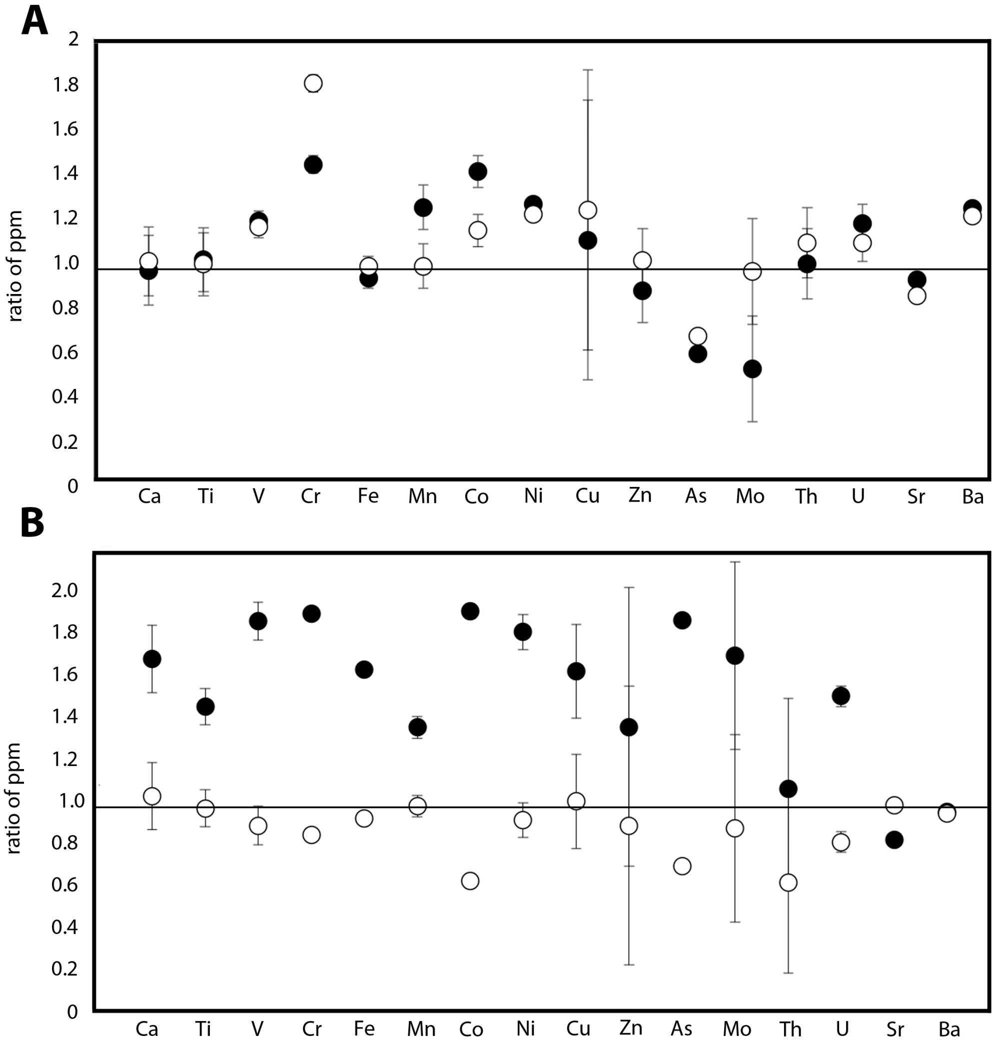
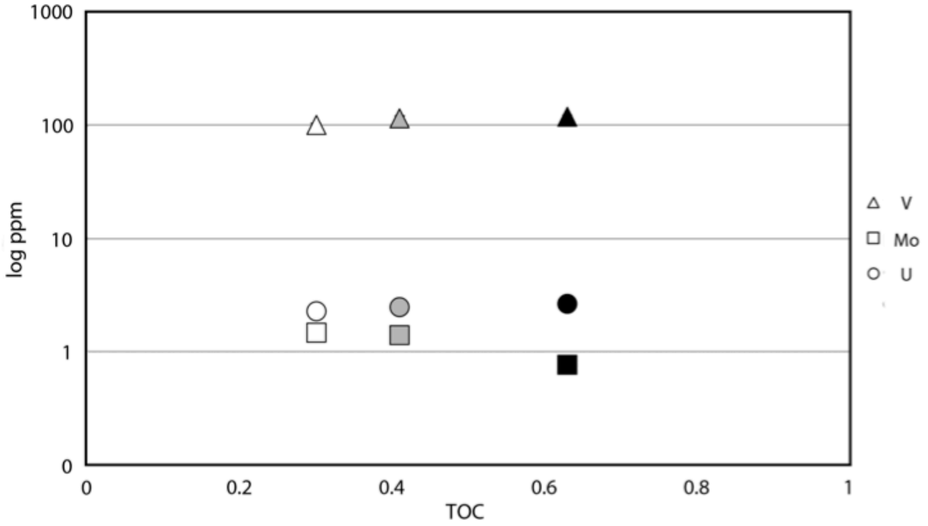


FIGURE 4— Inductively coupled plasma–mass spectrometry (ICP-MS) data for burrowed and host sediment. Relative enrichment or depletion of redox-sensitive trace elements normalized to host sediment. A: *Zoophycos* clay-rich burrow (black) and sand-rich burrow (white), B: *Phycosiphon* core (black) and burrow halo (white). Error bars represent analytical precision.

Trace element enrichment in both the sand-rich and clay-rich *Zoophycos* burrows is seen in vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), uranium (U), and barium (Ba) (Fig. 4). Manganese (Mn) is significantly enriched solely in the clay-rich burrow. Relative depletion in both arsenic (As) and strontium (Sr) is seen in both burrows while Molybdenum (Mo) is depleted solely in the clay-rich burrow. The trace elements from the two *Zoophycos* burrow show similar trends in enrichment or depletion relative to the host sediment. The majority of the enriched trace elements in the burrows are slightly more enriched in the finer grained, clay-rich sediment portion (Fig. 4). Measurements from the *Phycosiphon* burrow core and halo represent fractionation between both the fecal mud rich core and the sand rich halo of the trace fossil, relative to the host sediment (Fig. 4B). The majority of the redox sensitive trace elements is enriched in the finer grained core and is depleted in the sand rich halo (Fig. 4).

Several of the redox-sensitive trace elements that are systematically fractionated between burrowed and host sediment have an established response to variations in bottom water redox conditions in the depositional environment (Tribovillard et al., 2006 and references therein). These trace elements, most notably Ni, Co, Cu, V, Cr, U, Pb, and Mo, are commonly used in the reconstruction of paleoenvironmental conditions based on bulk rock data (Tribovillard et al., 2006; Forchielli et al., 2014). Multiproxy paleoredox and paleoproductivity analyses demonstrate that groups of trace elements with similar behavior patterns in response to varying redox conditions are reliable tools in these benthic condition reconstructions (Algeo and Maynard, 2004; Tribovillard et al., 2006). Trace elements such as U and V are reduced and will accumulate under denitrifying conditions, while trace elements like Ni, Mo, and Cu are enriched almost exclusively under sulfate-reducing conditions (Tribovillard et al., 2006). Several studies suggest that this contrasting relationship can aid in determining between sub-oxic-anoxic and euxinic sediments (Algeo and Maynard, 2004, Tribovillard et al., 2004, 2005, 2006). The distinction between sub-oxic and euxinic environments is also helped by the variation of U, V, and Mo enrichment with TOC values (Tribovillard et al., 2006). These groups of elements were plotted together to compare the redox signatures of the trace fossils with the surrounding host sediment (Fig. 5). The clay-rich *Zoophycos* burrows show a slight relative enrichment in the U and V concentrations and a relative depletion of Mo, relative to the host sediment (Fig. 5). Enrichment in U and V without a simultaneous enrichment in Mo is said to infer an environment that lacks free H_2S (Tribovillard et al., 2006). Pyrite has been previously documented with *Zoophycos* (Gong et al., 2007, 2008), but did not happen to be observed in thin sections created from the hand sample. The fecal core of the *Phycosiphon*-like trace fossil shows a relative increase in U, V, and Mo concentrations compared with the host sediment (Fig. 5). Concurrent enrichments in U, V, and Mo are linked to euxinic conditions at the sediment-water interface or in the water column (Tribovillard et al., 2006). In euxinic conditions Mo is often associated with pyrite and sulfur-rich organic material and Mo enrichment above certain TOC values accompanies U-V enrichment, and marks the development of euxinic conditions (Tribovillard et al., 2006). Rare pyrite was documented around the *Phycosiphon*-like trace fossil (Harazim et al., 2015).

A



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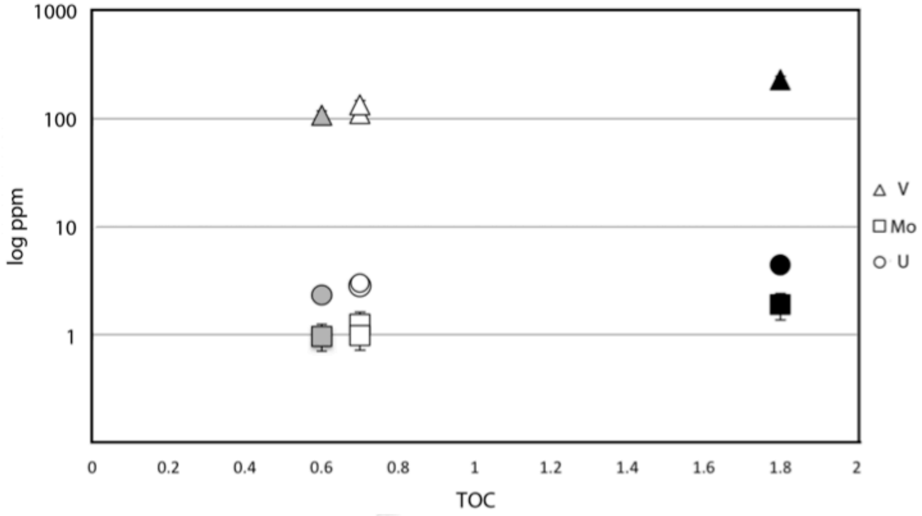

FIGURE 5— U, Mo, and V concentrations in trace fossil and host sediment for A: *Zoophycos* and B: *Phycosiphon*-like trace fossils. *Zoophycos* host sediment (TOC= 0.30), *Zoophycos* sand-rich burrow (TOC= 0.41), Phycosiphoniform halo (TOC= 0.6), *Zoophycos* clay-rich burrow (0.63), Phycosiphoniform host sediment (TOC=0.7), and Phycosiphoniform fecal core (TOC=1.8).

Based on the fractionation of several other important redox-sensitive trace elements between host and burrowed sediment (e.g. Cr, Co, Zn, Pb, Ni, Cu) it is possible to identify the paleoredox conditions prevalent in the sediment, from sub-oxic to euxinic (Tribovillard et al., 2006). When plotted with TOC values these trace elements show unique co-variation patterns, which can help distinguish between different paleoredox conditions (Tribovillard et al., 1994; Riboulleau et al., 2003; Cruse and Lyons, 2004; Algeo and Maynard, 2004; Tribovillard et al., 2004b; Tribovillard et al., 2005; Robinson et al., 2002). Sub-oxic to anoxic redox environments will show positive correlations in Ni, Cu, Cr, and Co values with increasing TOC. Ni and Cu are mainly brought to the sediment in organometallic complexes and are therefore considered valuable paleoproductivity proxies (Algeo and Maynard, 2004). Zn and Pb are among trace elements that are associated with sulfate reducing components and have a strong euxinic affinity. In the *Zoophycos* sample, similar to the decrease in Mo concentration in the burrows, Zn and Pb both display a similar relative depletion in the burrow component, which is consistent with a more anoxic rather than a euxinic trend in the data (Fig. 6). The Zn and Pb values are all within error in the *Phycosiphon* sample. In both the *Zoophycos* and *Phycosiphon* samples, the Cu data points are all within error, however the

Ni concentrations are relatively enriched in the burrow environment for both specimens (Fig. 7). Cr and Co values show concurrent enrichment in the burrow environments in both the *Zoophycos* and *Phycosiphon* trace fossils (Fig. 8).

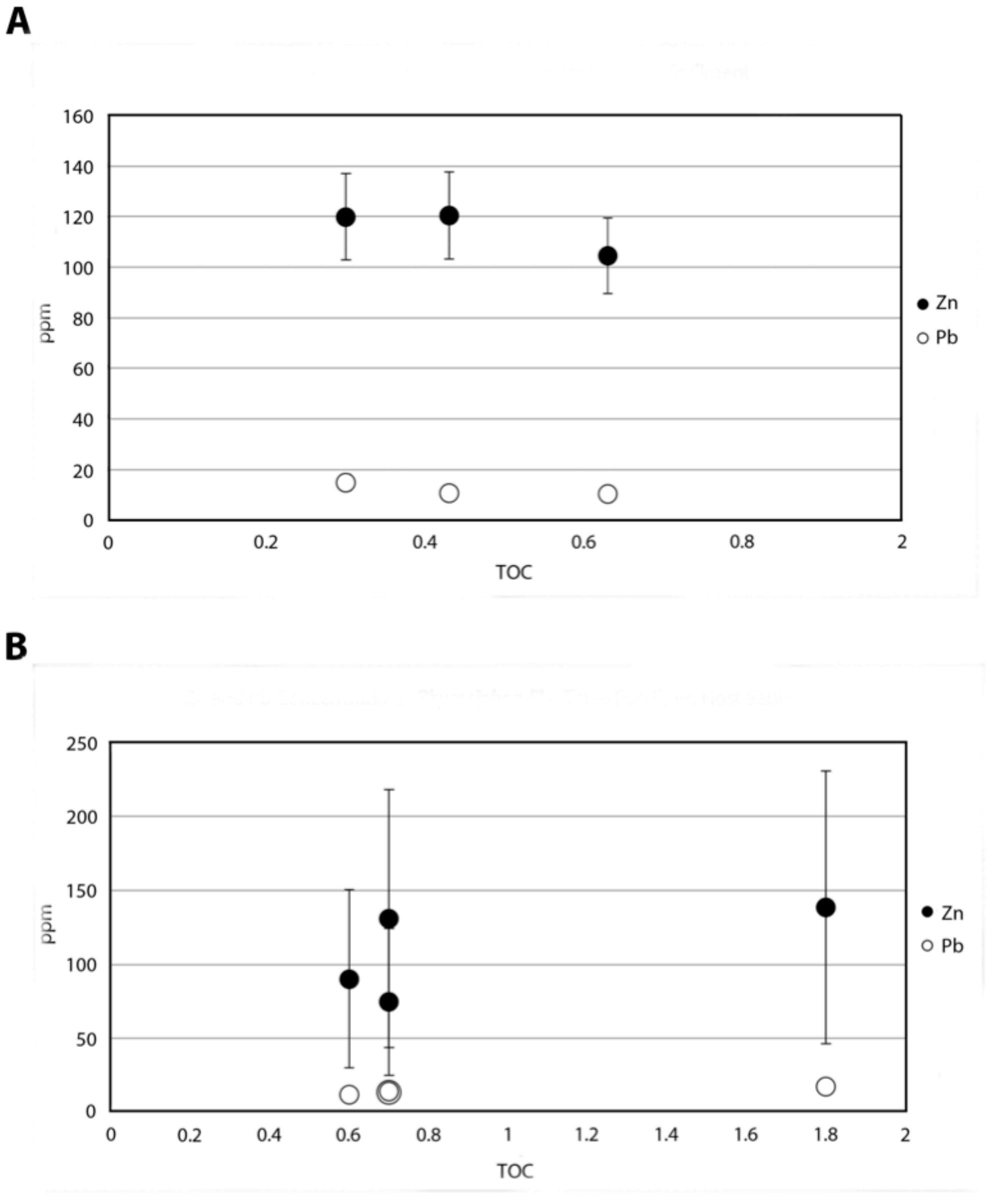

FIGURE 6— Zn and Pb concentrations for A: *Zoophycos* and B: *Phycosiphon*-like trace fossils from the Rosario Formation. *Zoophycos* host sediment (TOC= 0.30), *Zoophycos*

sand-rich burrow (TOC= 0.41), Phycosiphoniform halo (TOC= 0.6), *Zoophycos* clay-rich burrow (0.63), Phycosiphoniform host sediment (TOC=0.7), and Phycosiphoniform fecal core (TOC=1.8).

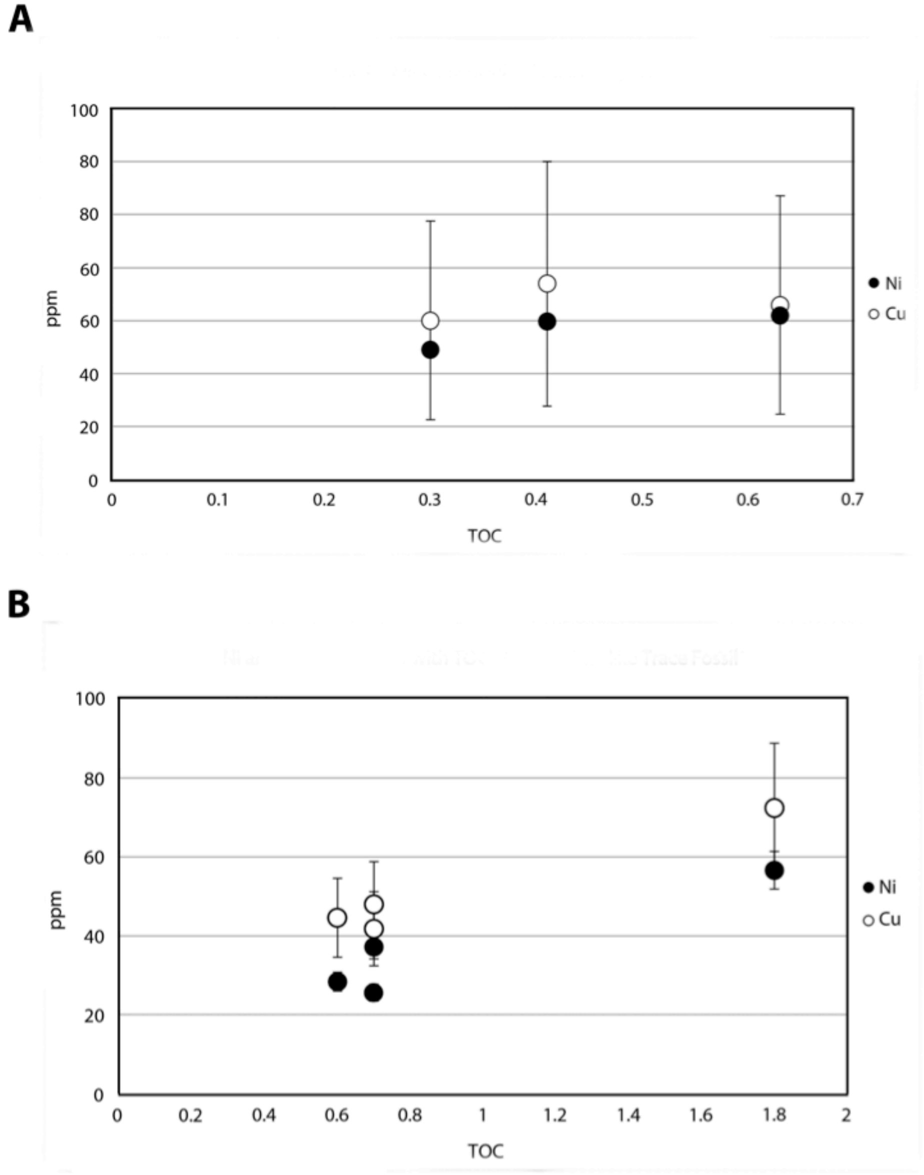

FIGURE 7— Ni and Cu concentrations for A: *Zoophycos* and B: *Phycosiphon*-like trace fossils from the Rosario Formation. *Zoophycos* host sediment (TOC= 0.30), *Zoophycos* sand-rich burrow (TOC= 0.41), Phycosiphoniform halo (TOC= 0.6), *Zoophycos* clay-rich

burrow (0.63), Phycosiphoniform host sediment (TOC=0.7), and Phycosiphoniform fecal core (TOC=1.8).

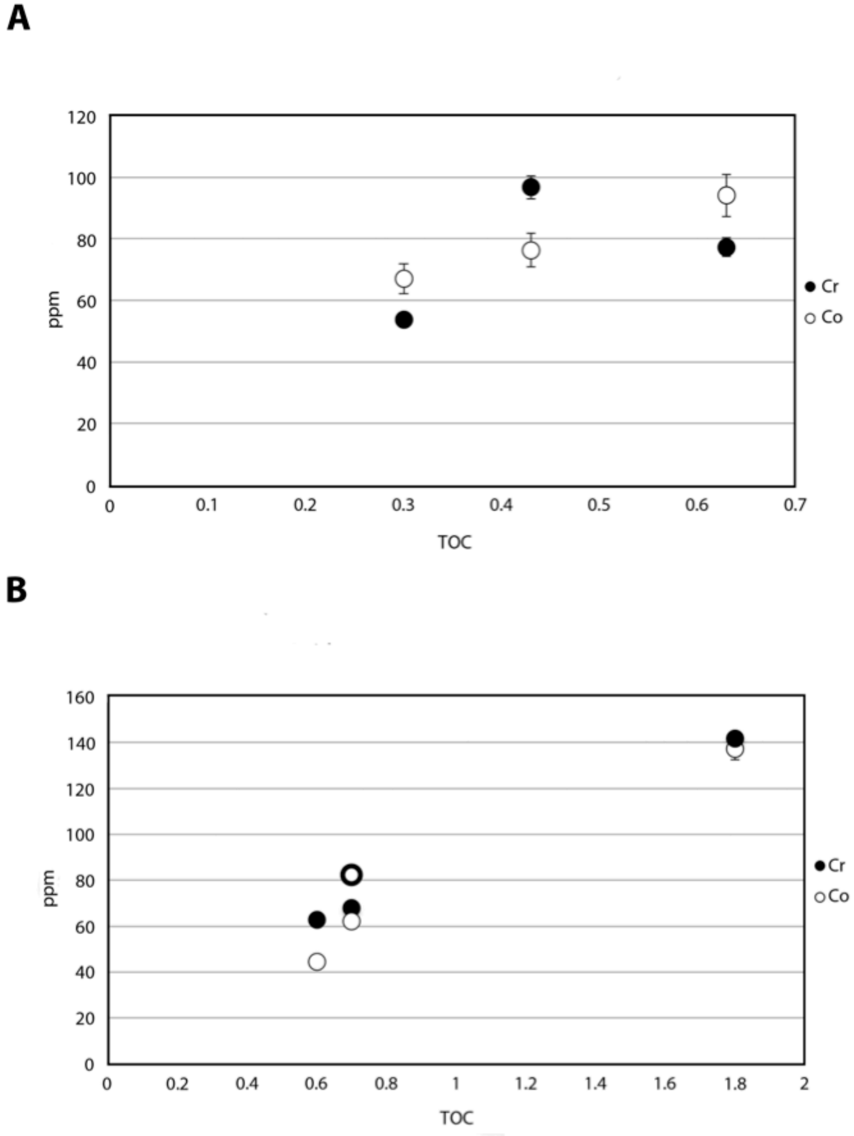

FIGURE 8— Cr and Co concentrations for A: *Zoophycos* and B: *Phycosiphon*-like trace fossils from the Rosario Formation. *Zoophycos* host sediment (TOC= 0.30), *Zoophycos* sand-rich burrow (TOC= 0.41), Phycosiphoniform halo (TOC= 0.6), *Zoophycos* clay-rich burrow (0.63), Phycosiphoniform host sediment (TOC=0.7), and Phycosiphoniform fecal core (TOC=1.8).

These correlations are most reliable in sediments with higher TOC values (Algeo and Maynard, 2004; Tribovillard et al., 2006). Trace element and TOC data from two sets of bioturbated and host sediment samples are plotted together (Fig. 9).

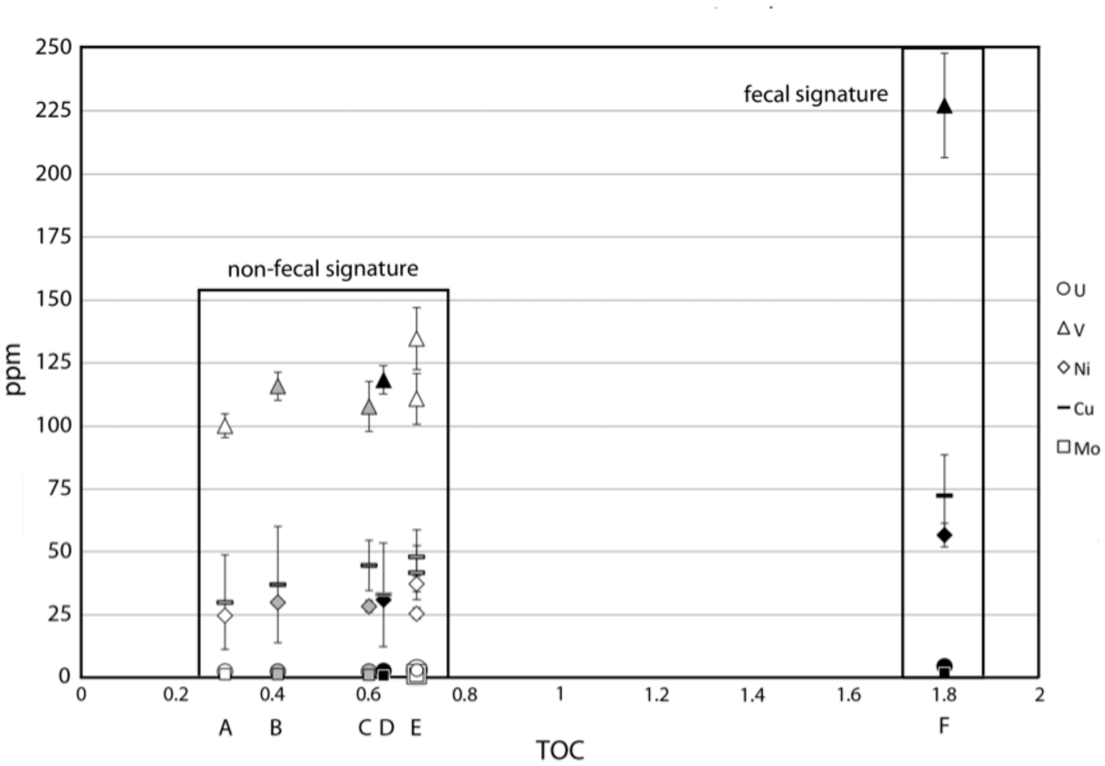

FIGURE 9— Trace element enrichment with increasing total organic carbon for *Zoophycos* and *Phycosiphon*-like trace fossils from the Rosario Formation. A: *Zoophycos* host sediment (TOC= 0.30), B: *Zoophycos* sand-rich burrow (TOC= 0.41), C: Phycosiphoniform halo (TOC= 0.6), D: *Zoophycos* clay-rich burrow (0.63), E:

Phycosiphoniform host sediment (TOC=0.7), and F: Phycosiphoniform fecal core (TOC=1.8). All TOC values are listed in wt % organic carbon.

Trace element and TOC data for both trace fossils are of similar concentration and organic carbon (wt %) values, apart from the values from the fecal core of the *Phycosiphon*-like burrows (Fig. 9). The trace elements in the fecal core are all significantly enriched, apart from Mo, when compared with the trace elements from the other sampled areas (Fig. 9). The increase in organic matter and redox sensitive trace element concentrations in the core of the *Phycosiphon* trace fossil indicates a more anoxic-euxinic signature than the other data points. The *Phycosiphon* core was previously demonstrated to be fecal in nature (Harazim et al., 2015). There is a relatively small fractionation in trace element enrichment between the host sediment and the sand-rich halo of *Phycosiphon*. This is expected in the *Phycosiphon* data, as the burrow halo represents cleaned host sediment, with clay minerals preferentially sorted and removed by the trace maker (Harazim et al., 2015). Several of these trace elements also function as micronutrients for microbes and macroorganisms (e.g. Collier, 1985; Calvert and Pedersen, 1993; Algeo and Maynard, 2004).

3.2 Biogeochemical characteristics of *Zoophycos* spreite: XRD Data

The peak widths and intensities of the major and minor minerals in all of the sampled components vary between the spreite and the host sediment (Fig. 10). These peaks are highlighted as enhanced, attenuated, or new, in relation to either burrow. Enhanced mineral peaks in the burrows are seen for muscovite at 19.9° and 23° 2θ (Fig.

10). Feldspar peaks for albite and anorthite are attenuated in both burrows at multiple, 2θ angles (23.8°, 24.1°, 27.9,° 29.1°, and 30.2°) (Fig. 10). At 22° 2θ, the peak for albite and anorthite is strongly attenuated in the clay-rich burrow, while the same peak is enhanced in the sand-rich burrow (Fig. 10). This could be due to the low clay component in the sand-rich burrow. New peaks for the mineral berthierine are seen in the burrows and are not present in the host sediment at 2θ angles 29.3° and 31.3° (Fig. 10). A peak for the mineral berthierine is also seen in the burrows at 33.8° 2θ, the appearance of which broadens a sharp peak in the host sediment, a feature that is characteristic of the introduction of new minerals (Fig. 10). The alteration of feldspars such as albite and anorthite and the production of the clay mineral berthierine have been linked to in-vivo weathering by organisms (McIlroy et al., 2003; Harazim et al., 2015).

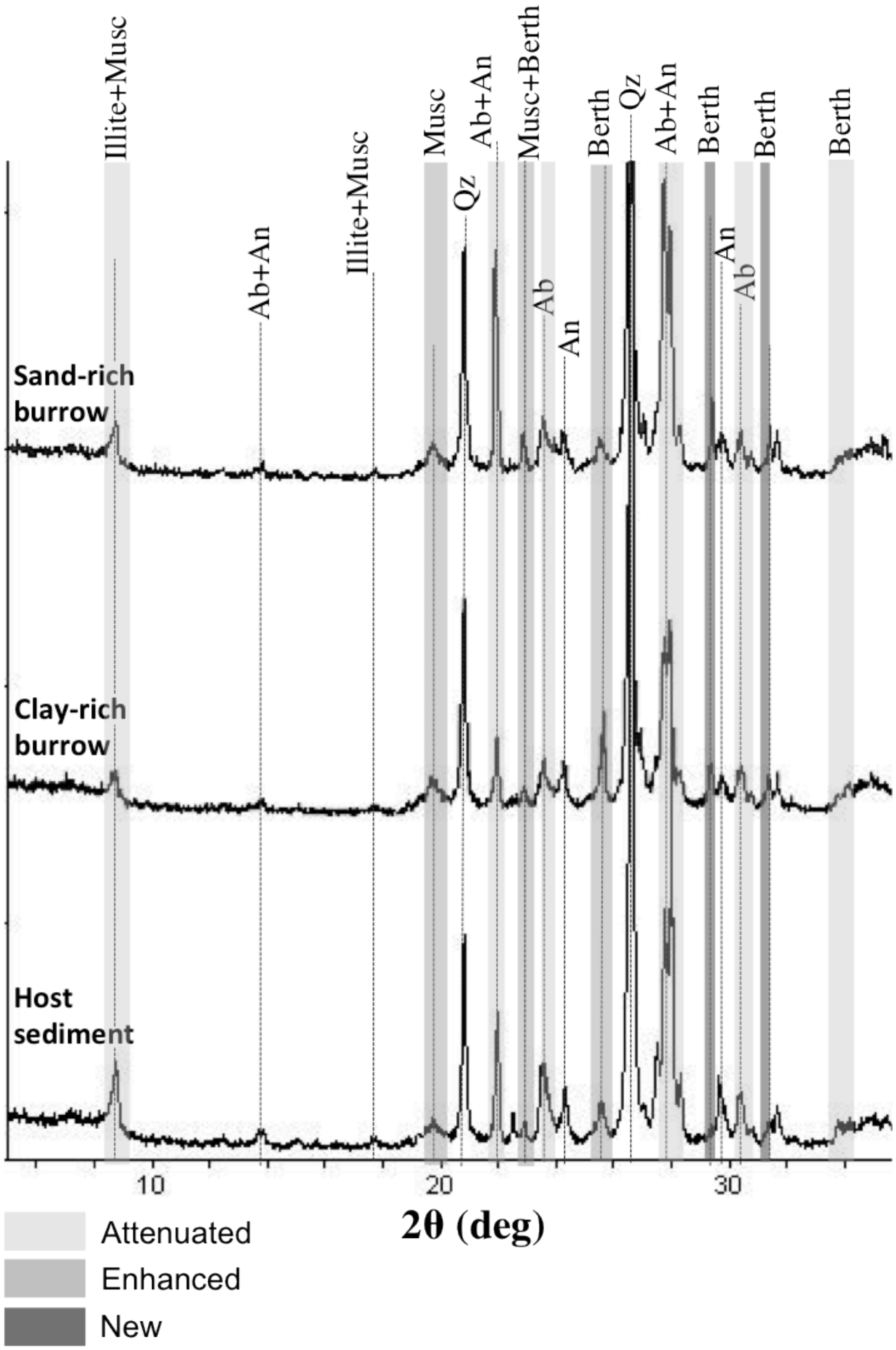

FIGURE 10— Comparative mineralogy of host sediment, clay-rich spreite, and the sand-rich spreite as determined by X-ray diffraction. Musc-muscovite; Ab-albite; An-anorthite; Qz-quartz. Attenuated, Enhanced, and New refer to changes in peak response

in the burrows relative to the host sediment. The plots show the formation of authigenic berthierine and decrease in the abundance of albite/anorthite in *Zoophycos* spreite relative to the host sediment.

3.3 Biogeochemical characteristics of *Zoophycos* spreite: Carbon and Sulfur Isotopes and TOC

The average TOC of the host sediment is 0.30 wt%, which is lower than average values of both the clay-rich (0.63 wt%) and the sand-rich (0.41 wt%) *Zoophycos* spreite. The concentration of organic matter in *Zoophycos* spreite relative to the host sediment, although slight, is significant for the interpreting the mode of life and feeding strategy of the *Zoophycos* trace-maker since TOC data only record residual organic matter rather than the original organic content of labile organic matter (DOM). The average $\delta^{13}C_{org}$ value of the host sediment is –24.04 ‰, with a slight variation of organic carbon quality between the spreite (clay-rich: –24.54 ‰, sand-rich: -24.23 ‰) (Fig. 11). The large amount of error in the analytical precision of the carbon isotopic signature for the sand-rich spreite burrow makes the data points insignificant. There is however a significant difference in the isotopic signature of the clay-rich burrow, which is slightly lighter than the host sediment (Fig. 11). The quantity and quality of the residual organic matter is therefore measurable different from the surrounding host sediment, information which would be lost using conventional bulk sediment sampling techniques.

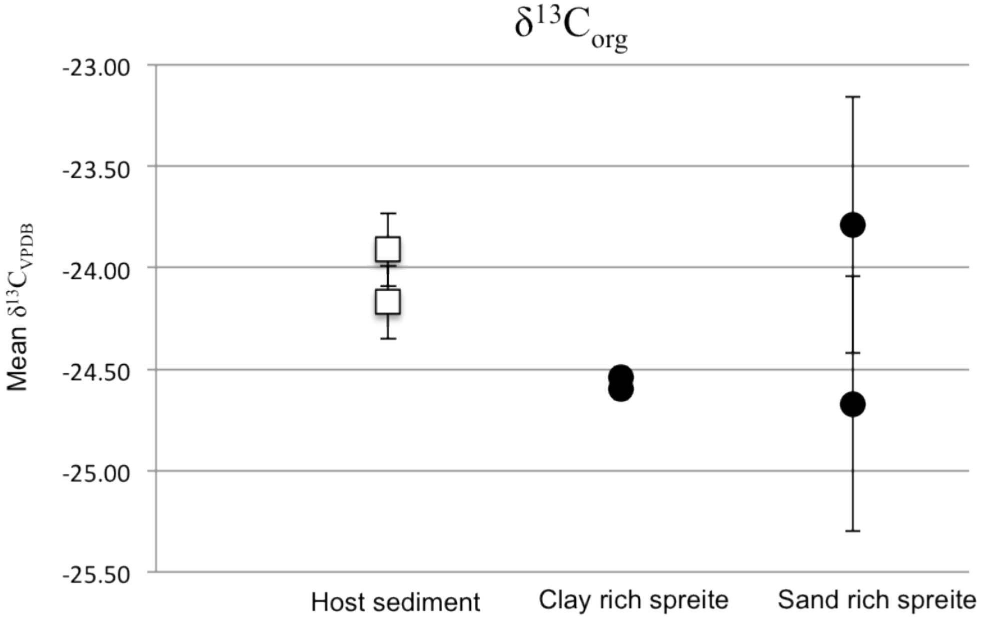

FIGURE 11— Mean $\delta^{13}C_{org}$ values from *Zoophycos* spreite and surrounding host sediment.

The $\delta^{34}S$ values between spreite and host sediment showed no significant fractionation. These results contained trace amounts of sulfur considered too low to be significantly accurate (Fig. 12).

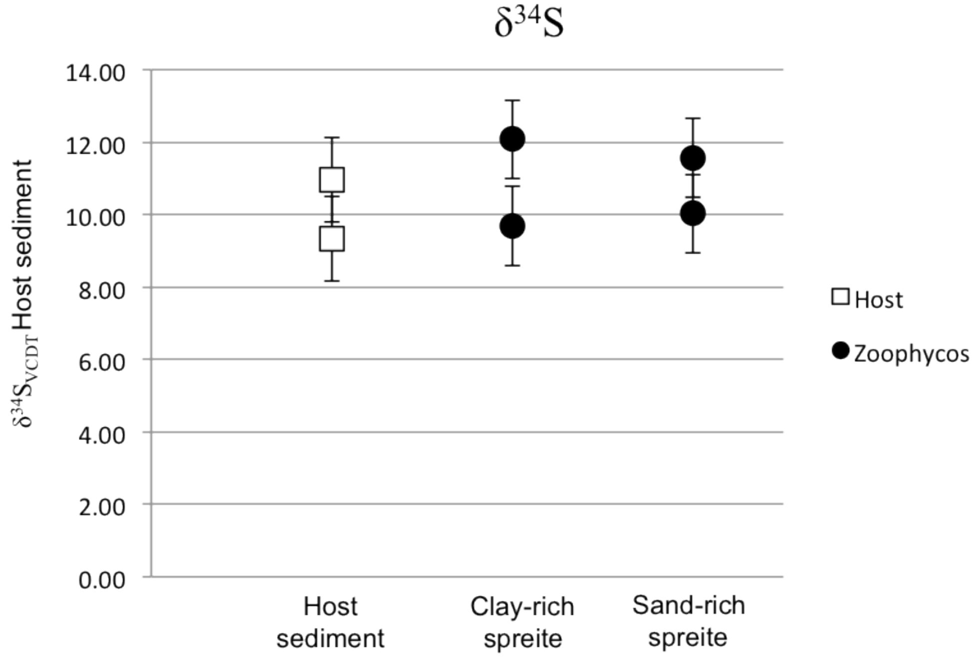

FIGURE 7— Mean δ^{34}S values from *Zoophycos* spreite and surrounding host sediment.

4.0 INTERPRETATION: COMPOSITIONAL ANALYSIS OF BIOTURBATED SANDSTONE FROM THE ROSARIO FORMATION

4.1 The spatial arrangement of redox-sensitive trace elements in bioturbated sandstones and the usefulness of paleoredox proxy data in ichnology

It has previously been found useful to relate the elemental composition of clay minerals to the feeding strategy of the fine-grained selective, deposit-feeding *Phycosiphon*-producer (Wetzel and Bromley, 1994; Bednarz and McIlroy, 2009; Izumi, 2014; Harazim et al., 2015). These studies highlight the validity and importance of combining geochemical studies with ethological analysis. Following this logic it is possible that further geochemical analyses can be developed to test against previously established ethological models to determine the most probable mode of life of a trace-making organism. It is also well known that certain groups of trace elements have a varied response to different redox conditions, and certain suites of redox sensitive trace elements are known to be associated with higher levels of organic matter (e.g. Tribovillard et al., 1994; Algeo and Maynard, 2004; Tribovillard et al., 2006). Independently sampling burrowed and host sediment allows for a detailed analysis of how the trace maker influences the distribution of sediment, and thus the arrangement of trace elements, mineralogy, isotope geochemistry, and TOC. The combination of these analyses not only provides information concerning the ethology of the trace maker, but can also determine the impact of the trace fossil on paleoredox proxies.

In the *Zoophycos* sample the trace elements that show significant depletion relative to the host sediment are Fe, As, Mo, Zn, and Sr (Fig. 4). The elements that show significant enrichment in the burrows are V, Cr, Co, Ni, U, and Ba (Fig. 4). In paleoredox studies trace elements are considered as ratios of one another, rather than being treated in isolation because their concentrations are affected by a number of parameters including: siliciclastic flux, primary productivity, and type of organic matter (Forchielli et al., 2014). Some groups of trace elements can exhibit varying sensitivities to redox conditions along an oxic to sulfidic gradient (Tribovillard et al., 2006). Certain suites of trace elements can accumulate under nitrifying conditions, such as Cr, U, and V, while other suites of trace elements are mainly only enriched under sulfate-reducing conditions, like Ni, Co, Cu, Zn, Cd and Mo (Tribovillard et al., 2006). The contrasting behavior of these two groups of trace elements may be used to recognize gradual redox trends in sediment (Tribovillard et al., 2006) (Fig. 5).

The combined use of U, V, and Mo enrichments can allow the distinction between sub-oxic environments from anoxic-euxinic ones. In the *Zoophycos* sample the U and V data from the fine-grained burrow was relatively enriched compared to the sand rich burrow and the host sediment (Fig. 5). The Mo values were relatively depleted in the fine-grained burrow. This elemental behavior is linked to a depositional environment with suboxic/anoxic redox conditions, without free H_2S (Algeo and Maynard, 2004; Tribovillard et al., 2006). In this case the H_2S could be incorporated into various iron-sulfide minerals. In the *Phycosiphon* sample, there is a relative enrichment of U, V, and Mo in the fine-grained core compared with the host sediment (Fig. 5). The data indicate a more euxinic signature in the core than in the surrounding host sediment, with free H_2S in the water column or surrounding pore water (Algeo and Maynard, 2004). Under euxinic conditions with free H_2S, insoluble metal sulfides can precipitate directly from the water column or at the sediment water interface (Algeo and Maynard, 2004). In each of the trace fossils the finer-grained portion of the sediment showed significantly different redox signatures than those from the host sediment.

Similar to their varying response to different redox conditions, the relative abundance of some trace elements may be identified based on their relation to the abundance of organic matter (Nameroff et al., 2002; Algeo and Maynard, 2004; Tribovillard et al., 2006). U and V will normally show good correlations with TOC when the TOC values stay below a certain threshold value. Above the threshold a significant Mo enrichment accompanies the U V enrichment, which demonstrates the development of euxinic conditions (Fig. 5). This threshold is thus identified as the boundary between anoxic and euxinic conditions. TOC value of this threshold can be highly variable, ranging from 1-1.5% in the Cariaco basin to 7% in the Kimmeridge Clay Formation (Ramanampisoa and Disnar, 1994; Tribovillard et al., 1994, 2005). Under anoxic conditions, Ni and Cu are largely deposited in the form of organometallic complexes and are released during organic matter decay with more limited diffusion of U and V into the sediments and precipitation as authigenic phases at the redox boundary (Tribovillard et al., 2006; Algeo and Maynard, 2004; Nameroff et al., 2002). Under oxic-dysoxic conditions, trace elements are mainly deposited in association with the detrital fraction of the sediment resulting in no co-variation with TOC (Algeo and Maynard, 2004; Tribovillard et al., 2006). Benthic oxygen levels can affect the quality and abundance of preserved organic matter in the sediment, which makes reconstructing redox trends or patterns in sediment a useful tool (Canfield, 1994; Van Cappellen and Ingall, 1994; Tyson, 1995; Algeo and Maynard, 2004). Trace metals that are considered proxies for increased levels of organic matter include Ni, Cu, Zn, Cr, Cu, and Cd. High abundances of these trace elements are associated with a high organic matter flux and evidence of reducing conditions, allowing for Ni and Cu fixation within the sediments (Tribovillard et al., 2006). The behavior responsible for the construction of the trace fossil is associated with an increase in these trace elements within the burrow (Figs 4, 6, 7, 8, 9). These redox-sensitive trace element ratios have been long considered as important indicators of paleoenvironmental conditions (Aller, 1982, 1988). Various combinations of these trace elements have been used extensively in the reconstruction of paleoenvironmental conditions involving trace element and TOC patters, redox conditions (oxidizing or reducing), organic matter abundance, and productivity (e.g. Aller, 1982, Tribovillard et al., 1994; Algeo and Maynard, 2004; Tribovillard et al., 2006; Forchielli et al., 2014).

When plotted with TOC, redox sensitive trace elements such as U, V, Mo, Ni, and Cu are all the most significantly enriched in the fine grained fecal core of the *Phycosiphon* trace fossil, which also has the highest value of TOC (Fig. 9). The data document that animals can influence the spatial patterns of pore-water solutes within sediment and can increase the rate of dissolved chemicals in both the surrounding sediment and the overlying water column (Jumars et al., 1990, 2015). Overall the *Zoophycos* data show signatures of a more sub-oxic/anoxic environment within the clay-rich spreite, while the *Phycosiphon*-like trace fossil shows more euxinic signatures in its clay-rich fecal core. The difference in the redox signature between host and trace fossil sediment may be attributed to biologic in-vivo processes within the guts of the respective trace makers. The organism may therefore alter redox condition signatures in heavily bioturbated sediments, which may affect the reliability of paleoredox reconstruction studies in heavily bioturbated units.

4.2 The Influence of the *Zoophycos* Trace maker on the Mineralogy of Bioturbated Sediment

The results of mineralogical composition analysis for the *Zoophycos* and host sediment samples were analyzed in this study (Fig. 10). The major minerals present in the host sediment include quartz, feldspar minerals (albite and anorthite), and clay minerals (illite, muscovite). Of the two burrows sampled, the major minerals include quartz, feldspars (orthoclase, albite, anorthite), calcite, sulfide related minerals sidpietersite and billingsleyite, and clay minerals berthierine, illite, and muscovite.

The ingestion and digestion of sediment—as preserved in trace fossils—has been shown to alter the mineralogical and biogeochemical composition sediments after deposition and before burial diagenesis (McIlroy et al., 2003; Harazim et al., 2015). The authigenic clay mineral berthierine is absent within the host sediment but found within the burrowed sediment (Fig. 10). Within the *Zoophycos* burrows new mineral peaks appear and peak broadening occurs in the traces for minerals including albite and anorthite (Fig. 10). The breakdown of feldspars and the presence of new clay minerals in *Zoophycos* spreite implies that clay-mineral authigenesis due to biological weathering (McIlroy et al., 2003; Harazim et al., 2015) was associated with the formation of *Zoophycos* spreite. The weathering of feldspars to clay minerals is associated with release of high-ionic-radius elements from the mineral crystal (Drake and Weill, 1975; Harazim et al., 2015). Elements with relatively smaller ionic radii can be incorporated into the crystal lattice of authigenic minerals, whereas high-ionic-radius trace elements tend to remain in solution. Data from the present study indicates a net loss of strontium in spreite relative to the host sediment suggesting that it may have been lost to solution. However the high-ionic-radius element Ba was not depleted and as such must be associated with an un-weathered mineral phase (Fig. 10). Several of these smaller ionic radii elements are relatively enriched in the burrows (i.e., V, Cr, Co, and Ni). Elements with small ionic radii (i.e., Ca) are most likely incorporated into authigenic minerals, which are seen in the mud-rich *Zoophycos* burrow (i.e. berthierine). The data herein demonstrates that bioturbating organisms may also alter the mineralogy of fine-grained sedimentary rocks, which can affect the usefulness of data in bulk geochemical analysis.

4.3 Organic Matter quality and quantity

The TOC of clay rich spreite material (0.63 wt%) and sand rich spreite (0.41 wt%) is slightly greater than that of the host sediment (0.30 wt%). The enrichment of TOC observed in the spreite material can have a number of implications for the probable function and mode of construction of *Zoophycos*. The quality of organic matter found within the spreite can be used to determine if the gardening of microorganisms has taken place within the burrow. The gardening model (Bromley, 1991) states that the trace maker introduces organic rich material to cultivate biomass from microorganisms and feeds on the organic material as a substrate. Since microorganisms fractionate heavily against ^{13}C, gardening activity within the spreite would create a noticeable shift in the $\delta^{13}C_{org}$ values of the organic material in the spreite to the host sediment (Löwemark et al., 2004). In our data the average $\delta^{13}C_{org}$ values of the host sediment are -24.04‰ while the average values of the burrow environment are between -24.57‰ (clay-rich) and -24.23‰ (sand-rich) (Fig. 6). This suggests a slight shift in isotopic values between the burrowed and host sediment, which is investigated in relation to trace maker ethology in the next section.

5.0 BIOGEOCHEMICAL GROUND-TRUTHING OF ESTABLISHED ETHOLOGICAL MODELS OF *ZOOPHYCOS*

Some work has been done to relate previously established trace maker behavioral models to biogeochemical data for the trace fossil *Phycosiphon* (Izumi et al., 2014, Harazim et al., 2015). These studies demonstrate that the fine-grained selective feeding strategy of the *Phycosiphon* trace maker can account for the redistribution of silt and clay sized grains from the area in the halo (Harazim et al., 2015). Following the methodology of Harazim et al. (2015), several ethological models are considered in this study for Rosario Formation *Zoophycos.* Based on a combination of field observations, a detailed three-dimensional reconstruction of the trace fossil, and biogeochemical data, these models are tested here against previously established ethological models for *Zoophycos.* These models include: 1) deposit-feeding (e.g. Seilacher, 1967; Wetzel and Werner, 1981; Ekdale and Lewis, 1991);, 2) detritus-feeding (Kotake, 1989, 1991); 3) microbial gardening and chemosymbiosis (Bromley, 1991); and 4) food caching (Bromley, 1991).

5.1 Cache Model

The cache model is best supported by the observation of spreite re-exploitation through coprophagy. This model is based on the need for an organism to store organic rich material in its burrow to use in times of low nutrient flux (Jumars et al., 1990; Bromley, 1991; Fu and Werner, 1995; Miller and D'Alberto, 2001; Bromley and Hanken, 2003). In the three-dimensional reconstruction of Rosario *Zoophycos* in this thesis*,* two *Zoophycos* abut, suggesting a re-visitation of the spreite as a potential cache. This observation coupled with a fecal biogeochemical signature and enrichment in TOC in the spreite would indicate the selective collection and storage of nutrient rich material (Löwemark et al., 2004). While the data does show an increase in TOC in the burrows, the cache model requires that the pellets in the spreite are fecal in nature. When plotted along with the fecal core of the Rosario *Phycosiphon*-like trace fossil, the *Zoophycos* burrow does not show the same fecal signature, nor is it as enriched in TOC (Fig. 5). An increase in TOC in the burrowed sediment is expected, as sediment reworked by the trace maker will naturally have higher carbon content than the local host sediment (Zhang et al., 2015). The cache model is therefore refuted as the primary function of this *Zoophycos*.

5.2 Gardening Model

The gardening model posits that organic material is collected on the seafloor and deposited within the burrow to act as a substrate for the cultivation of microorganisms as a labile carbon source, thus increasing the amount of TOC available to the organism (Löwemark et al., 2004). In order to facilitate the gardening of microorganisms, the trace maker must localize refractory, usually detrital carbon particles into an environment conducive to the production of labile biomass (Löwemark et al., 2004). The burrowing activities of the trace maker result in the creation of feces, which are cultivate and fed upon by symbiotic microbes (Bromley, 1991; Löwemark et al., 2004; Gong et al., 2008). Fractionation against ^{13}C is facilitated by sulfur oxidizing bacteria that fix carbon (Ruby et al., 1987) and by the ingestion and metabolism of the microbes and any remaining refractory organic carbon by the animal (Löwemark et al., 2004). These processes should result in a strong fractionation against ^{13}C in the spreite material, with heavier $\delta^{13}C_{org}$ values in the spreiten compared to the host sediment. In this study the $\delta^{13}C_{org}$ isotopes were slightly lighter in the clay spreite than the host sediment, which suggests that gardening of microorganisms was most likely not a defining factor behind the construction of this trace (cf. Löwemark et al., 2004, 2007).

5.3 Chemosymbiosis

Field observation and three-dimensional reconstruction showed that U-tube shaped *Zoophycos* specimens are present in the Rosario Formation (Fig. 1). This morphologic feature allows for the circulation of oxygenated water to be pumped through the burrow at depth in order to create conditions conducive to sustaining chemosynthetic bacteria. After the introduction of organic rich material to the burrow, these bacteria oxidize inorganic compounds, like sulfides or methane, to convert inorganic carbon molecules into organic matter (Dubilier et al., 2008). The carbon can be metabolized through a number of pathways as iron reduction, sulfate reduction, and methanogenesis are all available to donate terminal electron acceptors after porewater oxygen and nitrate have been exhausted (Whiticar et al., 1986; Tyson, 1995; Morasch et al., 2001). Bacterially produced carbon molecules have shown very light $\delta^{13}C_{org}$ signatures, as low as -110‰ in some cases (Whiticar et al., 1986). Many invertebrates have a symbiotic relationship with this type of chemoautrophic bacteria (Zuschin et al., 2001). An increase in TOC along with lighter $\delta^{13}C_{org}$ signatures in the *Zoophycos* spreite provides evidence that chemosymbiosis may have taken place within this trace fossil. This ethological model was discussed in relation to the upper Pliocene *Zoophycos* of Greece (cf. Bromley and Hanken, 2003). They described extending lobes of *Zoophycos* searching into *Thalassinoides* and ammonites, and indicated this may symbolize a search for sulfide-rich sediment (Bromley and Hanken, 2003). Sulfur isotopes did not show a significant deviation between the trace fossil and the host sediment, possibly due to the low quantity of sulfur in the samples. While the geochemical evidence of these data points is slight, it provides evidence that chemosymbiosis may have taken place in the trace fossil, even if it was not the primary motivation behind the construction of the burrow. The *Zoophycos* trace maker has been described as an adaptive organism, with more than a single mode behavior behind the construction of its spreite, perhaps in response to fluctuations in the availability of food (Löwemark, 2001).

5.4 Deposit-feeding (Strip mine)

The *Zoophycos* trace maker was first described as a strip-mining, deposit feeding style organism (Seilacher, 1967; Simpson, 1970; Wetzel and Werner, 1981; Ekdale and Lewis, 1991). In the deposit feeding model the animal sweeps broadly through the sediment and selectively processes nutrient rich particles. Each lateral movement of the burrow produces the spreite that alternately symbolize feeding exploration, and waste disposal (Seilacher, 1967; Simpson, 1970; Bromley, 1991). The spreite contain a large introduction of foreign material, and have higher TOC content than the surrounding host sediment, which have both been previously demonstrated to advocate against the deposit-feeding model (e.g. Leuschner et al., 2002; Löwemark and Schäfer, 2003).

5.5 Refuse Dump (Ballast)

The refuse dump model was described by Bromley (1991) to accommodate evidence of foreign material placed in a *Zoophycos* burrow (Kotake 1989, 1991). This model states that the animal feeds at depth in the sediment and deposits its fecal matter at the seafloor (Bromley, 1991). To main an open, narrow burrow cavity to sustain the flow of oxygenated water, sediment is transported down to the burrow and deposited as ballast. The material may be pelleted to optimize transport efficiency (Bromley, 1991). It is noted that the material conveyed downward may be by chance slightly enriched in refractory organic material relative to the host sediment (Bromley, 1991).

The U-shaped marginal tube morphology found in Rosario *Zoophycos* allows for many of these criteria to be met. The U-shape allows for the circulation of oxygenated water, and provides two openings at the seafloor, which may be each independently used for fecal matter deposition and a source of sediment ballast. The geochemical data mostly validate the possibility for this model. The burrow material showed no fecal signature, which supports the criteria that the organism excretes outside of the burrow environment. The average TOC values are slightly lower in the host sediment (0.30 wt. %) than in either the clay-rich burrow (0.63 wt. %) or the sand-rich burrow (0.41 wt. %). The refuse dump model does allow for the introduced material to, by chance, be somewhat slightly enriched in TOC. The geochemical evidence for the refuse dump model allows for it to be considered as a possible ethological strategy for the trace-making organism.

5.6 Detritus-feeder

The downward transport of sediment in *Zoophycos* was first commented on by Ekdale and Bromley (1983), and was eventually established as evidence for non-selective surface detritus feeding (Kotake, 1989, 1991). According to this model the *Zoophycos* producer dwelled in its burrow within the sediment and fed on nutrient-rich grains on the seafloor, around its burrow opening. Volcanic ash layers found at higher sediment levels than the burrow were determined to be the source of volcanic particles found in the *Zoophycos* spreite (Kotake, 1991), and after feeding the trace-maker deposited its fecal pellets in the spreite (Kotake, 1989, 1991). The abundant appearance of fine-grained, sometimes-pelleted sediment in the earlier *Zoophycos* 1 from Chapter, 2 of this thesis supports the idea that the sediment may have been conveyed downwards from a more mud-rich layer. Geochemical evidence did not show a strong fecal signature in the spreite sediment, which contradicts the detritus-feeder model for Rosario *Zoophycos*.

6.0 CONCLUSION

The results support the value of integrating geochemical analyses and other data (e.g. a three-dimensional morphology study) as a means to systematically evaluate preexisting ethologies as a means to explain the behavior behind the construction of a variety of trace fossils. This study can also offer a means to determine a working ethological model for the *Zoophycos* trace maker in the event the data suggests a behavioral style that has not yet been described for the trace maker.

1. The data has demonstrated that trace fossils have a measurable effect on sediment biogeochemistry. Detailed sampling of the trace fossil *Zoophycos* documented the impact of the trace-making organism on the spatial distribution of redox-sensitive trace elements, mineralogy, and TOC. The data supports the notion that box-model geochemical analysis on burrowed sandstones may not properly account for organism influence.
2. Combining these analyses with other types of investigative data, such as a three-dimensional study of a trace fossil or field observations, can aid in furthering the interpretation of organism behavior and determining the impact of an organism on sediment properties.
3. It has been documented here that *Zoophycos* trace makers can introduce sediment into their burrow environment from layers above the local burrow environment (eg. Kotake, 1989, 1991; Löwemark et al., 2004). This may complicate the

reconstruction of paleoredox conditions within sediment, by introducing geochemical signatures from a number of different stratigraphic levels.

4. This study has demonstrated the validity of detailed biogeochemical analysis in the evaluation of organism ethology. Significant biogeochemical differences in organic matter quality and quantity, supported by associated trace element and mineralogy data, can be used to prove or disprove an ethological analysis for the *Zoophycos* trace fossil. The data was tested against previously established ethological models to identify viable explanations for the construction of the trace fossil. This study showed that the *Zoophycos* trace maker may use a combination of behaviors in the creation of its burrow system. A combination of selective detritus feeding, chemosymbiosis, and refuse dump behaviors are suggested as possible behaviors behind the construction of this *Zoophycos* trace fossil.

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Chapter 4

Summary

4.1 Introduction

This study investigates the three-dimensional morphology and biogeochemical impact of the trace fossil *Zoophycos.* The morphology and ethology of *Zoophycos* were investigated through the creation of a three-dimensional model of the trace fossil and a whole rock model of the trace fossil bearing sample. Through a detailed biogeochemical analysis, the impact of *Zoophycos* on sediment properties was studied to determine how the *Zoophycos* trace maker alters the spatial geochemical characteristics of fine-grained sedimentary rocks. This research expands on the novel findings of bioturbation as a first order control on geochemical heterogeneity in sedimentary rocks (Harazim et al., 2015).

The study was motivated by the need to better understand the morphology and ethology of *Zoophycos*. Ichnologists have explored the morphology, evolution, and ethology of *Zoophycos* for almost 200 years and there remains no consensus on the trace fossil (Zhang et al., 2015). The three-dimensional reconstruction and detailed biogeochemical analysis produced herein helped to characterize the structure and biogeochemical impact of *Zoophycos*. These findings have not only improved the understanding of *Zoophycos* morphology, but have also aided in developing a systematic means to test pre-established behavioral models of *Zoophycos*. Understanding the morphological elements of at least one form of *Zoophycos* in combination with a detailed biogeochemical analysis will aid in the understanding and classification of this enigmatic trace fossil. The three-dimensional model can be sliced in any plane, a feature that will improve field and core-based diagnostics. Detailed biogeochemical analysis will help to narrow a list of possible behavioral models assigned to any sample of *Zoophycos*.

4.2 *Zoophycos* Morphology

The full morphology of the *Zoophycos* trace fossils in this study was investigated in detail, which allowed for the identification of new spreite morphology and novel insight into the complex opportunistic behavior of the *Zoophycos* trace-maker. The three-dimensional reconstruction of *Zoophycos* created in this study has revealed new details on spreite morphology not yet commented on in literature to date, and additional complexity that is superimposed upon many well-accepted models of *Zoophycos*. These models include deposit feeding (Wetzel and Werner 1981; Ekdale and Lewis 1991); detritus-feeding (Kotake 1989, 1990, 1991); refuse-dumping (Bromley 1991; Löwemark and Schäfer, 2003); food caching (Fu and Werner 1995; Bromley et al. 1999; Miller and D'Alberto 2001; Bromley and Hanken 2003; Löwemark and Schäfer, 2003); and microbial gardening (Bromley, 1991).

The morphology of the two *Zoophycos* burrows in the sample suggests that two different types of behavior formed them. Three-dimensional investigation of *Zoophycos* 1 revealed spreite formed by a U-tube shaped causative burrow (cf. Wetzel and Werner 1981). Successive images through the trace fossil showed that the composition of spreite is laterally discontinuous, with sand-rich spreite grading to mud-rich spreite near the distal portion of the trace fossil. These images also revealed that some distal spreite are comma shaped, a similar feature of spreiten morphology that has previously been described as a geopetal indicator created by a trace-maker during backfill activities (Seilacher, 2007). It is established that alternating sand-rich and clay-rich spreite in *Zoophycos* are created during successive periods of excavation and deposition, and that spreite are formed through the lateral displacement of the burrow (Häntzschel, 1975;

Löwemark and Schäfer, 2003). The spreite in *Zoophycos* 1 are significantly more mud-rich than the host sediment, indicating that it is possible the trace-maker performed grain-selective deposit feeding both at a higher stratigraphic level and by grain selective deposit feeding.

Zoophycos 2 has spreite that are significantly more clay-rich (~85%) than the sand-rich host sediment. The three-dimensional reconstruction revealed that the proximal position of *Zoophycos* 2 is positioned so that it corresponds to, and post-dates, the plane of *Zoophycos* lobe 1. This is interpreted to indicate that the trace-maker of lobe 2 elected to exploit lobe 1, rather than the host sediment, due to the local abundance of fine-grained sediment. Pellets discovered in *Zoophycos* 1 that are likely fecal in nature may indicate evidence for allocoprophagy (cf. Jumars, 1990, 2015). *Zoophycos* 1 was also bioturbated by other organisms, which provides additional evidence that the material in its spreite were an attractive nutrient source, or that the fine-grained sediment was attractive for other reasons. In either case *Zoophycos* 2 displays evidence of an opportunistic trace maker that sought out spreite of another *Zoophycos* by way of infaunal deposit feeding. This feature provides direct evidence that the *Zoophycos* trace maker was opportunistic and able to adapt to surrounding sediment characteristics.

4.3 *Zoophycos* biogeochemistry

The detailed biogeochemical study in this thesis has helped create a means whereby aspects of the pre-established ethological models for the *Zoophycos* trace-maker can be systematically tested. This study builds on the results from previous work concerning bioturbation as a control on the spatial geochemical characteristic of fine-grained sedimentary rocks (Harazim et al., 2015). The analyses utilized in this thesis can be applied to a variety of different trace fossils to identify how bioturbating organisms redistribute redox sensitive trace elements and sedimentary organic matter (cf. McIlroy et al., 2003; Harazim et al., 2015). These data have various implications on paleoenvironmental analysis and geochemical interpretation of potential hydrocarbon reservoir, source, and seal rocks (Harazim et al., 2015).

Detailed biogeochemical mapping of the *Zoophycos* trace fossil and surrounding host sediment revealed differences in mineralogy, trace element geochemistry, and organic matter quantity and quality. These data would otherwise be lost in box-scale geochemical studies on bioturbated sandstones and siltstones. A number of different research avenues can benefit from the identification of biogeochemical signatures from bioturbated sediment and those of local host sediment. Paleoredox reconstructions may be especially complicated in sediment units with *Zoophycos* bioturbation, since the *Zoophycos* trace maker has been documented to introduce sediment into their burrows from layers above the local burrow environment (e.g. Kotake, 1989, 1991; Löwemark and Schäfer, 2003). Based on the contrasting behavior of different groups of redox sensitive trace elements, groups of elements may be used to recognize redox trends in sediment (Tribovillard et al., 2006). The *Zoophycos* data show sub-oxic/anoxic signatures in the clay-rich spreite, while the *Phycosiphon*-like data shows more euxinic signatures in its clay-rich fecal core. Differences in redox signatures between host and trace fossil sediment can potentially be attributed to biologic in-vivo processes within the guts of the respective trace makers. These data therefore document alterations in redox signatures in bioturbated sediment, which may complicate paleoredox reconstructions in certain sedimentary units with heavy bioturbation.

Biologic in-vivo processes may also affect the mineralogy found in *Zoophycos* spreite in contrast to the host sediment. The authigenic clay mineral berthierine is present within the *Zoophycos* spreite, while absent from the host sediment. Ingestion and digestion of the sediment preserved in trace fossils has previously been shown to alter the mineralogical and biological composition of sediments after deposition and before burial diagenesis (McIlroy et al., 2003; Harazim et al., 2015). The data demonstrate that bioturbating organisms may alter the mineralogy of fine-grained rocks, data that would otherwise be lost to bulk geochemical analysis.

Detailed biogeochemical mapping also provided insight into the most probable, evidence-based explanation for the function of Rosario Formation *Zoophycos*. The ethology of the *Zoophycos* trace maker has long been a subject of contention (Seilacher, 1967, Simpson, 1970; Ekdale, 1977; Wetzel and Werner, 1981; Kotake, 1989, 1991, 1994; Ekdale and Lewis, 1991; Bromley, 1991; Fu and Werner, 1995; Löwemark and Schäfer, 2003; Olivero and Gaillard, 2007; Löwemark, 2015). This study suggests that the Rosario Formation *Zoophycos* trace maker most likely uses a combination of behaviours in the creation of its burrow system. A combination of selective detritus feeding, chemosymbiosis, and refuse dumping behaviors are suggested as possible functions of this *Zoophycos* trace maker. Selective detritus feeding is supported by the abundant appearance of fine-grained, sometimes-pelleted sediment in the *Zoophycos* 1 from Chapter 2 of this thesis. The abundance of fine-grained sediment in otherwise sand-rich host sediment supports the idea that the sediment may have been conveyed downwards from a more mud-rich layer. An increase in TOC along with lighter $\delta^{13}C_{org}$

signatures in the *Zoophycos* spreite provides evidence that chemosymbiosis may have taken place within this trace fossil. The refuse dump model is supported by the presence of foreign material in the *Zoophycos* burrow, which in this case is the abundant fine-grained sediment. Biogeochemical data also support this model, as there is no fecal signature noted in the *Zoophycos* spreite, and the refuse dump criteria dictates that the organism excretes outside of the burrow environment onto the contemporaneous seafloor.

4.4 Concluding statement

In order to fully understand complex trace fossils like *Zoophycos*, an integrated approach is essential. This thesis adds to the growing number of works that demonstrate how three-dimensional morphological reconstructions contribute to the proper characterization and understanding of trace fossils (Bednarz and McIlroy 2009; Bednarz and McIlroy 2012; Boyd et al. 2012; Bednarz et al. 2015; Leaman et al. 2015; Leaman and McIlroy 2015; Boyd and McIlroy 2016; Evans and McIlroy, 2016). Detailed biogeochemical mapping of trace fossils and local host sediment is a relatively new approach in fully characterizing the ethological models of different trace making organisms (Izumi, 2013; Harazim et al., 2015). This thesis highlights the validity of an integrated approach of three-dimensional morphologic reconstructions with detailed biogeochemical mapping as a means to fully characterize trace fossils. It also offers a means to select an evidence based ethological model for a trace-making organism. It is suggested that in future studies of complex trace fossils like *Zoophycos*, that a similar integrated approach be utilized to fully understand the structure and function of the trace fossil and trace-making organism.

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APPENDIX A

High-resolution geochemical analyses of host sediment, and two *Zoophycos* burrows (mud-rich and sand-rich spreite) from the Rosario Formation, Mexico.

This table contains high-resolution (sub-mm) trace element data obtained from host sediment and *Zoophycos* burrow sediment. These data are presented in my third thesis chapter. The table shows trace element concentrations (in ppm). The data were obtained via ICP-MS measurements.

K.Power
PPM Rock
Run = 1090
FileName = Aug13023

	Ca	Ti	V	Cr 52	Fe 54	Mn	Co
SB1 MUDBurrow AVG ppm	22817.576	4051.601	118.244	77.254	35965.792	535.418	93.992
1 sigma (ppm)	3543.03	574.75	5.64	2.98	1672.27	53.62	6.79
SB2 SANDBurrow AVG	23788.215	3974.907	115.727	96.714	37952.050	422.510	76.324
1sigma (ppm)	3693.750	563.868	5.520	3.735	1764.629	42.311	5.512
SH3 Light&Dark AVG	24595.154	3895.210	93.628	50.520	36715.358	427.269	100.214
1sigma (ppm)	3819.049	552.562	4.466	1.951	1707.127	42.787	7.237
SH1Light AVG	22791.405	3842.390	95.604	52.167	36336.462	331.245	24.883
1sigma (ppm)	3538.969	545.070	4.560	2.015	1689.510	33.171	1.797
SH2Dark AVG	23767.603	4304.674	111.110	58.712	43068.275	532.691	75.691
1sigma (ppm)	3690.549376	610.6477748	5.299350974	2.267454257	2002.51388	53.34453586	5.465859343
SHAverageTotal	23718.054	4014.091	100.114	53.800	38706.698	430.402	66.929
1sigma (ppm)	3682.855631	569.4265988	4.77489108	2.077743243	1799.716853	43.10109564	4.833160169
SCO-1 Average of 5 runs (ppm)	23344.058	3088.350	121.518	64.385	33594.851	355.775	9.931
SCO-1-1 PublishedStandard	18725	3777	130	68	35879	410	11
Host Sediment AVG(w/o error)	23718.054	4014.091	100.114	53.800	38706.698	430.402	66.929
Host Sediment AvgDev ppm	1335.957	278.224	7.378	3.322	3274.479	83.355	33.135
Host Sediment avg prop. Error	0.155276468	0.141856918	0.047694483	0.038619732	0.046496264	0.100141536	0.072212983
Host Sediment avg dev %	5.632660692	6.931189482	7.369409355	6.174793147	8.459721408	19.366699	49.50713525
Error calculation based on SC0 published values							
Stdev 1sigma	0.155276468	0.141856918	0.047694483	0.038619732	0.046496264	0.100141536	0.072212983
Stdev (1 sigma) %	15.52764677	14.18569181	4.769448268	3.861973233	4.649626375	10.01415361	7.221298271
SD%*AVG Sample	362478.2899	43810.38839	579.5716566	248.6523724	156203.5053	3562.78448	71.71619174
SD*AVG Sample	3624.782899	438.1038839	5.795716566	2.486523724	1562.035053	35.6278448	0.717161917

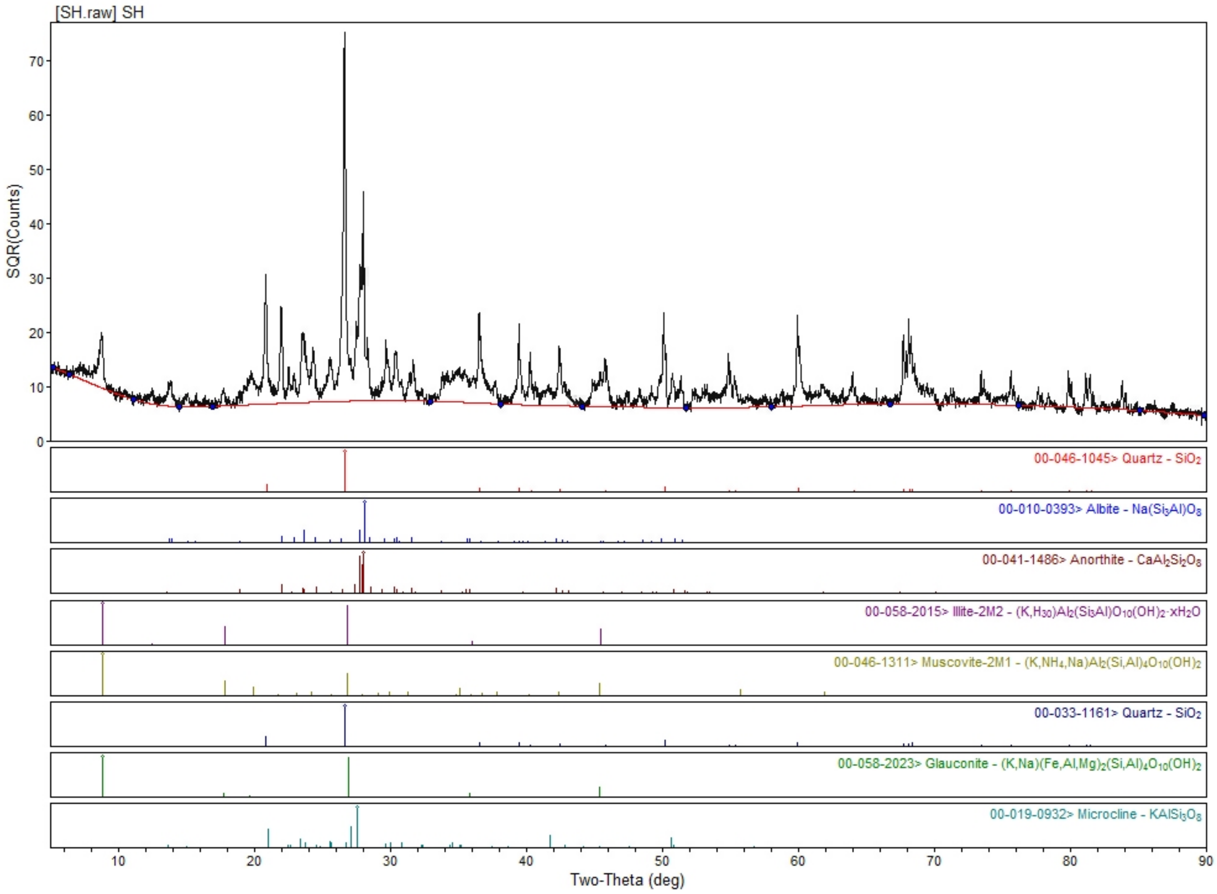
Ni	Cu	Zn	As	Mo	Th	U	Sr	Ba
30.915	32.950	104.504	9.899	0.769	11.891	2.680	221.816	948.292
0.92	20.58	14.92	0.30	0.12	1.85	0.18	7.17	6.23
29.799	36.987	120.432	11.183	1.406	13.019	2.483	204.794	922.336
0.885	23.105	17.192	0.334	0.215	2.022	0.168	6.623	6.062
23.932	30.282	115.085	15.511	1.312	12.817	2.214	245.345	791.301
0.711	18.916	16.429	0.464	0.201	1.991	0.150	7.934	5.200
22.166	28.046	114.740	15.058	1.302	11.701	2.291	238.226	727.886
0.658	17.520	16.379	0.450	0.200	1.817	0.155	7.704	4.784
27.576	31.737	129.760	19.697	1.797	11.455	2.355	239.623	775.928
0.818762031	19.82490434	18.52345796	0.588961011	0.275300491	1.779179809	0.159650977	7.749161337	5.09935325
24.558	30.021	119.862	16.755	1.470	11.991	2.286	241.065	765.039
0.72915849	18.7534889	17.11047208	0.5010132	0.225264421	1.862474903	0.155019695	7.795781061	5.027787434
25.890	74.888	122.455	11.503	1.740	12.094	2.862	162.399	564.727
27	29	100	12	1.4	9.7	3.15	170	570
24.558	30.021	119.862	16.755	1.470	11.991	2.286	241.065	765.039
2.330	2.873	6.821	2.118	0.218	0.750	0.085	9.286	29.751
0.029691581	0.62466983	0.142751626	0.029901596	0.153228876	0.15532482	0.067798878	0.032338958	0.00657194
9.487359593	9.57055496	5.690935837	12.63803073	14.80809983	6.252906118	3.724474035	3.852214842	3.888843672
0.029691581	0.62466983	0.142751626	0.029901596	0.153228876	0.15532482	0.067798878	0.032338958	0.00657194
2.969158142	62.46698297	14.27516257	2.99015961	15.32288764	15.53248199	6.779887786	3.233895821	0.657193982
76.87024851	4678.04857	1748.061073	34.39598598	26.66554361	187.8439377	19.40260534	525.1814472	371.135089
0.768702485	46.7804857	17.48061073	0.34395986	0.266655436	1.878439377	0.194026053	5.251814472	3.71135089

APPENDIX B

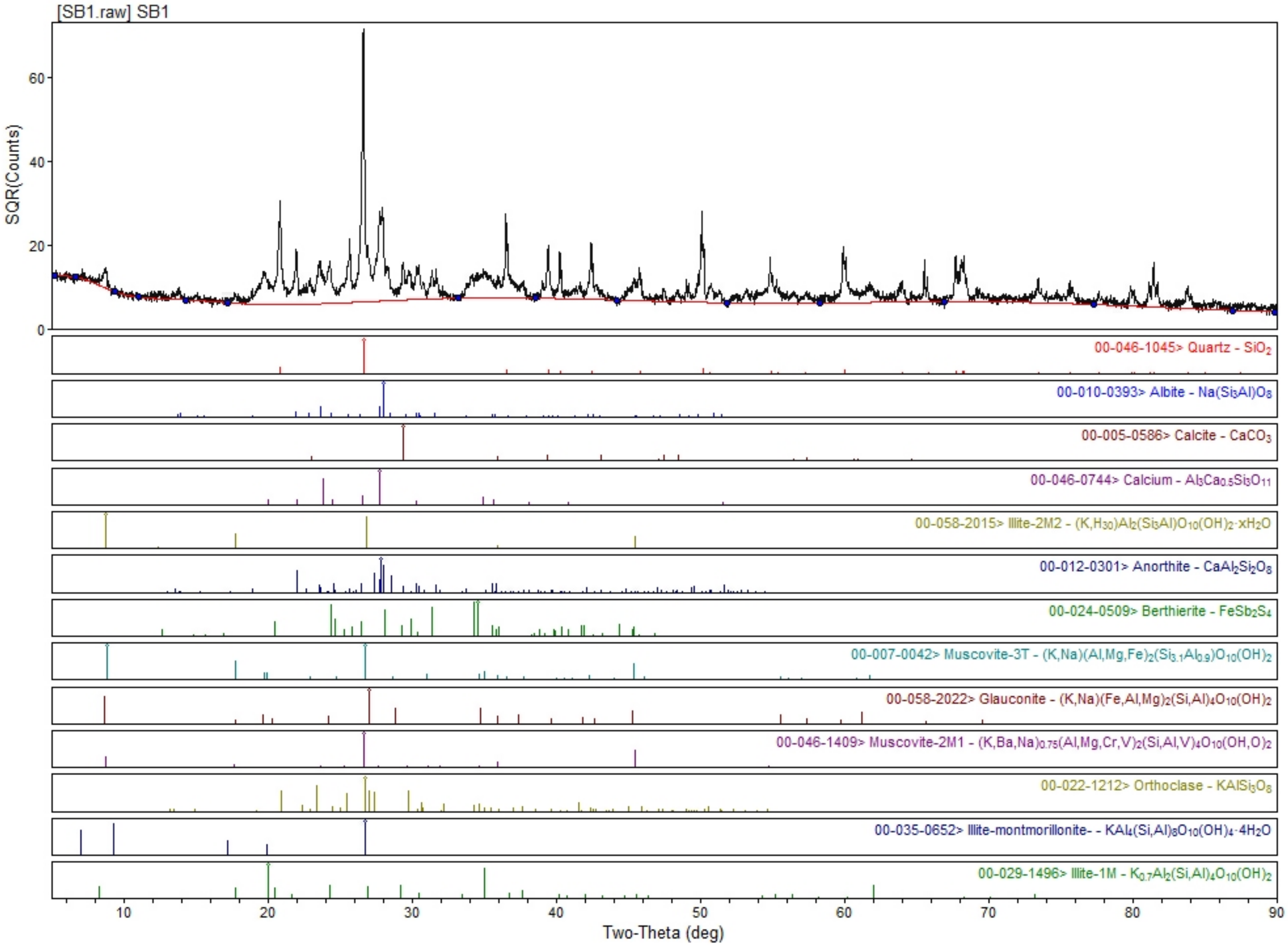
Phase identification using X-Ray Diffraction

This appendix contains the phases identified via X-ray diffractometry for host sediment, mud-rich *Zoophycos* spreite, and sand-rich *Zoophycos* spreite. The X-ray diffractometer was operated at 40 kV and 44 mA current, using a scintillation counter (1 mm divergent slit, 0.6 mm detector slit, 1.0 mm anti-scatter slit and a graphite monochromator). Samples were scanned with a step size of 0.02° and a count time of 2 s per step. All samples were analyzed in air-dried state.

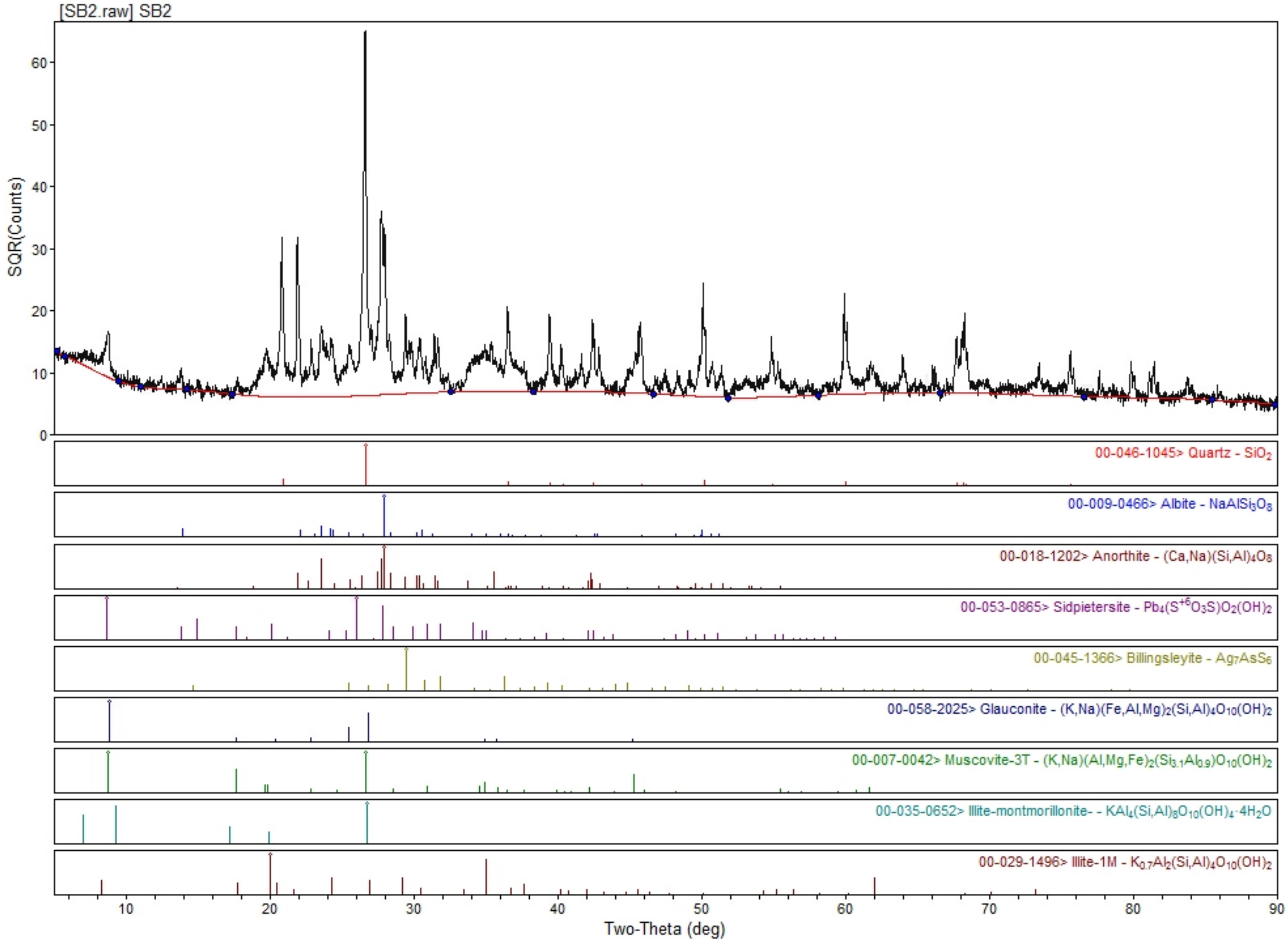
SH- Host Sediment



SB1- Mud-rich *Zoophycos* spreite



SB2-Sand-rich *Zoophycos* spreite



APPENDIX C

High-resolution geochemical data including isotopic data and TOC

Appendix C contains data that are presented in the third chapter of the thesis. The table lists the sample number, isotopic value ($\delta^{13}C_{org}$, δ^{34} S, ‰,) and Total Organic Carbon (TOC wt%). TOC was measured using a Carlo Erba NA 1500 Series 2 elemental analyzer and $\delta^{13}C_{org}$ was measured using a Thermo Electron Delta V Plus mass spectrometer.

Sample Name	$\delta^{13}C_{org}$ (‰, PDB)	TOC (wt%)	$\delta^{34}S$ (‰, VCDT)
SHost	-23.91	0.30	10.97
SHost*	-24.17	0.29	9.32
SB1	-24.60	0.60	9.68
SB1*	-24.54	0.65	12.08
SB2	-24.67	0.42	10.03
SB2*	-23.79	0.40	11.57

* Duplicate measurements

APPENDIX D

High-resolution geochemical analyses from host sediment and phycosiphoniform burrow elements (core and halo) from the Pelican System (Rosario Formation, Mexico) from Harazim et al., (2015).

This table contains the high-resolution (sub-mm) trace element data obtained from host sediment,burrow halo, and burrow core from sample ROS1. The table shows trace element concentrations (in ppm). The data were obtained via ICP-MS measurements.

The sample (~0.1 g) was dissolved via HF and HNO3 treatment (Jenner et al. 1990). The sample solution was sprayed into the inductively coupled argon plasma (~8000°C) of a HP 4500 plus mass-spectrometer, allowing all analyte species to be atomized, ionized and thermally excited in order to be detected.

Name	**Ca**	**Ti**	**V**	**Cr 52**	**Fe 54**
Host sediment, sample 1 (ppm)	15001.08	3886.38	110.77	67.85	22690.97
1 sigma (ppm)	2407.65	340.03	10.11	2.04	661.61
Host sediment, sample 2 (ppm)	14593.42	4229.96	134.62	82.24	26735.89
1 sigma (ppm)	2342.22	370.10	12.29	2.47	779.55
HALO (ppm)	15089.42	3896.93	107.73	62.72	22529.15
1 sigma (ppm)	2421.83	340.96	9.83	1.89	656.89
PHYCO CORE (ppm)	24746.18	5863.01	227.28	141.60	40077.11
1 sigma (ppm)	3971.73	512.98	20.74	4.26	1168.55
FER-4 standard average of 3 runs (ppm)	19748.7	370.8	12.5	9.4	268390.0
FER-4 standard published (GeoREM, ppm)	15723.0	419.7	11.0	9.0	279690.0
Host sediment average (without error)	14797.3	4058.2	122.7	75.0	24713.4
Host sediment average dev (ppm)	5506.5	1652.5	50.0	32.4	10689.7
Host sediment average, prop. error	0.227	0.124	0.129	0.043	0.041
Host sediment average dev (%)	37.2	40.7	40.8	43.2	43.3
Halo excess (ppm)	292.2	-161.2	-15.0	-12.3	-2184.3
Core excess (ppm)	9948.9	1804.8	104.6	66.5	15363.7
Error calculation based on FER-4 published values					
Stdev (1 sigma, ppm)	**2846.58**	**34.58**	**1.07**	**0.28**	**7990.31**
Average (ppm)	17735.83	395.20	11.76	9.20	274040.00
Stdev (1 sigma)	0.1605	0.0875	0.0913	0.0301	0.0292
Stdev (1 sigma, %)	**16.05**	**8.75**	**9.13**	**3.01**	**2.92**

Mn	Co	Ni	Cu	Zn	As	Se 77	Br 79	Ag 107	Cd
266.40	62.27	25.58	41.80	74.72	11.74	-1.90	1178.32	0.28	0.96
14.03	2.18	2.14	9.37	49.64	0.32	0.00	0.00	0.00	0.00
286.22	82.39	37.26	48.02	130.92	16.27	7.65	1059.26	0.42	1.44
15.07	2.89	3.12	10.77	86.99	0.45	0.00	0.00	0.00	0.00
268.38	44.44	28.41	44.59	90.23	9.60	-13.45	1078.06	0.33	2.00
14.13	1.56	2.38	10.00	59.95	0.26	0.00	0.00	0.00	0.00
372.07	137.33	56.58	72.43	138.57	25.98	1.64	1125.25	0.63	1.38
19.59	4.81	4.74	16.24	92.07	0.71				
1585.2	1.9	9.0	17.9	69.3	3.8	0.5	0.7	2.1	2.4
1471.4	2.0	8.0	13.0	25.0	4.0				
276.3	72.3	31.4	44.9	102.8	14.0	2.9	1118.8	0.3	1.2
116.6	31.2	13.0	15.8	30.5	6.1	3.8	497.2	0.2	0.5
0.074	0.050	0.118	0.317	0.940	0.039	0.000	0.000	0.000	0.000
42.2	43.1	41.4	35.2	29.7	43.4	133.0	44.4	44.4	44.4
-7.9	-27.9	-3.0	-0.3	-12.6	-4.4	-16.3	-40.7	0.0	0.8
95.8	65.0	25.2	27.5	35.8	12.0	-1.2	6.5	0.3	0.2
80.47	**0.07**	**0.71**	**3.46**	**31.33**	**0.11**				
1528.26	1.95	8.50	15.45	47.15	3.92				
0.0527	0.0350	0.0837	0.2243	0.6644	0.0275				
5.27	**3.50**	**8.37**	**22.43**	**66.44**	**2.75**				

Sn	Sb	Te	I	La	Ce	Pr	Nd	Er	Tm
2.80	1.30	0.36	23.45	29.73	55.92	6.51	25.17	1.78	0.22
-6.56	1.39	0.00	0.00	0.12	73.52	8.74	34.90	2.23	0.13
2.95	1.46	3.22	13.84	39.12	76.29	9.04	33.91	2.28	0.36
-6.91	1.55	0.00	0.00	0.16	100.31	12.14	47.01	2.86	0.21
2.40	1.34	1.45	16.68	29.72	57.84	6.88	25.89	1.82	0.27
-5.63	1.42	0.00	0.00	0.12	76.04	9.25	35.90	2.28	0.16
3.50	2.67	3.53	16.74	38.13	72.28	8.71	33.07	2.78	0.41
-8.20	2.84			0.15	95.04	11.70	45.85	3.49	0.24
-4.0	9.0	14.5	1.7	8.0	0.4	0.1	0.1	8.3	0.2
1.0	1.3			8.0	11.0	2.0	8.0	0.5	0.1
2.9	1.4	1.8	18.6	34.4	66.1	7.8	29.5	2.0	0.3
4.2	0.1	1.4	8.3	15.2	8.4	1.1	4.1	0.2	0.1
3.315	1.507	0.000	0.000	0.006	1.859	1.900	1.961	1.773	0.824
146.0	3.8	75.5	44.4	44.3	12.8	13.6	13.9	10.5	27.3
-0.5	0.0	-0.3	-2.0	-4.7	-8.3	-0.9	-3.6	-0.2	0.0
0.6	1.3	1.7	-1.9	3.7	6.2	0.9	3.5	0.8	0.1
3.56	**5.44**			**0.03**	**7.49**	**1.38**	**5.60**	**5.52**	**0.10**
-1.52	5.11			8.02	5.70	1.03	4.04	4.40	0.17
-2.3443	1.0655			0.0041	1.3148	1.3434	1.3863	1.2537	0.5823
-234.43	**106.55**			**0.41**	**131.48**	**134.34**	**138.63**	**125.37**	**58.23**

Lu	W	Hg	Pb	Bi	Th	G/KG
0.20	444.30	0.30	13.59	0.28	17.47	0.02
0.28	0.00	0.00	3.19	0.00	7.50	0.00
0.30	579.66	-0.24	14.26	0.40	12.46	0.02
0.42	0.00	0.00	3.35	0.00	5.34	0.00
0.22	369.81	-0.21	12.24	0.18	9.06	0.02
0.30	0.00	0.00	2.88	0.00	3.89	0.00
0.39	612.84	-0.19	17.48	0.58	15.78	0.02
0.53			4.11	0.00	6.77	
7.1	0.0	2.6	5.7	0.0	1.5	0.0
0.1			8.0		0.8	
0.3	512.0	0.0	13.9	0.3	15.0	
0.0	227.5	0.2	4.8	0.2	3.3	
1.944	0.000	0.000	0.332	0.000	0.607	0.000
15.4	44.4	690.7	34.3	44.4	22.3	
0.0	-142.2	-0.2	-1.7	-0.2	-5.9	
0.1	100.9	-0.2	3.6	0.2	0.8	
4.93			**1.61**		**0.49**	
3.58			6.86		1.15	
1.3747			0.2350		0.4291	
137.47			**23.50**		**42.91**	