



MASTERARBEIT

Feeder pipes – Expression of the uppermost plumbing system in Oligocene methane seep deposits, Washington State (USA).

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This work is dedicated to my loving man, friend and scientist-companion...

without you this journey would be unwritten

1. – Introduction

Plumbing systems of cold methane seeps are complex pathways along which hydrocarbon enriched fluids migrate over long distances upward through the marine sedimentary column. At greater depths corresponding to several hundreds of meters, fluid flow is enabled by tectonic faulting and fracturing of consolidated marine sediments (Hooper, 1991; Talukder, 2012). At shallower depths corresponding to the first few meters below the sediment-water interface, fluid and gas seepage is facilitated by conduits which are often subsequently cemented by methane-derived carbonate mineral phases. These subsurface features have been described in detail by Nyman et al. (2010) from Late Miocene cold seeps of New Zealand. A wide variety of tubular concretion morphologies was recognized, ranging from cylindrical pipes to sinuous tubes and other conduits. These tubular concretions are several meters in length and diameter. With the aid of stable carbon and oxygen isotopes, it was shown that the passing fluids were rich in methane and that carbonate precipitation within the conduits was induced by microbial activity. Nyman et al. (2010) linked concretion morphologies to variations in subsurface fluid flux. Similar insights were attained by De Boever et al. (2009; 2011), who investigated giant Early Eocene tubular carbonate concretions associated with subsurface plumbing systems from Bulgaria. The Bulgarian concretions are several meters high and one meter in diameter. Their biomarker inventory revealed that the flux of reduced fluids enriched in methane triggered the formation of the concretions. Similarly, Mazzini et al. (2008) observed subsurface plumbing systems in the Black Sea and discussed mechanisms of fluid seepage and carbonate precipitation. Direct geological evidence for an ancient plumbing network was reported by Clari et al. (2004), who investigated Miocene carbonate pipes within the setting of a mud volcano from northwestern Italy. Cylindrical concretions were interpreted as direct pathways for methane-enriched fluid expulsion. A further study on this topic by Aiello et al. (2001) centered on Miocene calcite concretions from Santa Cruz, California. Several types of tubular features were distinguished, showing variable orientations. One type of conduit was positioned parallel to bedding, implying a horizontal fluid flow, others were aligned with a high angle to the bedding planes. An early work by Orpin (1997) discussed the possibility that large carbonate concretions from New Zealand represent fossilized carbonate chimney structures. All aforementioned studies are in accord with carbonate precipitation from reduced fluids and coupled to sulfate dependent anaerobic oxidation

of methane (AOM). This process is carried out by a consortium of methane oxidizing archaea and sulfate reducing bacteria (Hinrichs et al., 1999; Boetius et al., 2000). Methane in the marine environment is produced biologically by anaerobic methanogenic archaea (Jørgensen and Kasten, 2006; Reeburgh, 2007) and thermogenically at higher temperatures and pressures deeper within the sediments (Claypool and Kaplan, 1974; Sassen et al., 1999). The two most important pathways of methanogenesis are CO₂ reduction by hydrogen and the transformation of acetic acid (Rullkötter, 2006). AOM is considered to be the trigger for authigenic carbonate precipitation at cold seeps (Ritger et al., 1987; Suess and Whiticar, 1989; Peckmann et al., 1999), as it increases alkalinity and reduces the solubility of carbonate minerals.

Tubular carbonate concretions have received particular attention, as they have been interpreted to represent integral parts of ancient, shallow cold-seep plumbing systems (Nyman et al. 2010). Most subsurface seep plumbing models from the above mentioned studies on tubular concretions do not discuss the factors that govern the establishment of fluid conduits leading to the tubular structure of the precipitates. Nelson et al. (2004) explicitly excluded the possibility of a biogenic origin for tubular carbonate concretions from New Zealand. While many studies have discussed large concretions within meters from the seabed, the uppermost region of these plumbing systems has received less attention (Wetzel, 2013). Only recently, Wetzel (2013) investigated the bioturbated zone in association with authigenic carbonate formation. Various open and partly connected tubes were found within a carbonate nodule collected from the South China Sea. To expand the knowledge of the uppermost plumbing network of ancient cold seep, this work investigates mineralized fluid pipes with a distinct paragenetic sequence, here referred to as feeder pipes, which occur below an Oligocene seep deposit within the Lincoln Creek Formation in Washington State. This study describes the paragenetic sequence of authigenic minerals making up the feeder pipes and relates it to phase specific rare earth element content and the isotopic composition of carbon and oxygen. As already suggested by Peckmann et al. (2007) and Wetzel (2013), carbonate pipes and tubular concretions in the bioturbated zone may have primarily represented burrows of seafloor dwelling organisms, although it may not be always obvious which organisms generated the burrows. The burrows represent conduits that offer migration pathways for methane-rich fluids, as these always take the path of lowest resistance through the sediment column (cf. Hovland et al., 2010).

2. – Tectonic and geologic setting

Induced through thrust faults and followed by the subduction of the oceanic Juan de Fuca plate beneath the continental North American plate approximately 35 million years ago, a former basaltic terrane docked on the North American continent and built up the Coast Range Terrane (intra-Pacific-seamount). Contrariwise a forearc or a backarc rifting and spreading scenario for the origin of the basalts at the North American margin have been suggested (marginal basin; Brandon and Vance, 1992). During these tectonic processes the Cascadian accretionary wedge started to form. While the accretionary wedge belongs to a tectonic unit called the Olympic Subduction Complex or Olympic Structural Complex, which is exposed in the Olympic Mountains and developed through frontal accretion plus underplating, the overlying Coast Range Terrane is a unit informally called the Peripheral sequence (Fig. 1A; Brandon and Vance, 1992; Brandon et al., 1998). Both units are separated by the major Hurricane Ridge Fault. The aforementioned structural units with their respective formations have been exposed due to exhumation and subsequent erosion (Fig. 1B). The accretionary wedge is locally uplifted, forming the Cascadian forearc high in the center of the Olympic Mountains, a process that started approximately 18 million years ago. Since 14 million years a steady exhumation rate is adopted and in general the whole area around the Cascadia forearc high is uplifted and eroded, supported by ongoing accretion and thickening of the wedge (Brandon et al., 1998). The lowest unit of the Coast Range Terrane is the Crescent Formation, which consists of ophiolitic crust such as pillow and massive basalts (Coast Range Basalts). This formation is overlain by early to late Eocene sedimentary rocks followed by mostly marine Oligocene through lower Miocene marine and clastic rocks (Brandon and Vance, 1992; Beikman et al., 1967; Rau, 1967). The carbonate rocks studied here derive from a marine sedimentary succession of the allochthonous Coast Range Terrane of the Olympic Peninsula, precisely the Lincoln Creek Formation (LCF). The formation, which is widespread in western Washington, is exposed best in various river valleys on the south side of the Olympic Mountains, ranging to the northern shore of the Columbia River (Kiel, 2010).

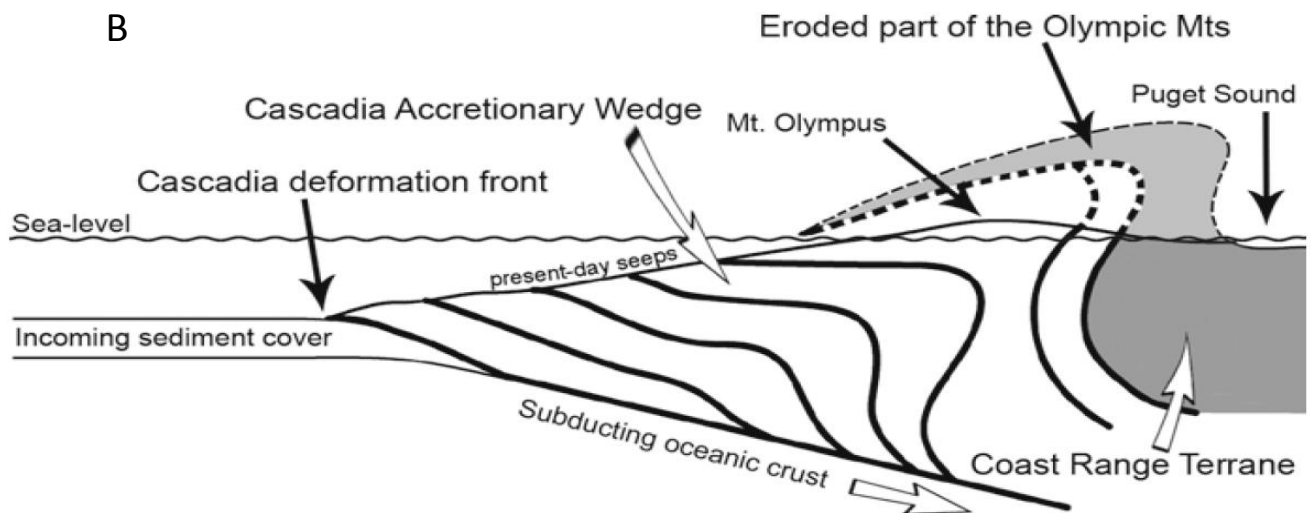
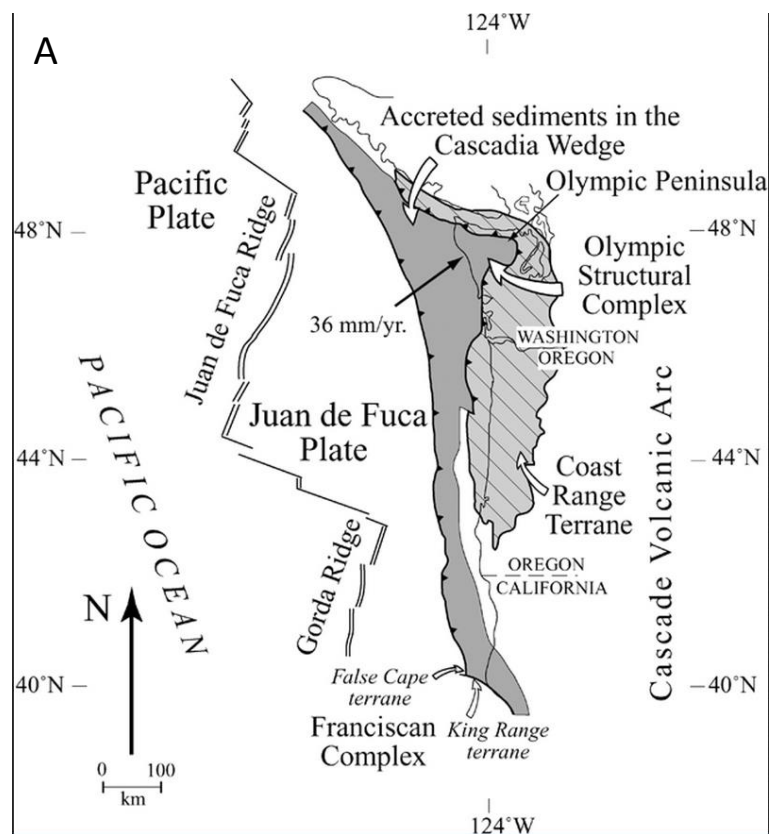


Fig. 1. A: Tectonic situation of the study area (Stewart and Brandon 2004) B: Cascadia subduction zone shown in in cross section (Kiel, 2010, redrawn from Stewart and Brandon 2004).

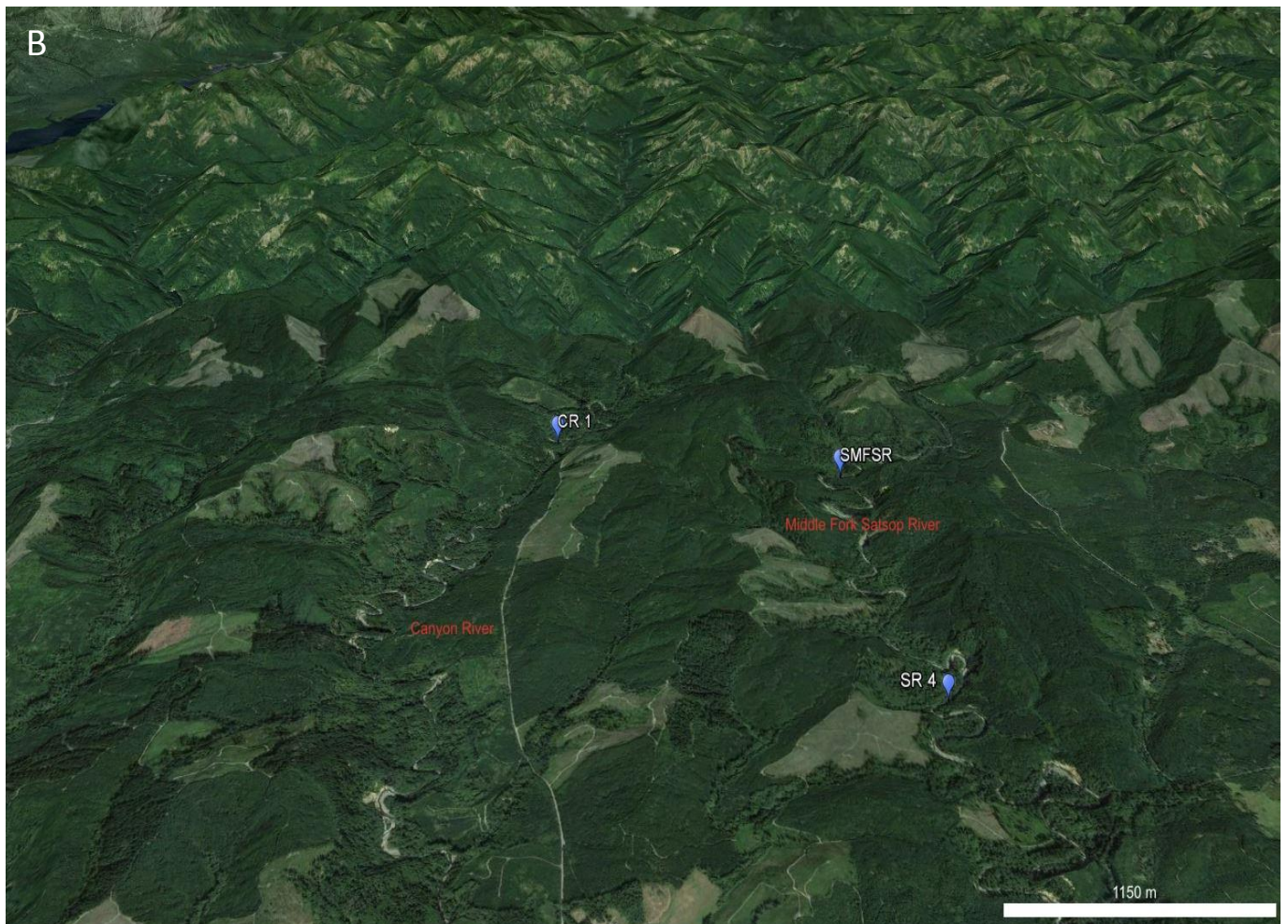


Fig. 2. A: Location of the study area. B: Overview of the three localities from where the samples were collected (<http://earth.google.com>).

The Lincoln Creek Formation consists of tuffaceous siltstone and minor amounts of feldspathic sandstone as well as calcareous concretions. These marine deposits have a dark gray to olive gray color. In the lower part of the formation thin bedded, laminated, bioturbated, fine to medium grained and graded micaceous sandstone is present. In some places the formation contains thin layers of basaltic and glauconitic sandstone, especially at the base. The upper part of the formation is massive to laminated, bioturbated, and contains poorly bedded siltstones and mudstones (Wells, 1989; Beikman et al., 1967; Goedert et al., 2000). The Lincoln Creek Formation is mainly Late Eocene to Oligocene in age. The samples discussed here derive from the early and late Oligocene part of the formation (Fig. 4 B). The studied outcrops are exposed along the Satsop and Canyon River beds (Fig. 2B, 3), where the Lincoln Creek Formation is approximately 3000 m thick (Beikman et al., 1967; Peckmann et al., 2002). Most seep deposits are allochthonous and range in size from 0.45 to 2 m (Peckmann et al., 2002). Carbonate pipes and masses are exposed on the south side of the Middle Fork of the Satsop River (SMFSR; Fig. 4 A, C; 47°17'40.50"N, 123°28'48.93"W). SMFSR records show widespread seepage and a large tube was horizontal with respect to bedding. Smaller curved pipes were found approximately 1.5 m stratigraphically above the horizontal tube, and ended at a small mass with a few bivalves. The other Satsop River site (47°16'18.01"N, 123°28'56.15") is the SR4 deposit of Peckmann et al. (2002). Carbonate pipes are apparently most abundant just beneath the base of the SR4 deposit, associated with small vesicomid bivalves. SR4 has the greatest taxonomic diversity compared to other seep deposits nearby, containing bivalves, gastropods, cephalopods, decapods and anthozoa among others (Peckmann et al., 2002). The Canyon River samples were collected at a site (47°18'7.61"N, 123°30'31.74"W) in the vicinity of the CR1 deposit of Peckmann et al. (2002). CR1 is an allochthonous seep deposit, which is stratigraphically equivalent to SMFSR. It is fragmented and spatially separated by sharp contacts from the surrounding siltstone, suggesting that the limestone was transported and faulted (Goedert et al., 2000) This deposit contains vestimentiferan worm tubes and scarce modiolid bivalves (Goedert et al., 2000).

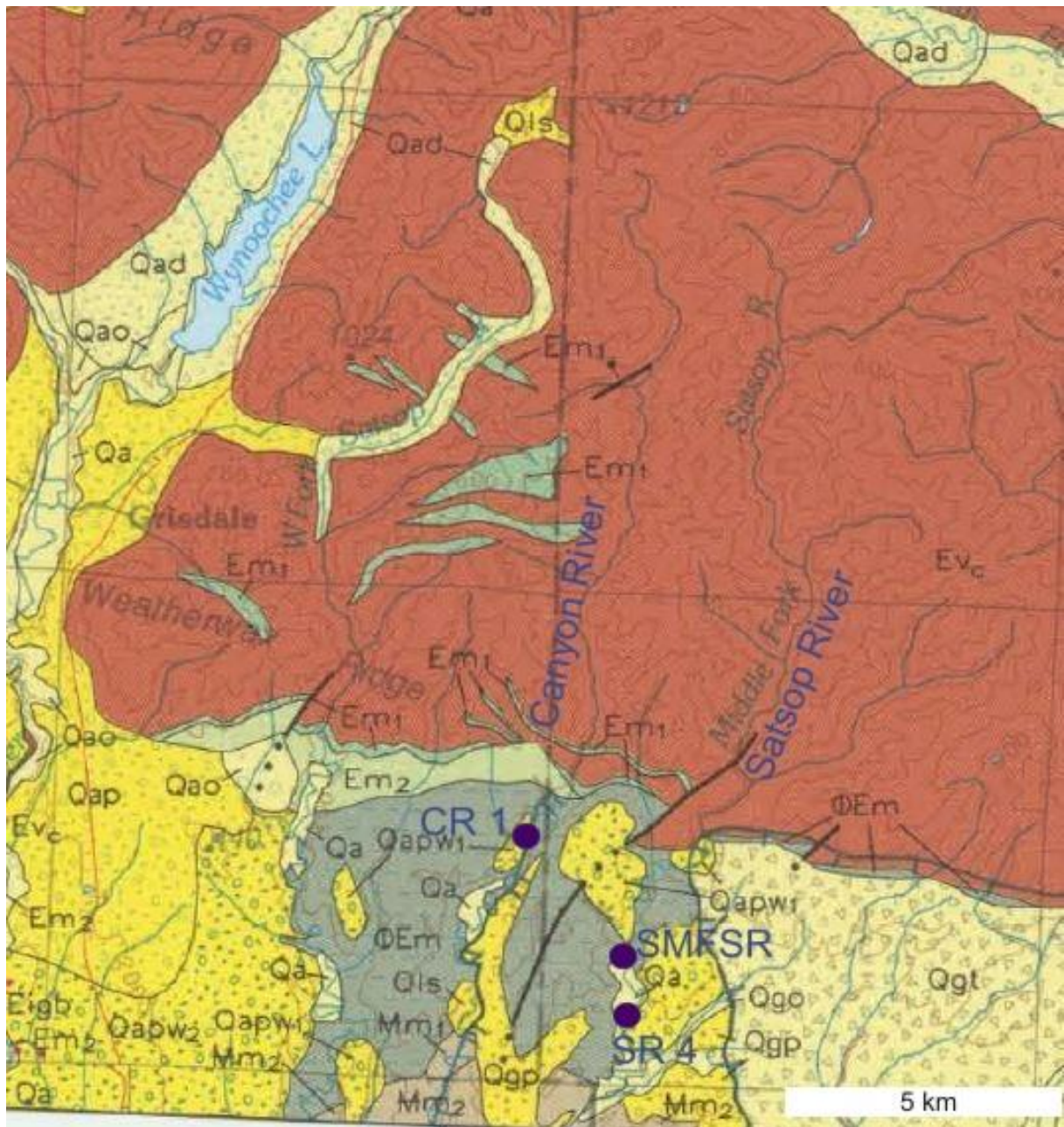


Fig. 3: Geologic map of the study area showing the Canyon River (CR1), South of Middle Fork Satsop River (SMFSR) and Satsop River (SR4) deposits (modified after Dragovich et al., 2002).

Unconsolidated sediments

	Landslide debris – Clay, silt, sand, gravel and larger blocks; unstratified and poorly sorted (Quaternary, nonglacial)
	Alluvium – Sorted combinations of silt, sand and gravel deposited in streambeds and alluvial fans (Quaternary, nonglacial)
	Glaciolacustrine deposits – Sand, silt and clay deposited in proglacial lakes (Quaternary, glacial continental)
	Undifferentiated outwash – Recessional and proglacial stratified sediments (Quaternary, glacial continental)
	Till – Unsorted, unstratified, highly compacted clay, silt, sand and gravel glacial deposits (Quaternary, glacial continental)
	Undifferentiated drift of pre-Fraser age – Till and outwash sand and gravel (Quaternary, glacial continental)
	Late Wisconsinian alpine outwash – Stratified sand and gravel not deeply weathered (Quaternary, glacial alpine)
	Early Wisconsinian alpine drift – Till and outwash sand and gravel (Quaternary, glacial alpine)
	Older pre-Wisconsinian alpine drift – Outwash sand and gravel, till and lacustrine silt and clay (Quaternary)
	Younger pre-Wisconsinian alpine drift – Outwash sand and gravel, till and lacustrine silt and loess (Quaternary)

Sedimentary deposits and rocks

	Lower-middle Miocene marine sedimentary rocks – Fine grained, silty, feldspathic sandstone; contains abundant siltstones with fragments of carbonaceous material. <i>Consists of the Astoria Formation.</i>
	Middle-upper Miocene marine sedimentary rocks – Coarse – to fine grained, silty, friable, lithofeldspathic or feldspatholithic sandstones; local conglomerate, siltstone and claystone.
	Oligocene - Eocene marine sedimentary rocks – Thick-bedded, light gray tuffaceous siltstone and fine grained tuffaceous sandstone; discontinuous basaltic and glauconitic sandstone beds in lower part. <i>Includes the Lincoln Creek Formation</i>
	Eocene marine sedimentary rocks – Very thick to medium bedded conglomerate, sandstone and pillow basalt
	Lower-middle Eocene marine sedimentary rocks – Sandstone, siltstone, mudstone argillite, conglomerate and breccia
	Middle-upper Eocene marine sedimentary rocks – Sandstone, siltstone, argillite, conglomerate and pillow basalt

Volcanic deposits and rocks

	Lower-middle Eocene Crescent Formation – Tholeiitic basal flows, basaltic flow breccia and volcanoclastic conglomerate
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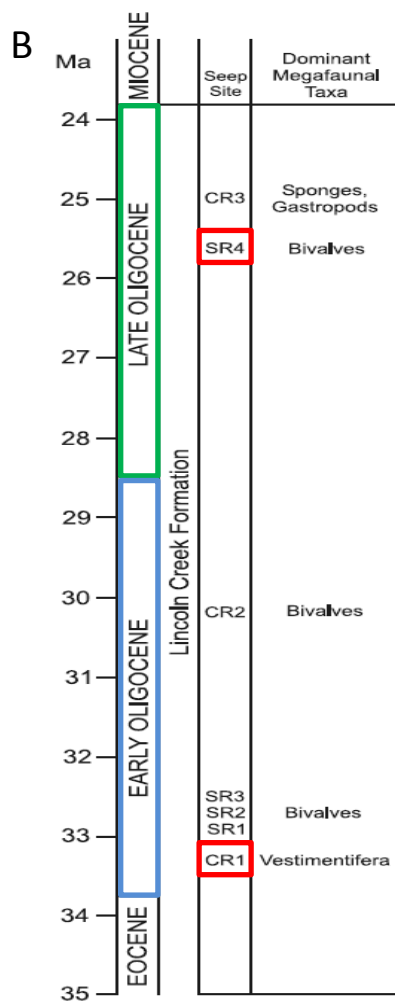


Fig. 4 A: Picture of the outcrop in the Satsop River bed at locality SMFSR. B: Chronostratigraphic chart of the study area (modified from Peckmann et al., 2002) C: Closer look of the seep deposit.

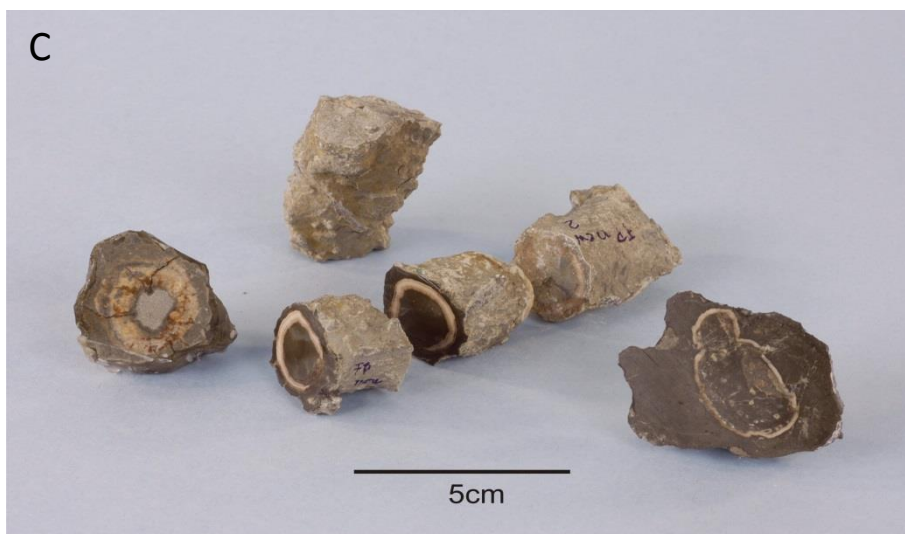


Fig. 5 A: Picture of the outcrop in the Satsop River bed at locality SMFSR. B: Chronostratigraphic chart of the study area (modified from Peckmann et al., 2002) C: Closer look of the seep deposit.

3. – Materials and methods

Samples were collected by James L. Goedert (Burke Museum of Natural history and Culture in Seattle, Washington). They were taken along the river beds at water level low stand. In order to determine the paragenetic sequence of authigenic mineral phases within the feeder pipes, petrographic microscopy was applied to thin sections (7.4 x 9.7 to 5 x 5 cm) using a Leica DM4500 P polarization microscope. Photographs were taken with a Leica DFC 420 camera using the Leica Application Suite 3.2.0 software.

Fluorescence microscopy was performed on a Nikon SMZ 1500 stereomicroscope with a Prog.Res Speed XT core 5 camera as well as a Nikon Optiphot-2 optical microscope. The software Prog.Res Capture pro 2.8.8. was used for image analysis. UV and blue filters (377/50 409 LP and 480/40 510 LP, respectively) were used. To discriminate carbonate minerals, some thin sections were partly stained with a mixture of potassium ferricyanide and alizarin red solution, dissolved in 0.1% HCl (cf. Dickson, 1966). Some thin sections were partially stained with Feigl's solution (cf. Füchtbauer, 1988) to distinguish aragonite and calcite. Powdered samples of two pipes (SR4) for the powder X-ray diffraction were prepared with a hand-held microdrill. Measurements were carried out at the Department for Geodynamics and Sedimentology at the University of Vienna. The powdered samples were analyzed with a Panalytical PW 3040/60 X'Pert PRO (CuK α radiation, 40 kV, 40 mA, step size 0.0167, 5 s per step) diffractometer. The X-ray diffraction patterns were interpreted using the Panalytical software "X'Pert High score plus". Samples for carbon and oxygen stable isotope analysis were taken from the surface of the sliced pipes using a hand-held microdrill. Sample powders were reacted with 100% orthophosphoric acid in a vacuum at 75°C, and the evolved CO₂ gas was analyzed with a Finnigan MAT 251 mass spectrometer at the University of Bremen. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported relative to the Vienna Peedee-Belemnite standard (standard deviation smaller than 0.04‰), and appropriate correction factors were applied. The total carbon (TC) and organic carbon (TOC) content from three samples (SR4) were determined with a LECO RC-612 Carbon Analyzer (St. Joseph, MI, USA), equipped with a solid-state infrared detector at the Department of Environmental Geosciences at the University of Vienna. The TC was determined by measuring the released carbon dioxide at a temperature of 1000°C. Prior to sample measurements a pure CaCO₃ standard (Co. Merck) was measured, revealing relative standard deviation of 0.06%. The TOC contents were determined at 550 °C.

A Synthetic Carbon Leco 502-029 (1.01 ± 0.02 carbon%) standard was measured prior to sample analyses and a standard deviation of 0.005% was calculated.

CaCO₃% contents were calculated according to the equation:

$$\text{CaCO}_3\% = (\text{TC} - \text{TOC}) \times 8.333$$

Rare earth element and Y and other trace element contents were analyzed from two feeder pipe samples (SR4) by laser ablation inductively coupled plasma mass spectrometry on a ThermoFinnigan Element2 mass spectrometer at the University of Bremen. The laser (NewWave UP193ss) was operated with a 5 to 10 Hz pulse rate for point and line ablation, respectively. Two samples from site SR4 were analyzed, whereby the beam diameter was set to 75 µm for the first, and to 100 µm for the second sample. Pre-ablation was made with a 120 µm beam diameter and 5 Hz pulse rate before analysis. The produced data were calibrated against the synthetic SRM (Standard Reference Material) 610 and 612 silicate glasses from the National Institute of Standards and Technology (NIST; Jochum et al., 2012), and BCR-2G basalt glass from the USGS and BHVO-2G basalt glass were used as unknown measured standards. Due to different ablation yields of samples and calibration standards, ⁴³Ca was used as an internal standard. This practice also balanced temporal variations of the ablation signal. All elements were referred to the internal standard to allow quantitative analyses. A calcium content of 40% was adopted for clear and yellow aragonite of the analyzed samples, for matrix micrite, microspar, and brownish calcite measured Ca contents were used. The GeoPro software by Cetac was used for data evaluation. Raw data for each analysis were examined offline in order to choose segments of time when the laser was ablating through a homogeneous vertical section of a sample. Such sections are typified by time-resolved signals of all the elements that are more or less parallel in a logarithmic plot.

4. – Results

4.1 Sample description – Satsop and Canyon River feeder pipes

Feeder pipes from SR4, CR1 and SMFSR have mean diameters of 2.3, 2.3 and 3.3 cm, respectively. The lengths of the fragmented pipes ranges from 6 to 10 cm as a function of how much could be retrieved during sampling. All carbonate pipes of the Satsop (SR4; SMFSR) and Canyon Rivers (CR1) are enclosed by siltstones and mudstones (Figs. 5, 6). The matrix micrite forming the outer part of the pipes is dark brown in color and rich in detritus, represented by carbonate fragments, monaxon and triod sponge spiculae, benthic foraminifera, clay minerals such as glauconite, pieces of wood and organic material, as well as quartz and feldspar (Fig. 7 A, 8 A). The matrix micrite reveals little variability among the studied samples and shows no autofluorescence (Fig. 18). Pyrite occurs mainly as framboids and spherical aggregates, or subordinate as dispersely distributed grains (Fig. 8 B). Pyrite is also found in association with glauconite grains, which are covered to variable degrees by the sulfide mineral (Fig. 9 A) or are interspersed by pyrite along fractures within grains (Fig. 9 B). Glauconite grains vary from 50 to 500 μm in diameter. All studied samples contain oval to spherically shaped fecal pellets (Fig. 7 B), some of which are identified as the ichnogenus *Palaxius*, commonly assigned to callianassid decapod crustaceans. Structured crustacean microcoprolites vary 200 to 600 μm in diameter, however their typical crescent-shaped canals are not well preserved. The phase postdating matrix micrite in the paragenetic sequence is well-preserved yellow aragonite cement (Fig. 10 A). The contact between micrite and yellow aragonite is rather diffuse, with a cloudy transition into the outer matrix. Yellow aragonite shows a micro- to cryptocrystalline texture. It extends into veins and fractures of the matrix micrite. Yellow aragonite is pervaded by pyrite and dark inclusions, interpreted to represent organic matter. In places, yellow aragonite forms irregular layers of variable thickness. In SR4 samples, the thickness of layers varies widely from 10 to 1500 μm . In CR1 samples, thickness varies from 50 to 1550 μm . Yellow aragonite is always closely associated with clear aragonite, the phase that is next in the paragenetic sequence and the volumetrically most abundant phase after matrix micrite (Figs. 10 A, 11, 12, 13).

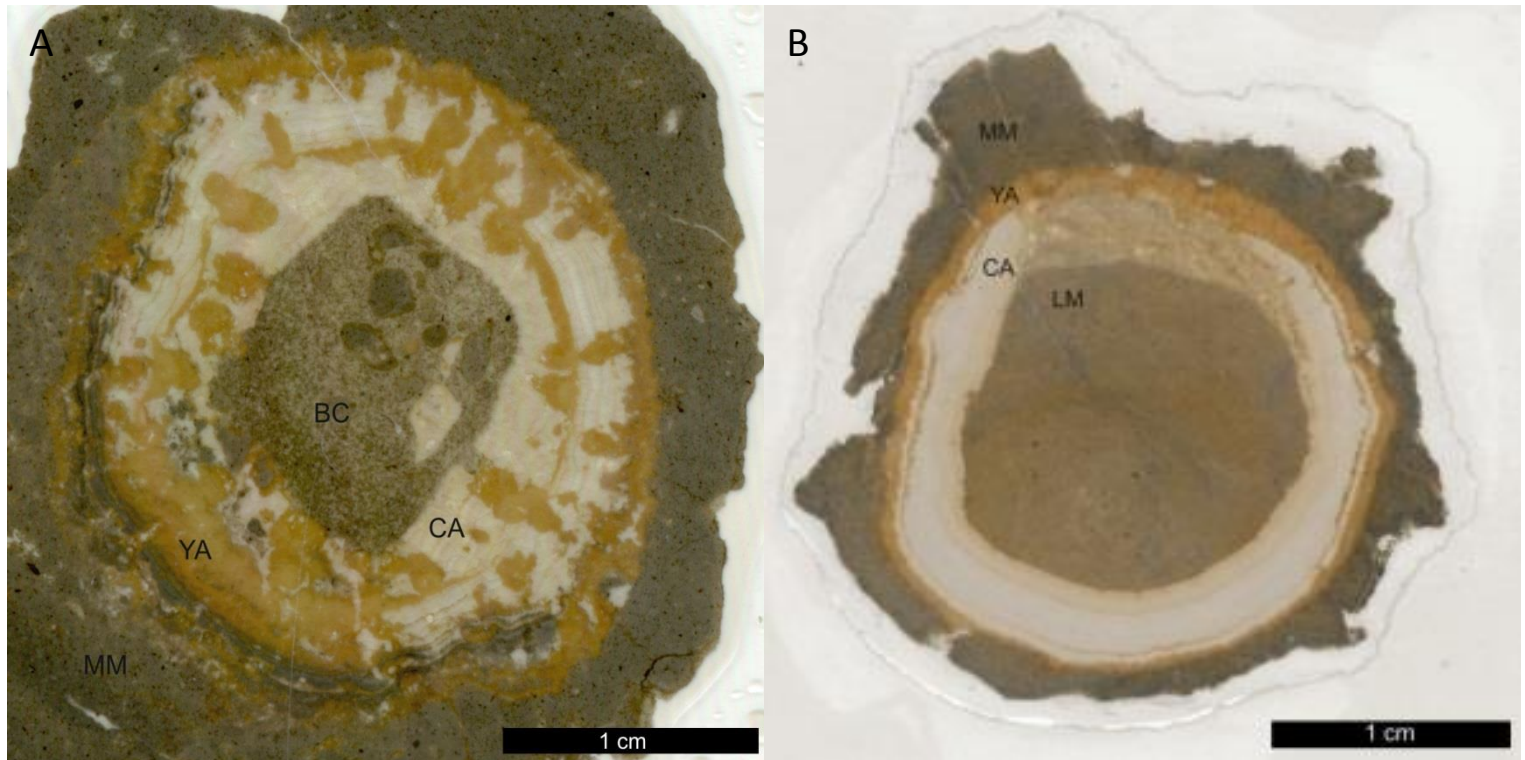


Fig. 6 A: Feeder pipe thin section scan from SR4 showing the common paragenetic phase sequence. B: Feeder pipe thin section scan from CR1. Matrix micrite (MM), yellow aragonite (YA), clear aragonite (CA), late micrite (LM) and brownish calcite (BC).

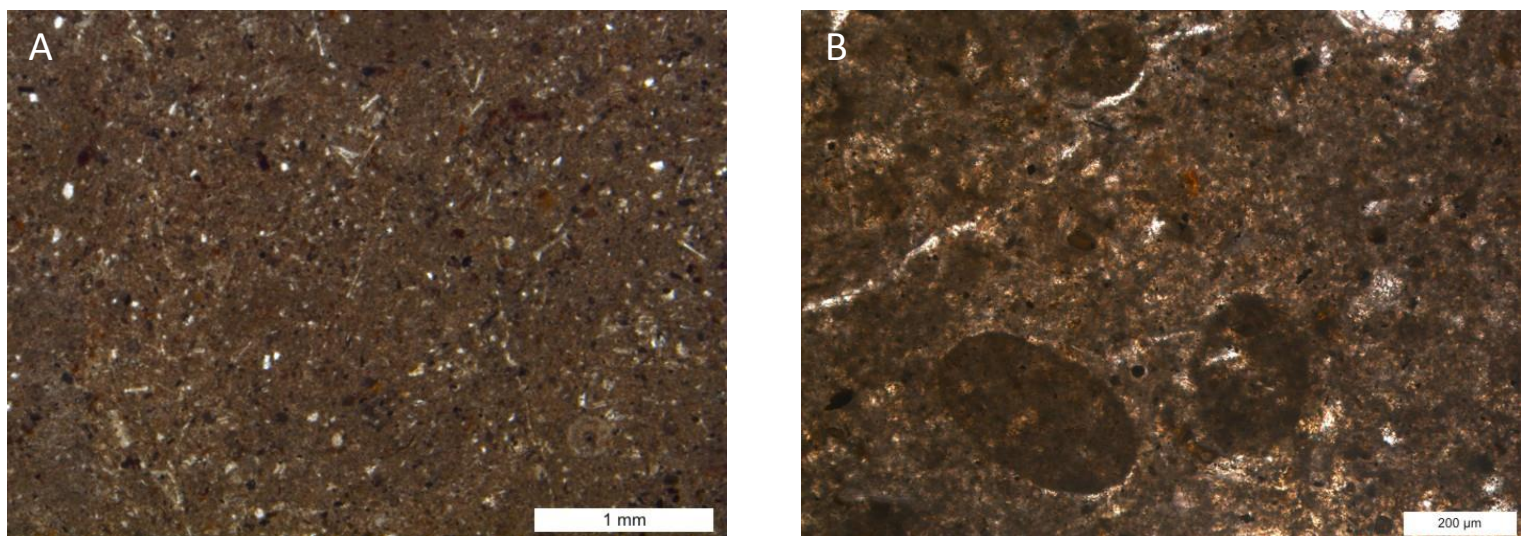


Fig. 7 A: Matrix micrite comprising abundant detrital components (SMFSR). B: Oval and spherical fecal pellets within the matrix micrite (SMFSR).

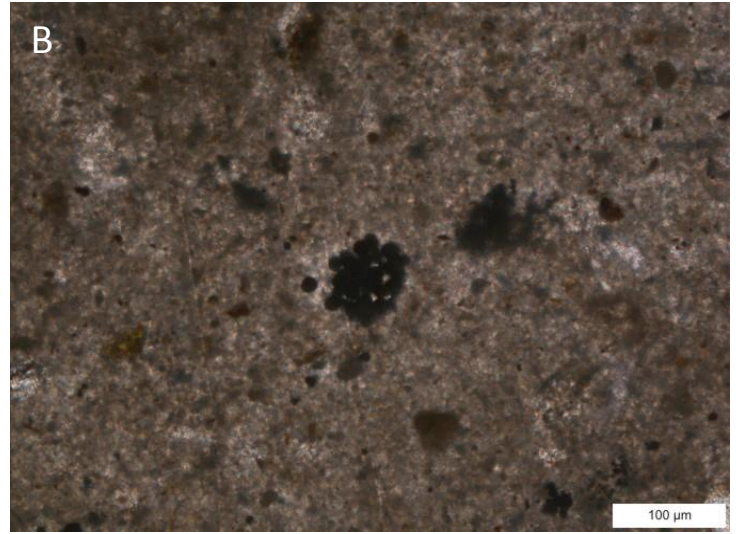
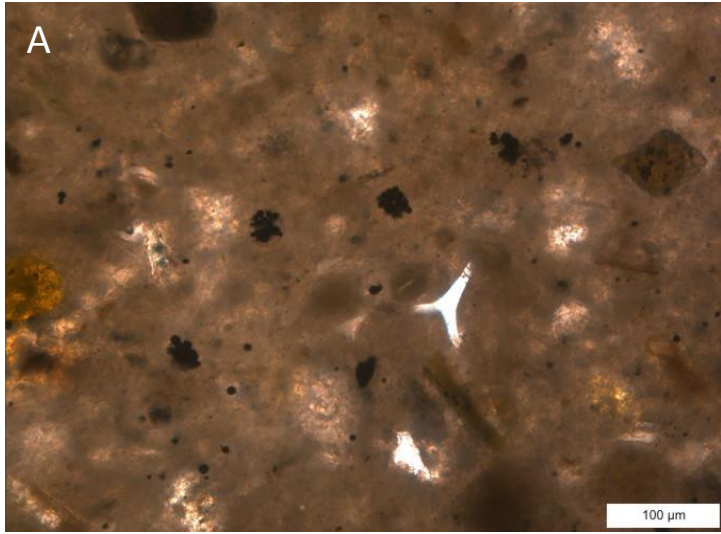


Fig. 8 A: Small spherical aggregates of framboidal pyrite and triod sponge spicule within the matrix micrite (SR4). B: Single pyrite cluster enclosed in matrix micrite (SMFSR).

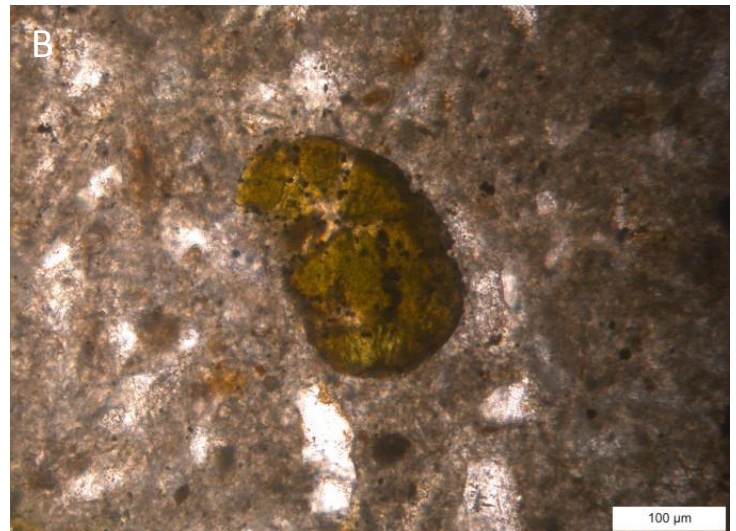
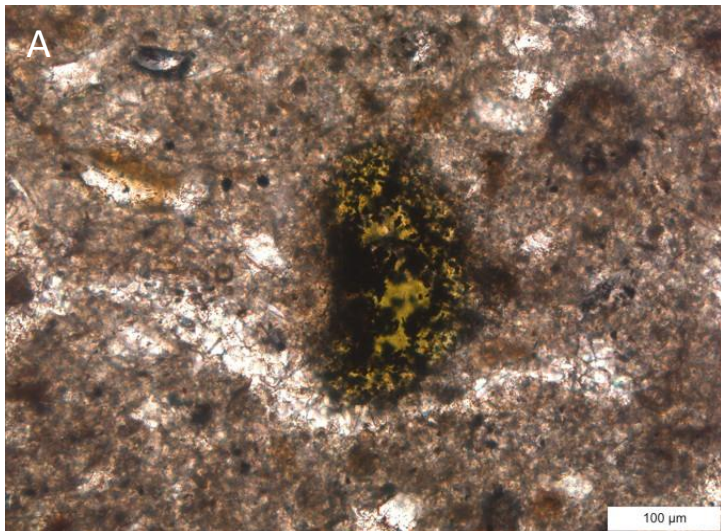


Fig. 9 A, B: Glauconite grains and associated pyrite (SMFSR).

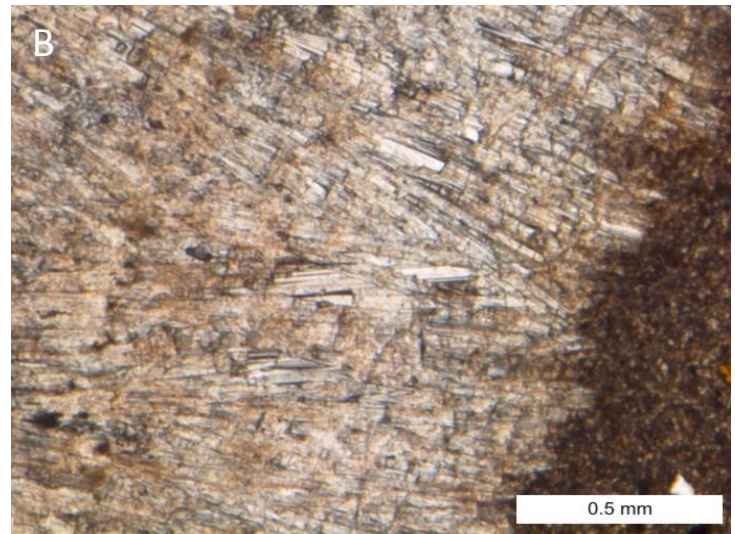
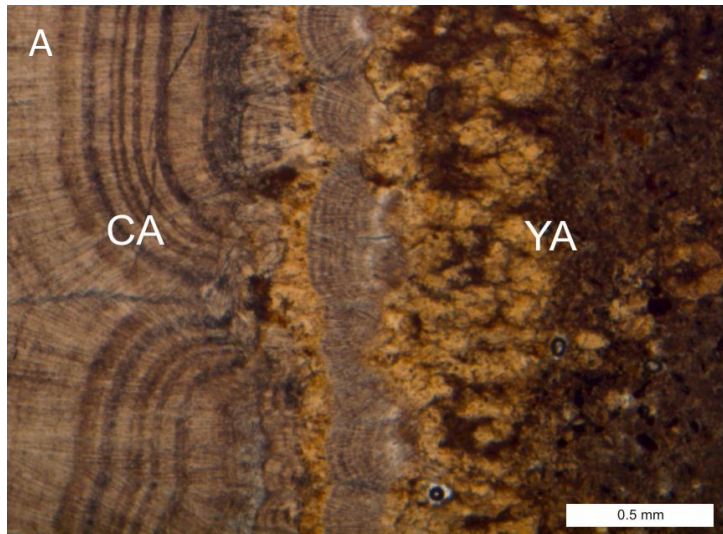


Fig. 10 A: Yellow aragonite (YA) in association with clear aragonite (CA) (CR1). B: Bundles of fine aragonite needles showing terminations orthogonal to growth direction (SR4).



Fig. 11 A: Yellow aragonite (YA) intercalated with clear aragonite (CA) (CR1). B: Clear aragonite isopachous cement showing peroidic inclusion-rich and inclusion-poor bands (CR1).

Clear aragonite is banded and botryoidal and consists of isopachous aggregates of fibrous crystals (Fig. 11). Crystal fibers occur in a fan-shaped form and needle tips point towards the center of pipes. The fibrous crystals exhibit orthogonal habits (i.e. flat crystal terminations, Fig. 10B). Isopachous crystal bands show a thickness 235 to 3000 μm in SR4 pipes. In CR1 pipes bands vary from 300 to 3400 μm , in SMFSR pipes they range from 1000 to 3200 μm . Botryoids and isopachous bands show a layered growth habit, whereby inclusion-rich and inclusion-poor layers alternate. Some botryoids show pyrite rims at their periphery (Fig. 12 A). Single botryoids of SR4 pipes vary from 1200 to 2070 μm in length and 1560 to 2060 μm in width. In CR1 pipes botryoids measure approximately 2700 μm in length and 1500 μm in width. In SMFSR samples botryoids range from 850 to 1100 μm in length and 580 to 1400 μm in width. Both, yellow and clear aragonite cements are intercalated and form isopachous layers. Yellow aragonite also intrudes clear aragonite orthogonal to the banded layers (Figs. 12 B, 13). Yellow aragonite fills irregular cracks within clear aragonite. Yellow aragonite predates clear aragonite, in other places clear aragonite appears to be dissolved and replaced by yellow aragonite (Fig. 12 B). Thin section staining revealed that calcium carbonate phases are stained red. Clear and yellow aragonites show a pink to red color in all thin sections, thus confirming their mineralogy. Staining with Feigl's solution indicates that clear and yellow aragonites are indeed aragonite, as are both covered with black dots of manganese oxide and metallic silver. Yellow aragonite reveals the strongest autofluorescence, which is expressed by a reddish to brownish color (Figs. 18, 19, 20). Clear aragonite exhibits a noticeably weaker fluorescence (Figs. 18, 19, 20). The later phases in the paragenetic sequence are a homogenous micrite, microspar, and in some samples brownish calcite (cf. Peckmann et al., 2002). In CR1 samples, the latest phase is late, homogenous micrite containing detrital grains. However when compared to matrix micrite, the late pipe-filling micrite has less detritus and is lighter in color (Fig. 14). The detritus comprises mostly carbonate fragments. Framboidal pyrite is scattered within pipe-filling micrite. In SR4 pipes, microspar or brownish calcite are the latest phases, occurring in the center of pipes. Microspar is light brown to grayish and contains pyrite, quartz, and glauconite grains (Fig. 15). Gypsum and clay minerals associated with the microspar were only detected by X-ray diffraction. Microspar crystals are more or less uniformly sized, subhedral to euhedral and measure 10 to 15 microns in diameter.

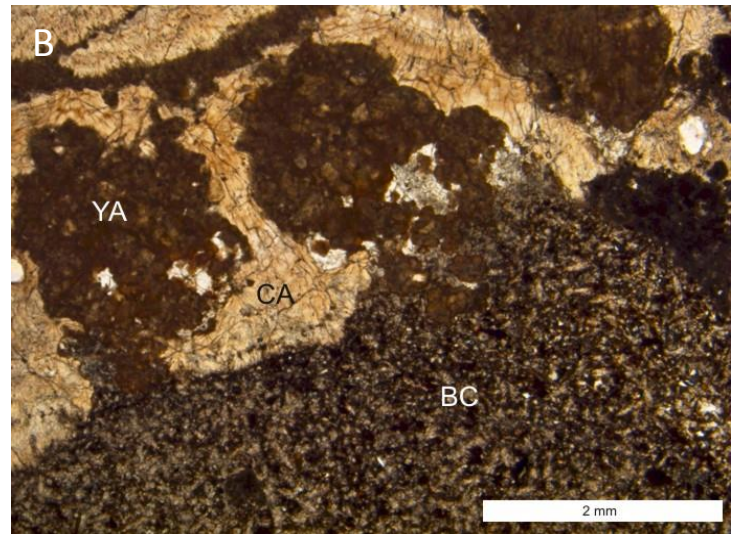


Fig. 12 A: Bundles of aragonite needles pointing towards the center of the pipe rimmed by pyrite crystals (SMFSR). B: Co-occurrence of yellow (YA) and clear (CA) aragonites at the boundary to brownish calcite (BC) (SR4).

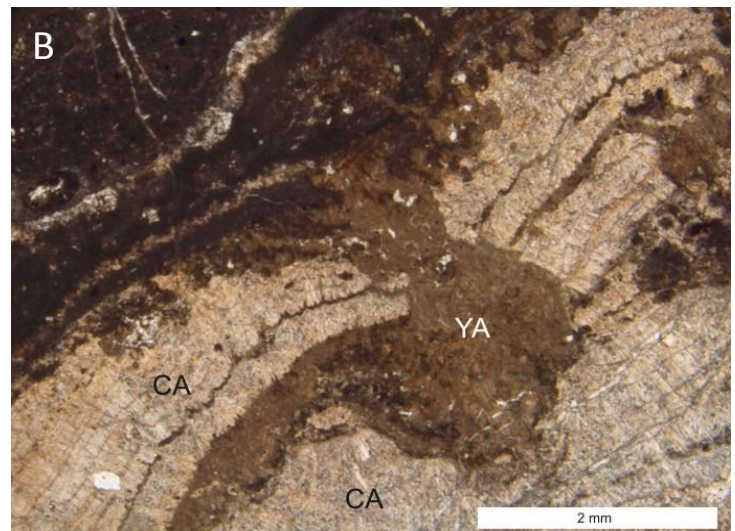
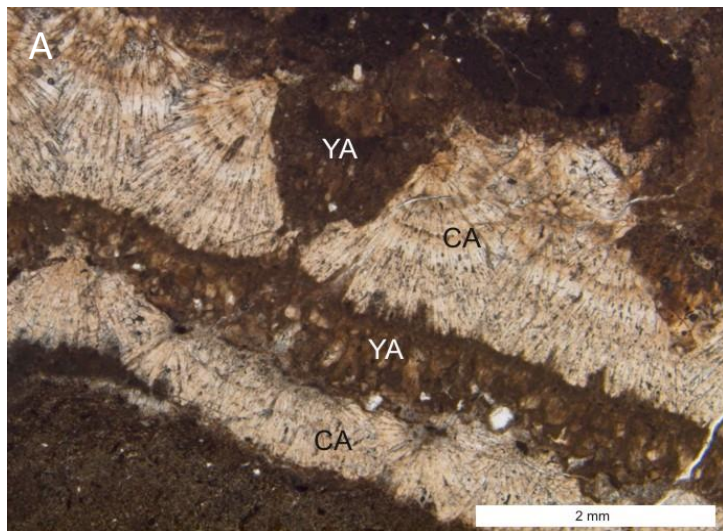


Fig. 13 A, B: Yellow aragonite (YA) filling cracks within clear aragonite (CA).

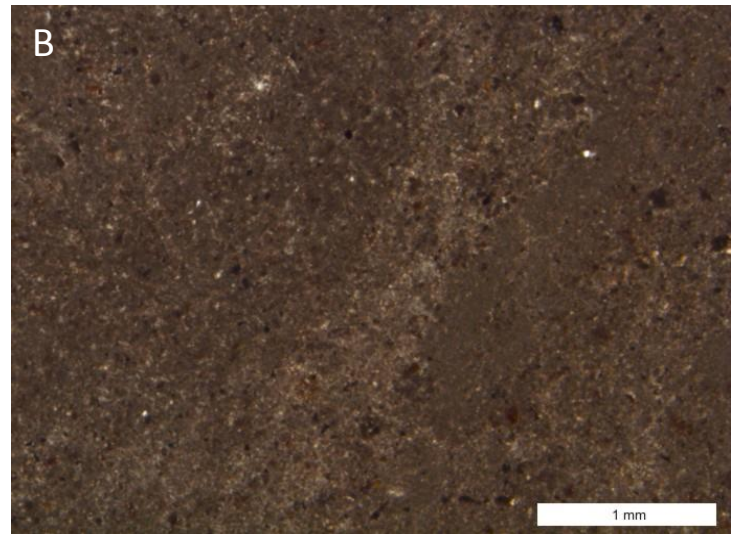
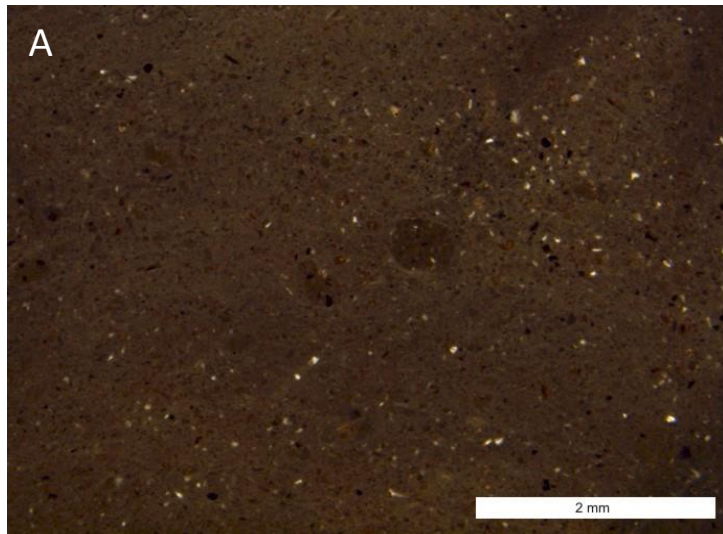


Fig. 14 A: Inner micrite filling the center of the pipe (CR1). B: Inner micrite from Satsop River deposit (SR4).

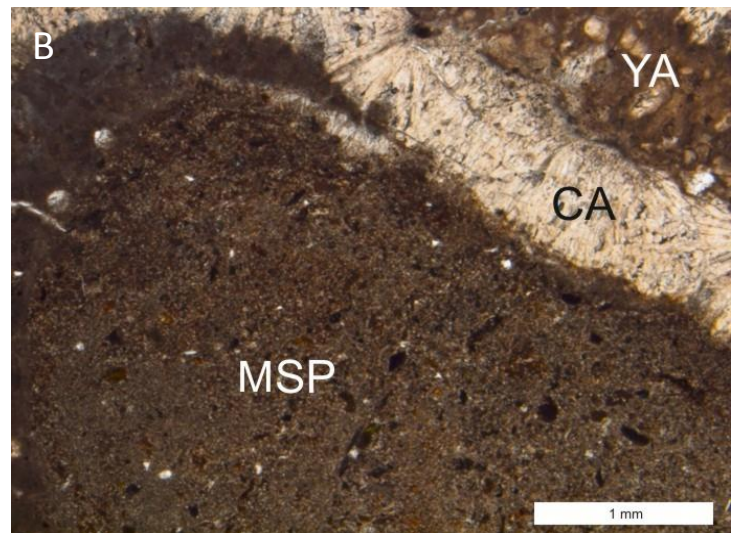
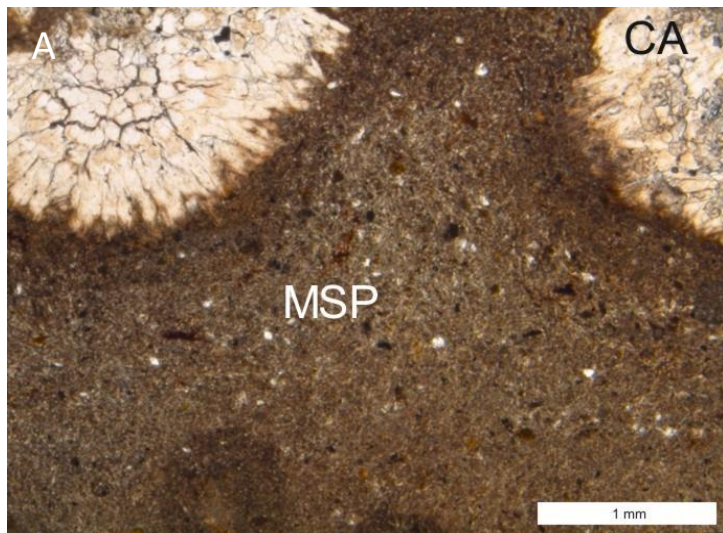


Fig. 15: Microspar (MSP) with detritus filling the pipes of Satsop River feeder pipes (SR4).

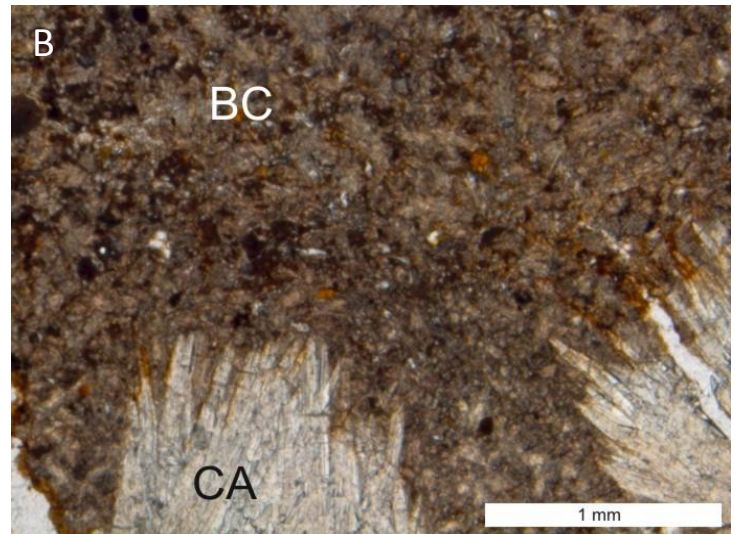
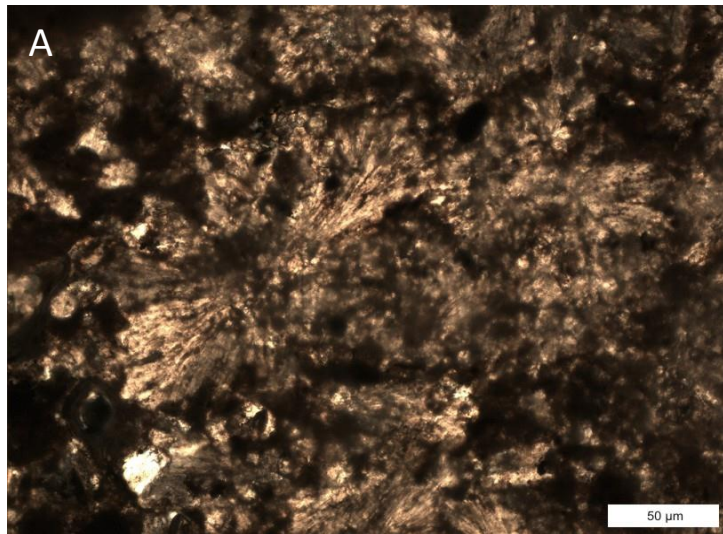


Fig. 16 A: Botryoidal to dumbbell shaped calcite crystal aggregates (SR4). B: Brownish calcite (SR4).

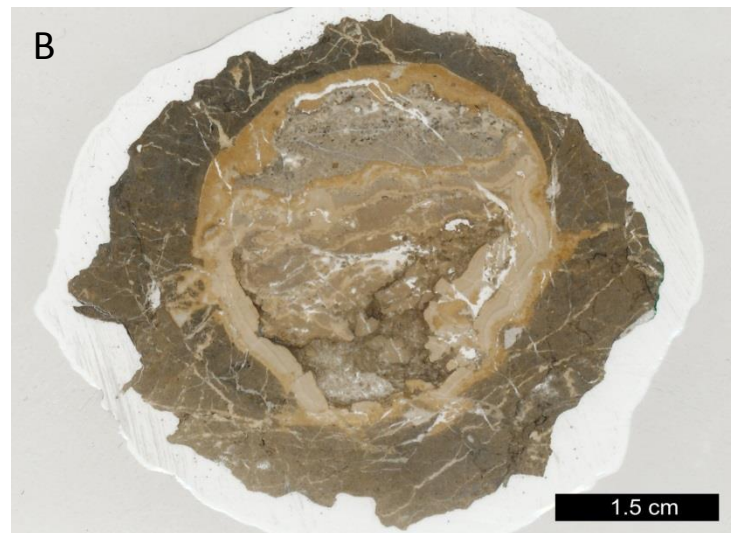
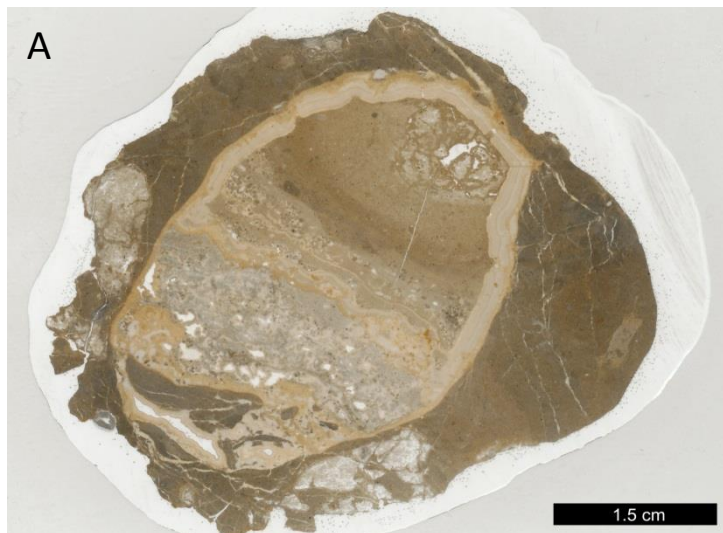


Fig. 17 A: Geopetal feeder pipe filling from SMFSR. B: Fractured feeder pipe with geopetal filling from SMFSR.

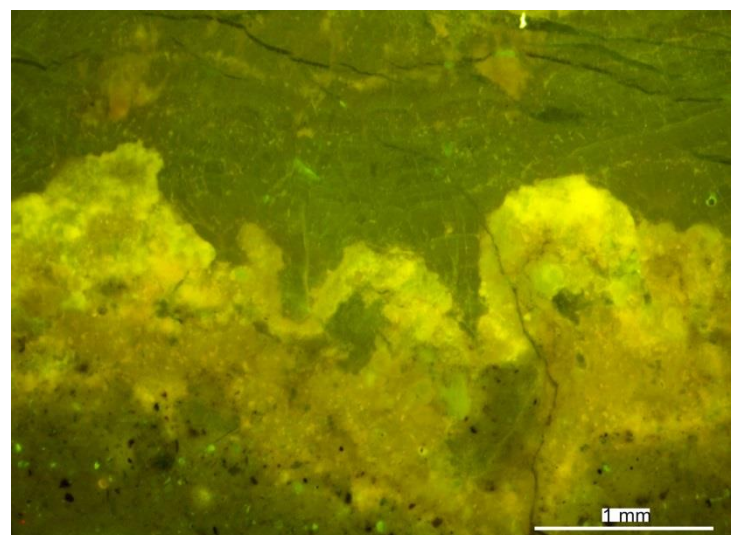
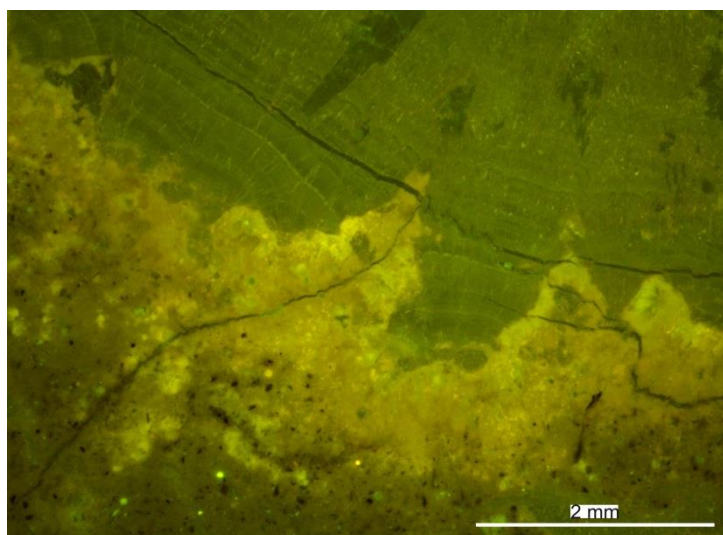
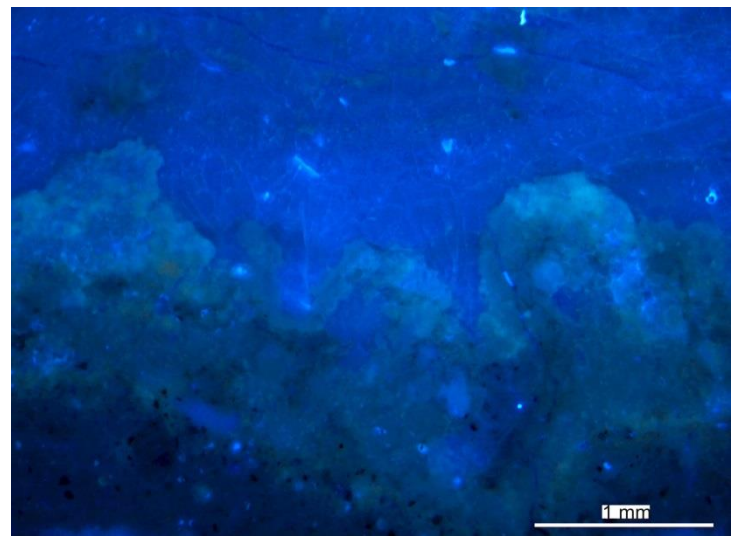
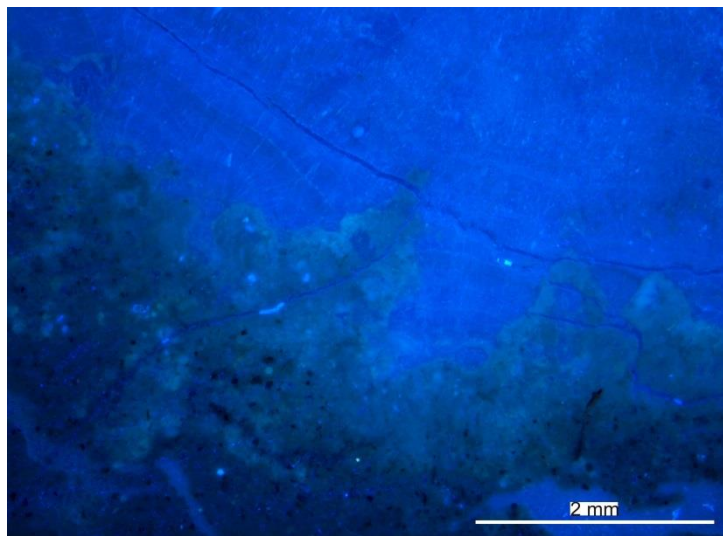
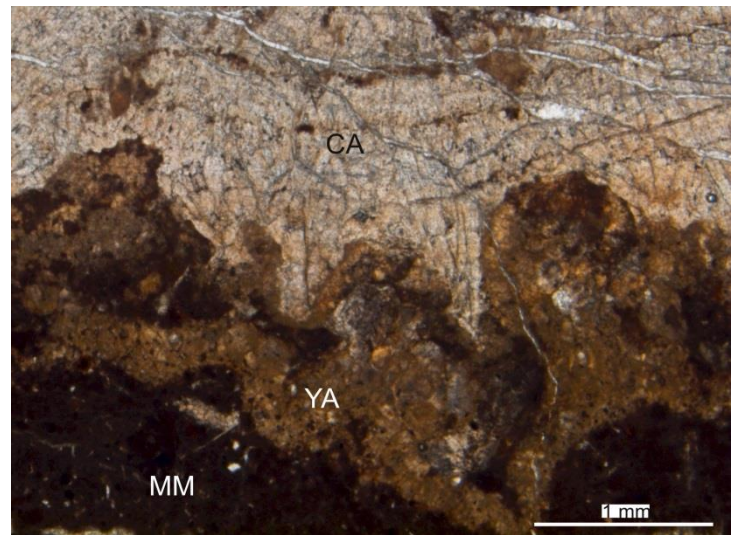
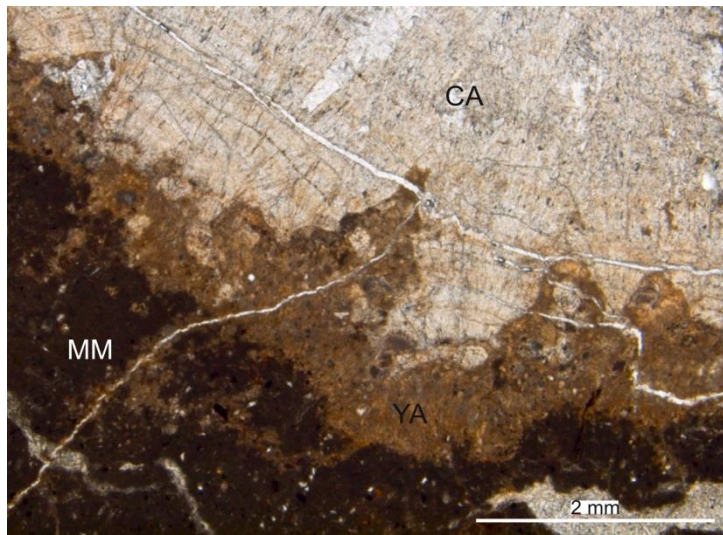


Fig. 18 top: Photographs of SR4 samples under plane polarized light. 18 middle: Epifluorescence photograph showing matrix micrite (MM), and fluorescent yellow (YA) and clear (CA) aragonite with UV filter. 18 bottom: Same as middle photographs with blue filter.

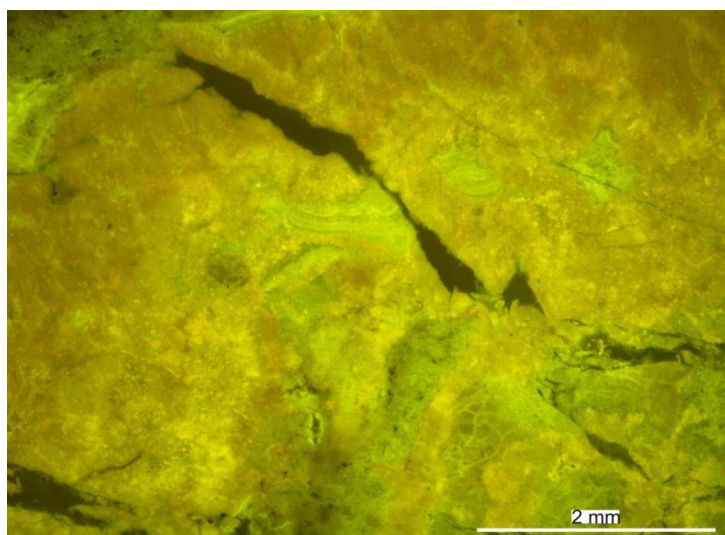
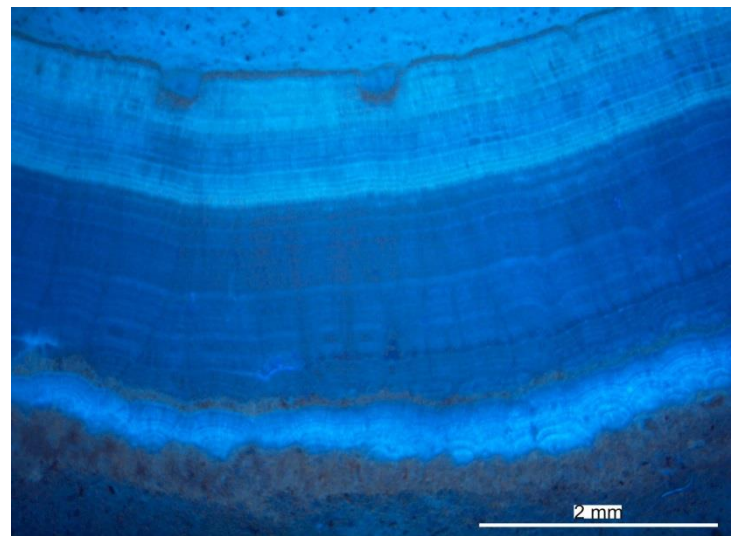
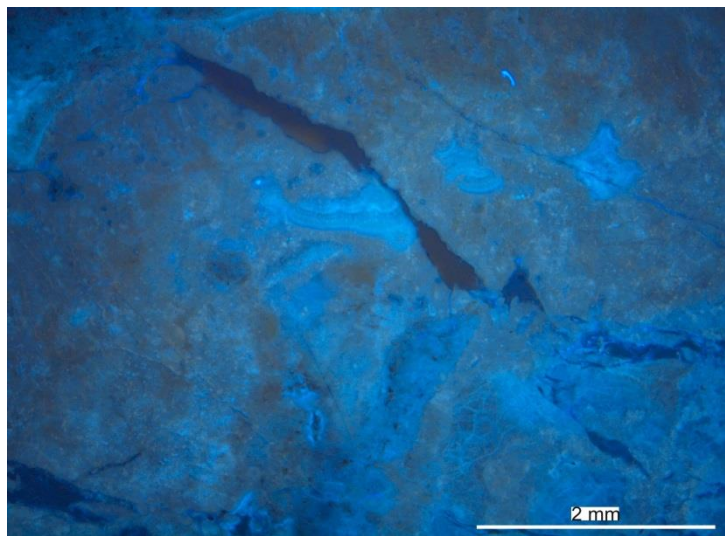
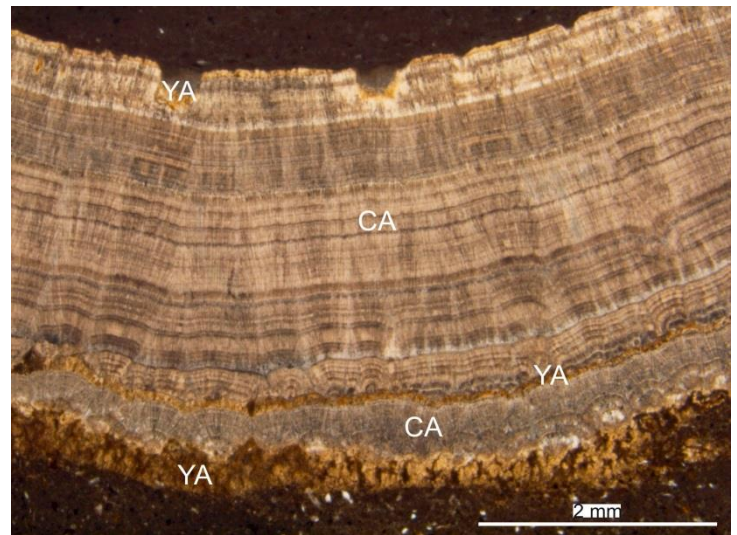
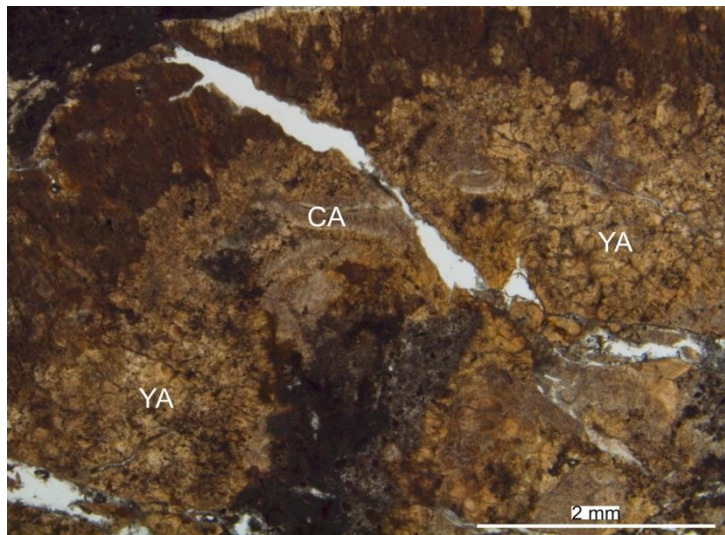


Fig. 19 top: Photographs under plane polarized light. 19 middle: Epifluorescence photograph showing matrix micrite (MM), and fluorescent yellow (YA) and clear (CA) aragonite with UV filter. 19 bottom: Same as middle photographs with blue filter. Left column from SMFSR, right column from CR1

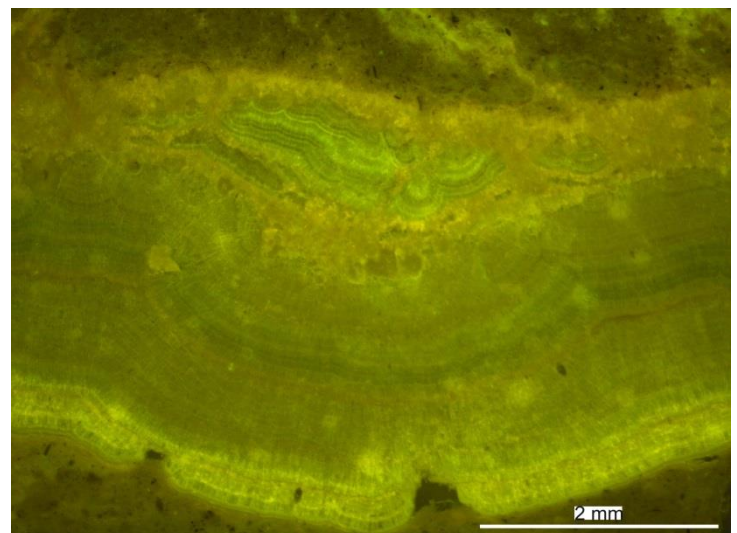
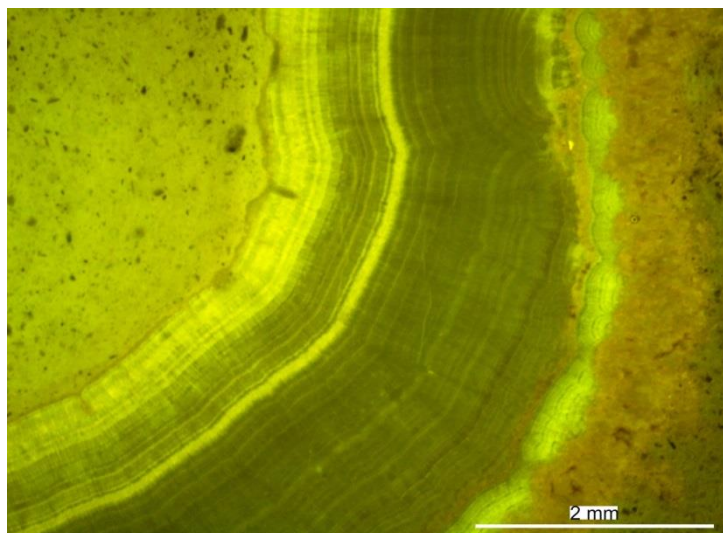
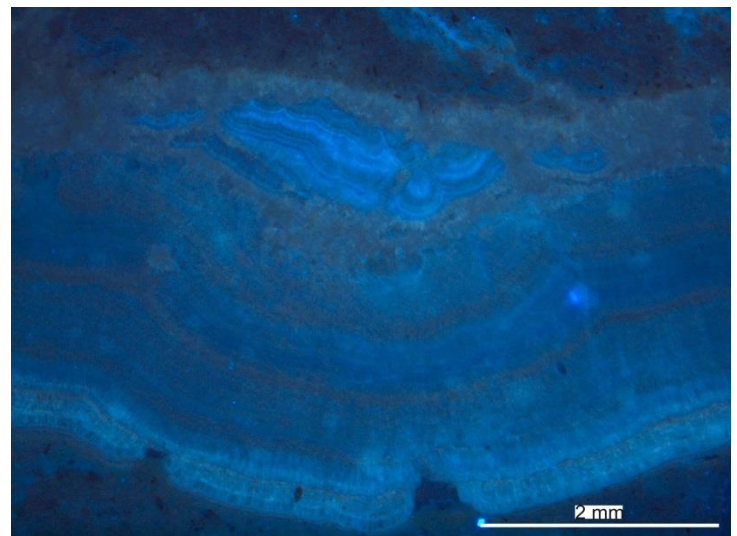
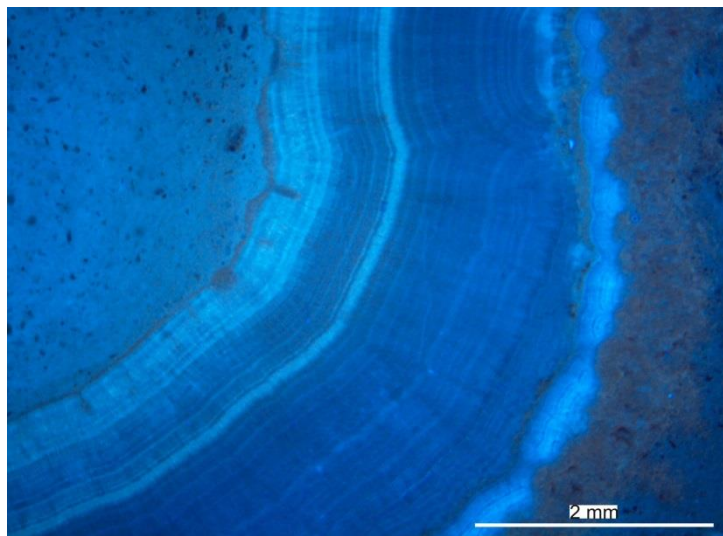
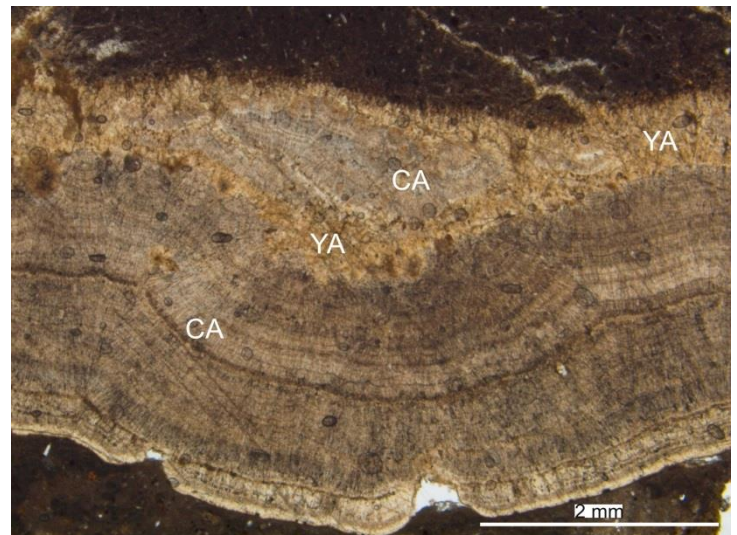
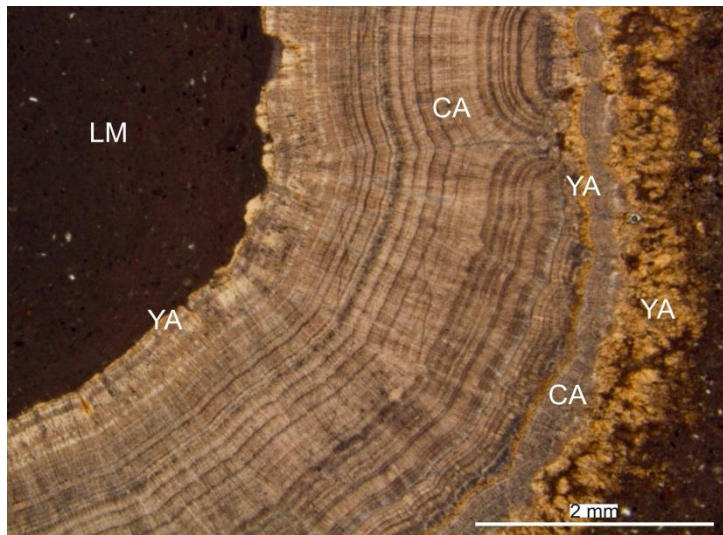


Fig. 20 top: Photographs under plane polarized light. 20 middle: Epifluorescence photograph showing late micrite (LM), and fluorescent yellow (YA) and clear (CA) aragonite with UV filter. 20 bottom: Same as middle photographs with blue filter. Left column from CR1, right column from SMFSR.

Microspar encloses dispersal distributed grains of pyrite as well as framboidal pyrite. Brownish calcite exhibits rod-shaped crystal aggregates, in some cases a dumbbell-shaped (Fig. 16). The aggregates are up to 50 μm in length. Unidentified brownish schlieren cover the crystal aggregates of brownish calcite in most places. Glauconite and pyrite also occur within brownish calcite. Brownish calcite revealed a blue stain after treatment with the combined potassium ferricyanide and alizarin red stain, indicating the presence of ferrous iron within this carbonate lattice. Pipe-filling micrite, microspar and brownish calcite have a very weak, dull fluorescence (Fig. 20). Most feeder pipes show a distinct paragenetic sequence starting with matrix micrite followed by yellow aragonite and clear aragonite. These pipes were then filled by different later phases, pipe-filling micrite, microspar and brownish calcite. There are however, deviations from this common sequence such as geopetal fillings occurring in the feeder pipes from SMFSR (Fig. 17). These fillings show a chaotic fabric and are pervaded by numerous fractures. In such sequence yellow aragonite is sometimes absent and clear aragonite is directly adjacent to matrix micrite.

4.2 X – Ray diffraction

The XRD analysis was conducted for brownish calcite (Fig. 21). This phase was analyzed because of the unique blue stain resulting from treatment with combined potassium ferricyanide and alizarin red solution, indicating a high Fe content in the carbonate lattice. XRD results, however, indicate a Low-Mg-calcite composition with 0.97 mole% Ca and 0.03 mole% Mg. XRD further reveals that approximately 1 to 2% quartz and the same amount of tentatively identified albite are present.

4.3 Stable C and O isotopes

The carbonate mineral phases making up the feeder pipes from the SR4 deposit were analyzed for stable carbon and oxygen isotope compositions. A total of 42 samples was analyzed (Fig. 22). The $\delta^{13}\text{C}$ values of yellow and clear aragonite were lowest, whereby values of clear aragonite range from -50.6 to -42.1‰ , and values of yellow aragonite range from -47.9 to -41.2‰ . Matrix micrite also revealed exclusively negative $\delta^{13}\text{C}$ values ranging from -40.5 to -19.2‰ . The $\delta^{13}\text{C}$ values of pipe-filling micrite (-2.3 to -0.3‰) and microspar (-0.4 to $+3.9\text{‰}$) are considerably more positive. The only phase that shows exclusively positive $\delta^{13}\text{C}$ values is brownish calcite. Its $\delta^{13}\text{C}$ values spans from $+0.3$ to $+2.5\text{‰}$. Stable oxygen isotope compositions vary noticeably from phase to phase. Clear and yellow aragonite both show overall positive $\delta^{18}\text{O}$ values ranging from $+0.9$ to $+1.8$ and $+0.9$ to $+1.6\text{‰}$, respectively. Matrix micrite yielded values from -3.9 to $+0.1\text{‰}$, whereas pipe-filling micrite exhibits values from -4.4 to -4.1‰ . Microspar and brownish calcite both show negative $\delta^{18}\text{O}$ values spanning from -5.0 to -4.5‰ and from -6.5 to -5.6‰ , respectively.

4.4 Carbonate content, trace and rare earth element contents

Matrix micrite showed the lowest carbonate contents of all phases ranging between 63.1% and 70.8%. For clear aragonite, a carbonate content of 96.5% was determined. It is, thus, the purest carbonate phase. Microspar has a carbonate content of 76.5% and brownish calcite carbonate content ranges from 61.4% to 72.2%. The highest content of $\Sigma\text{REE}+\text{Y}$ is represented by the matrix micrite with a mean value of 26.1 mg/kg, followed by yellow aragonite with 11.4 to 16.6 mg/kg. Clear aragonite shows $\Sigma\text{REE}+\text{Y}$ mean values of 0.3 to 3.9 mg/kg. Microspar has considerably lower contents with a mean value of 10.0, whereby clear aragonite has the lowest $\Sigma\text{REE}+\text{Y}$ contents amounting to total mean values ranging from 0.3 to 3.4 mg/kg. Brownish calcite exhibits a mean $\Sigma\text{REE}+\text{Y}$ content of 31.8 mg/kg. The REE+Y patterns vary among the different carbonate phases. All phases show enrichment of heavy rare earth elements (HREE) and depletion in the light rare earth elements (LREE), except for yellow aragonite, which displays an opposite trend with LREEs enrichment and HREEs depletion (Figs. 23, 24). $\Sigma\text{REE}+\text{Y}$ patterns of matrix micrite, yellow and clear aragonite from sample 03 show positive Eu anomalies. In sample 07, only brownish calcite exhibits a positive Eu anomaly (Fig. 24). Yttrium to Ho ratios of sample 03 vary considerably among the different carbonate phases. Matrix micrite, yellow aragonite, and microspar have rather similar mean ratios of 25.8, 25.5, and 27.7, respectively. Only clear aragonite shows a higher mean value of 44.2. By comparison, yellow aragonite and brownish calcite from sample 07 exhibit mean ratios of 26.2 and 28.2, respectively. Clear aragonite from this sample revealed a mean ratio of 36.6.

For comparison, we highlight the Ni and Ba contents of the aragonite phases, whereas Mg and Sr contents are plotted for all mineral phases (Fig. 25). Nickel and Ba are both more abundant in yellow aragonite compared to clear aragonite. Magnesium is enriched in microspar and brownish calcite. Conversely, Sr is more abundant in the aragonite cements than in microspar and brownish calcite.

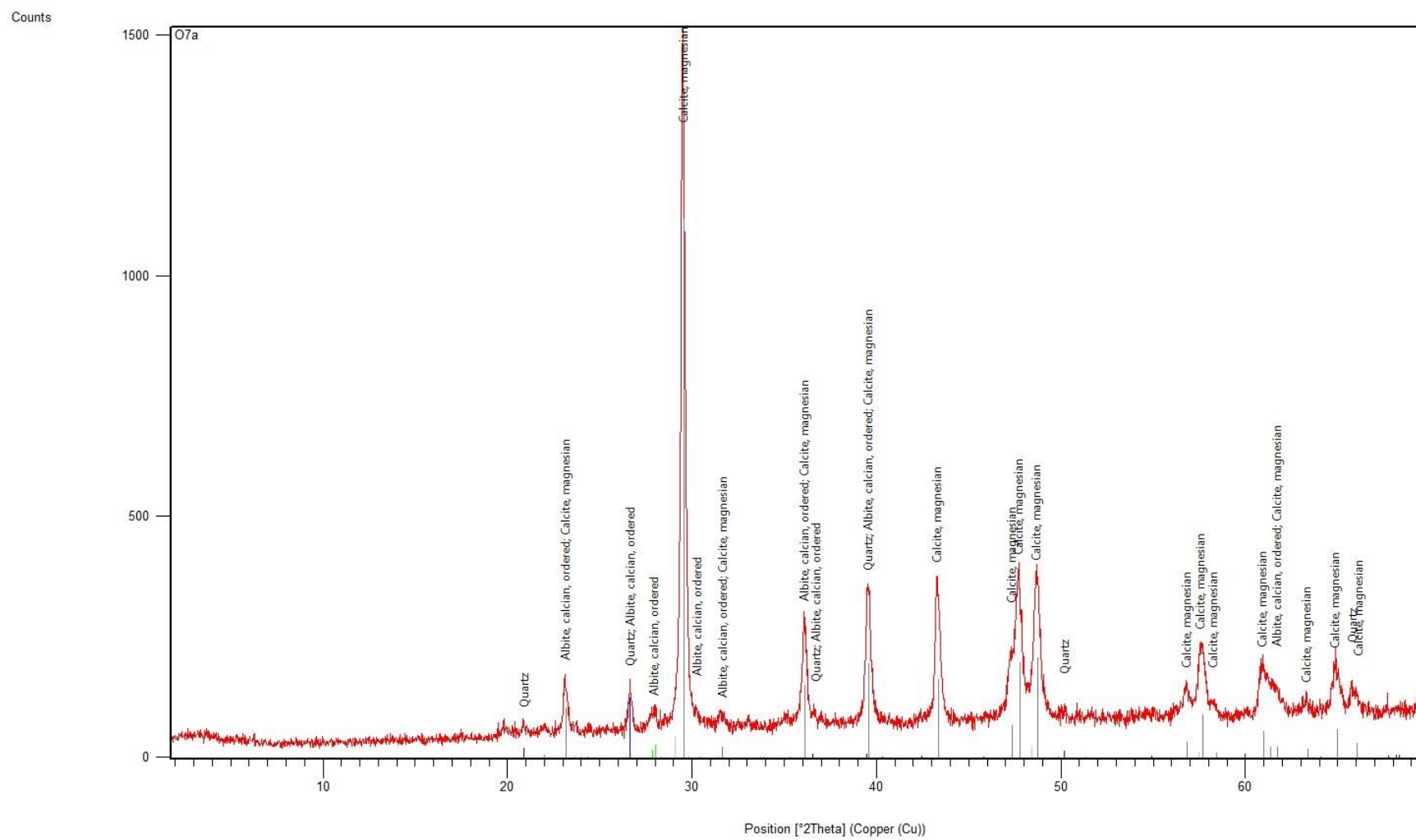


Fig. 21: XRD pattern of brownish calcite

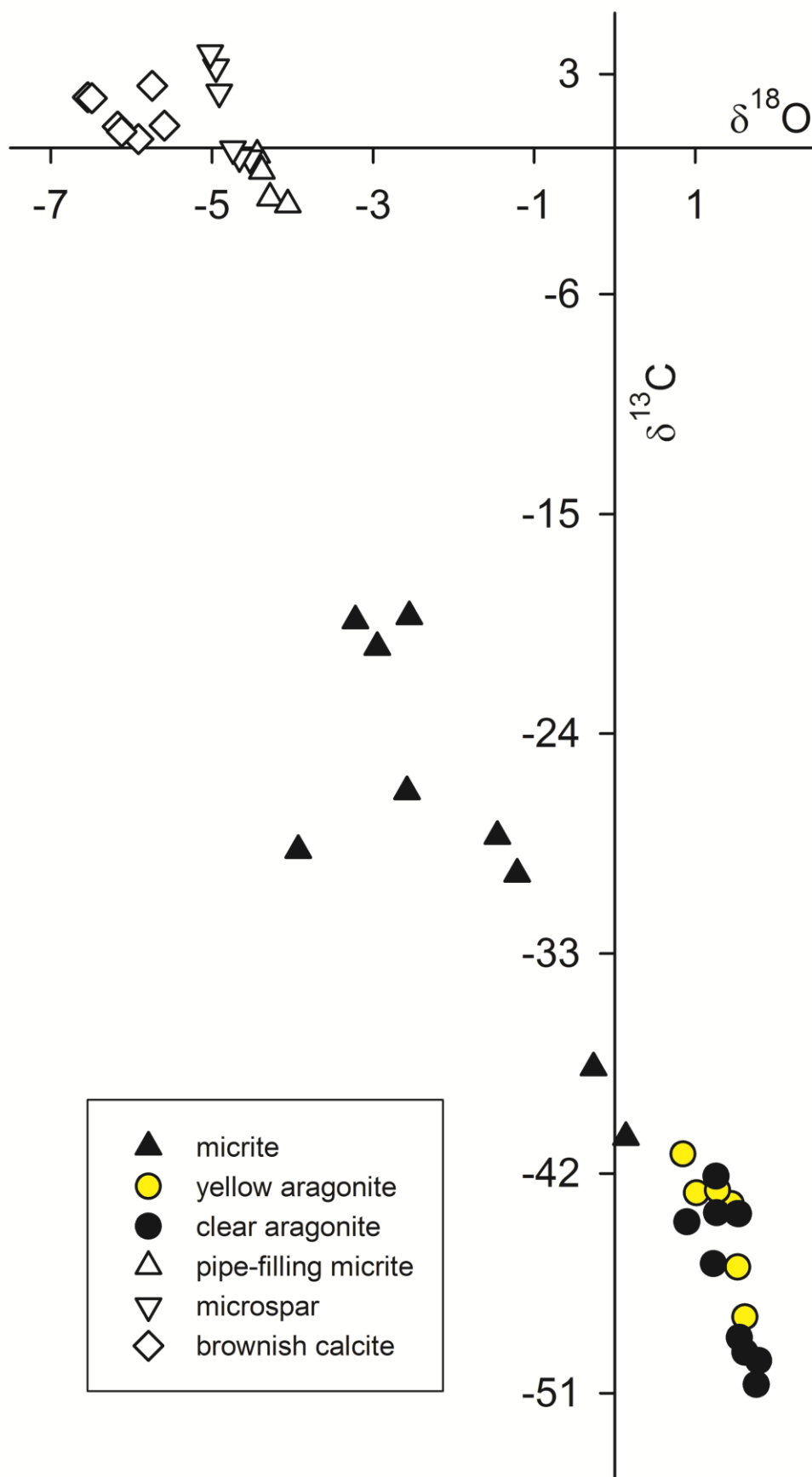


Fig. 22: Stable carbon and oxygen isotope plot the phases making up SR4 feeder pipes. Values are relative to VPDB standard

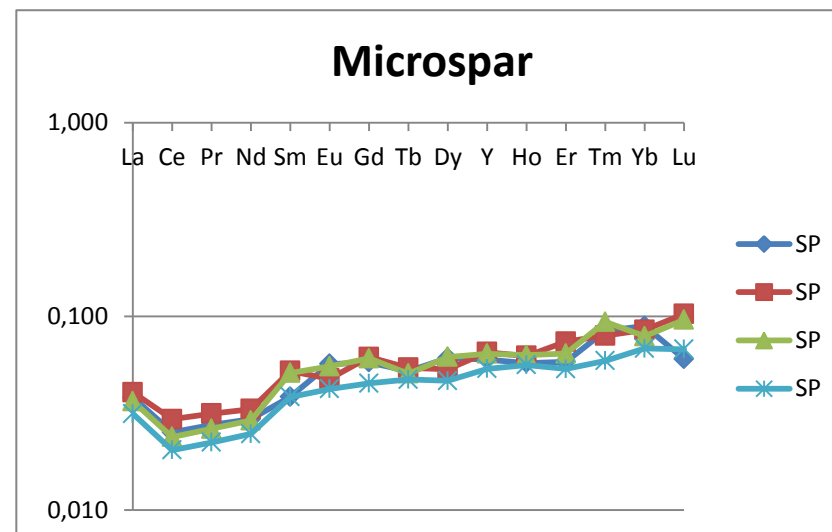
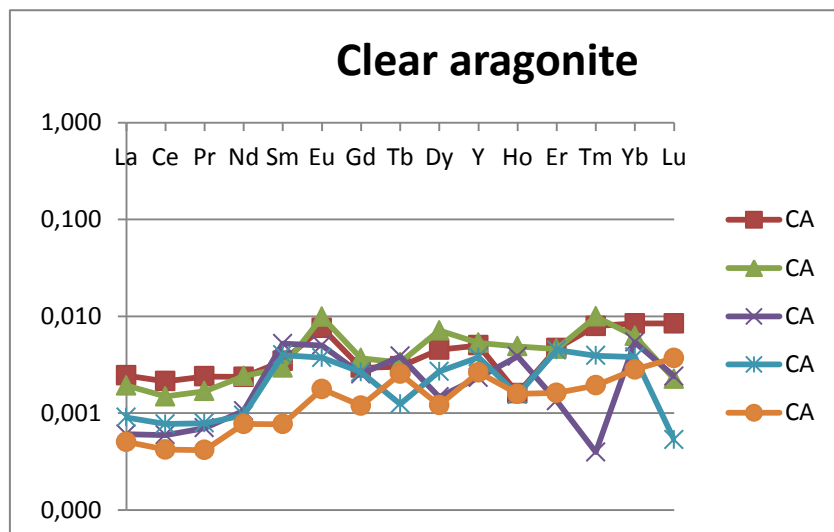
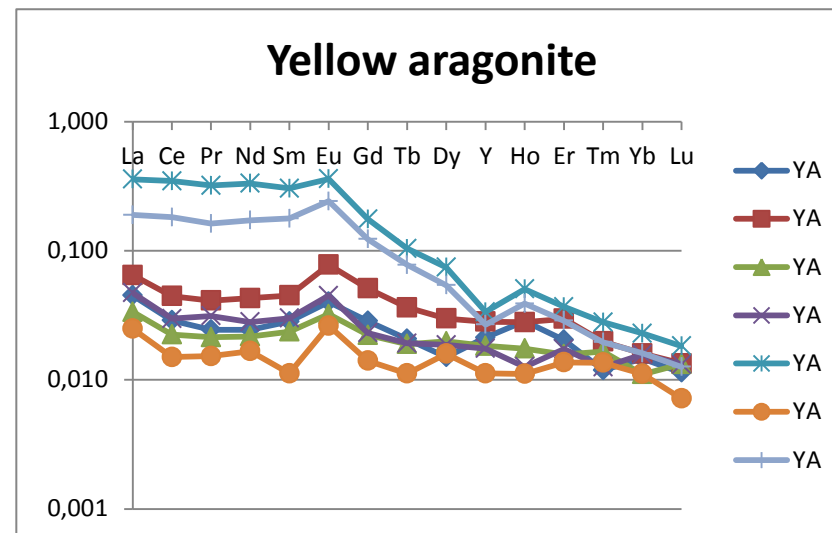
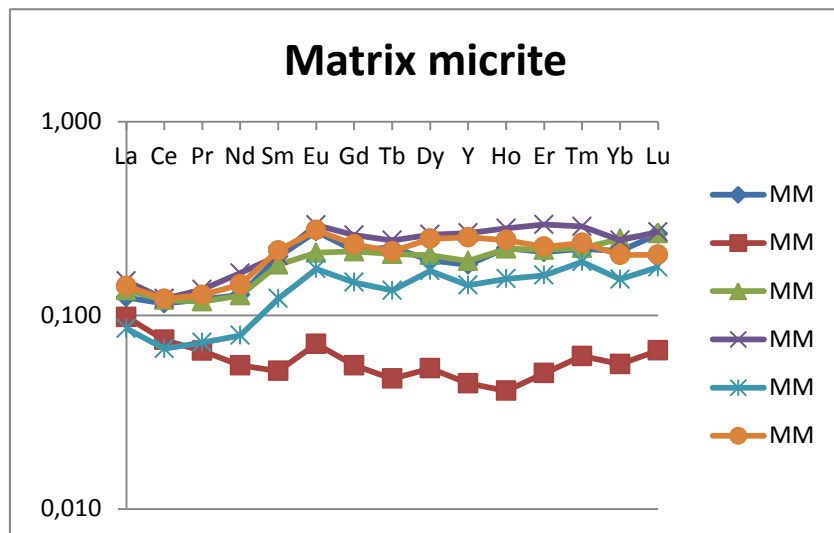


Fig. 23: Phase-specific, PAAS normalized rare earth elements + yttrium values for sample 03 (SR4) obtained with LA ICP-MS. **Vertical-axis = sample/PAAS.**

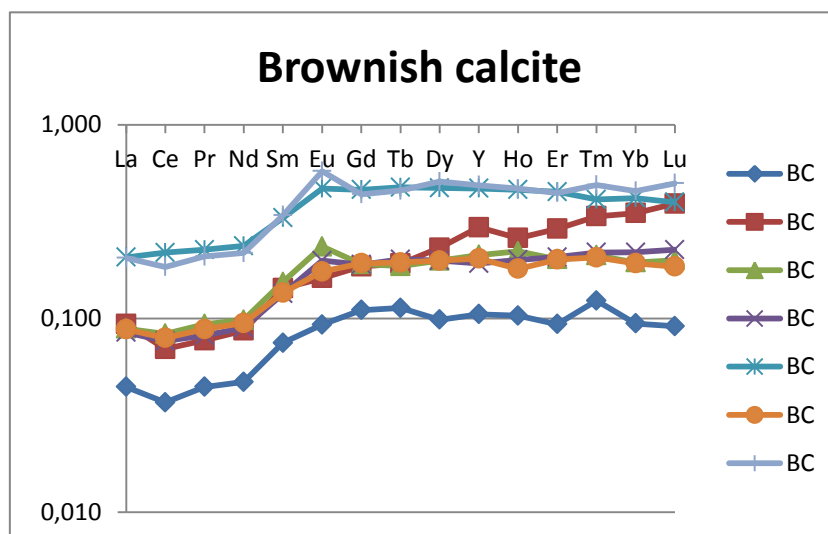
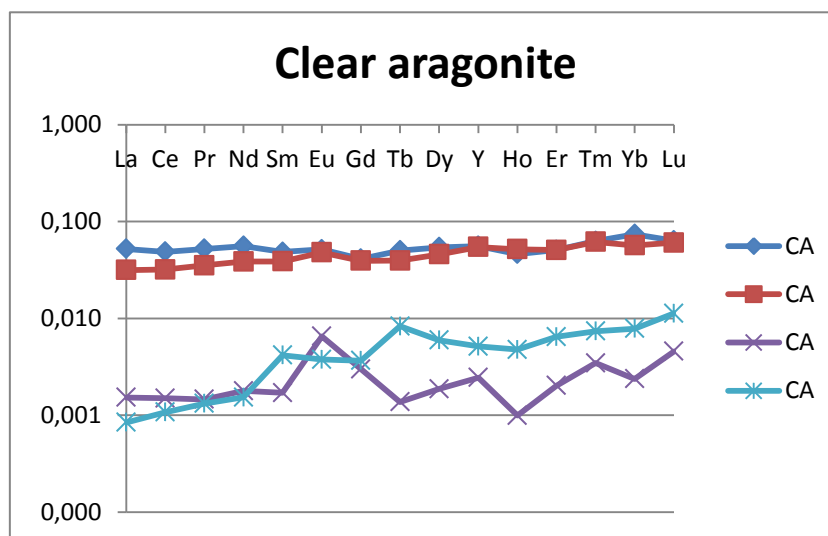
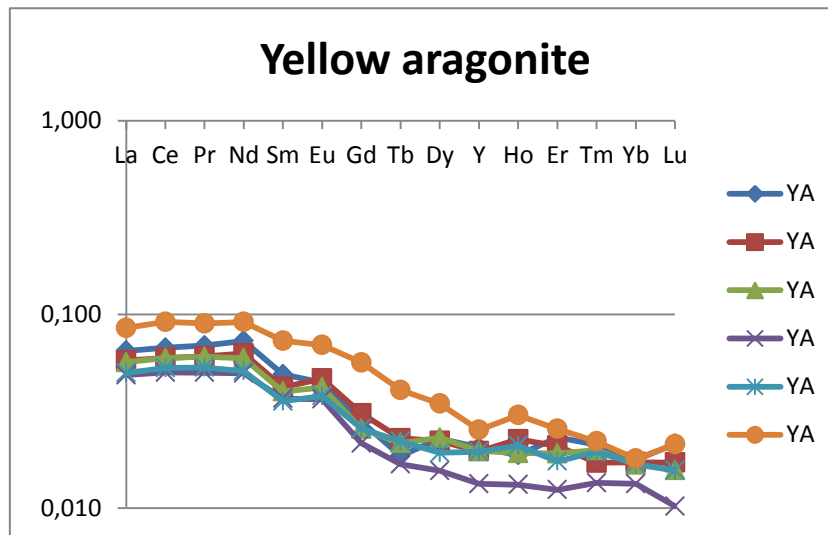


Fig. 24: Phase-specific, PAAS normalized rare earth elements + yttrium values for sample 07 (SR4) obtained with LA ICP-MS. **Vertical-axis = sample/PAAS.**

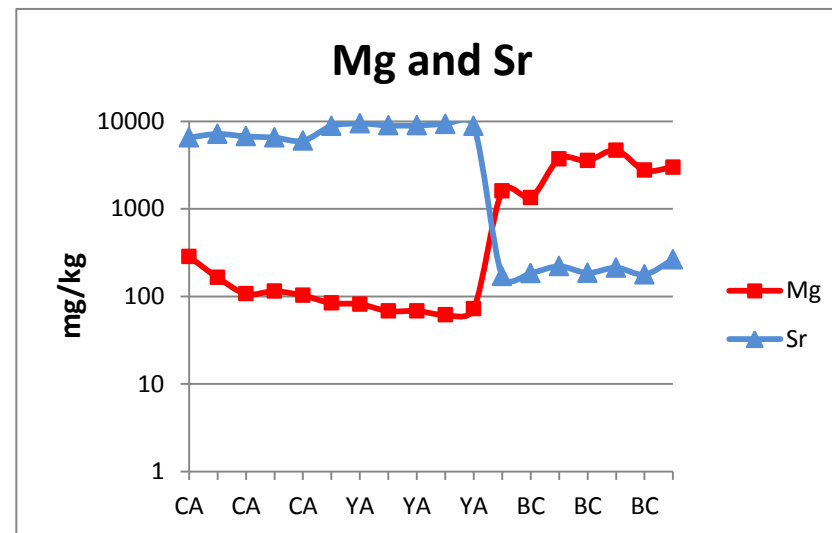
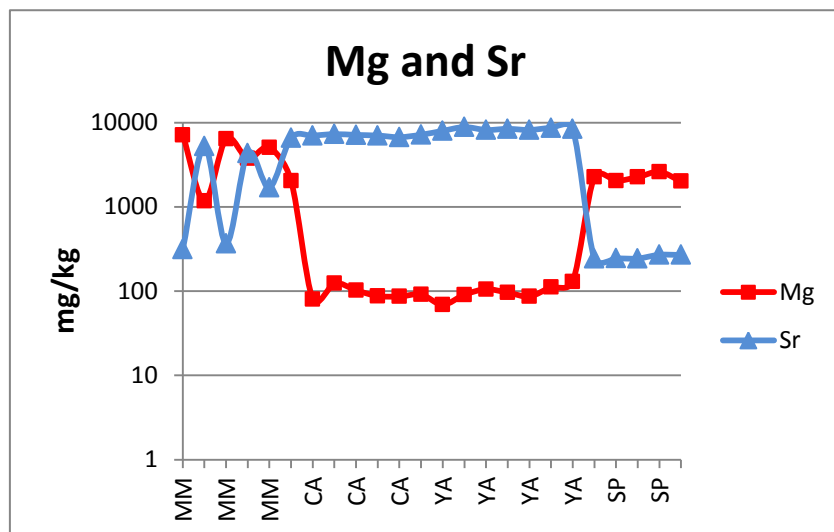
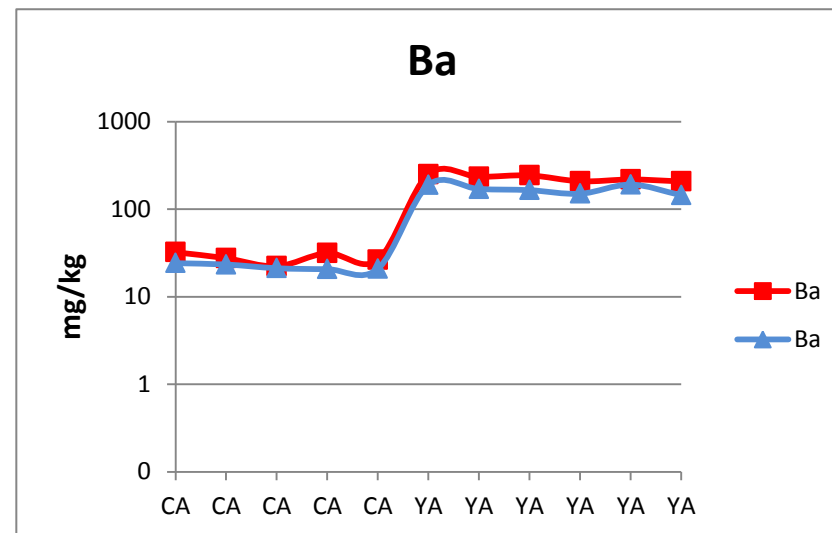
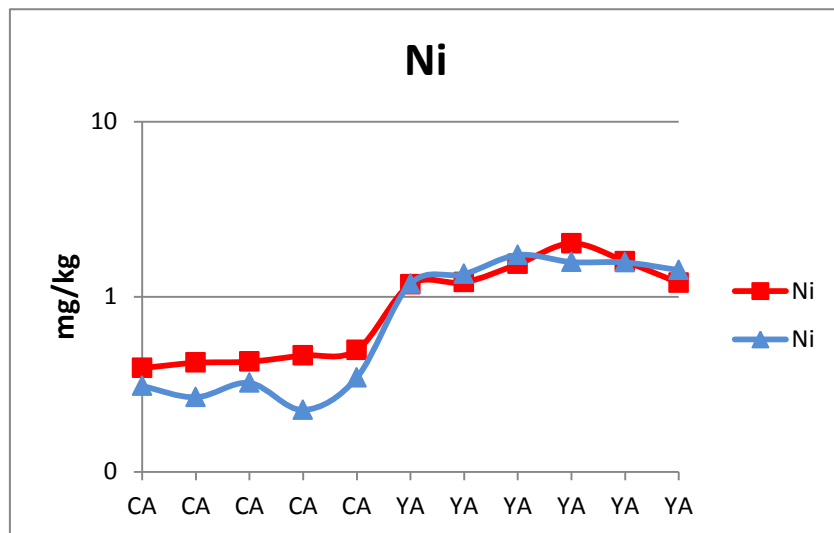


Fig 25: Contents of major and trace elements. A and B: Ni and Ba contents in aragonite cements. Red line with squares is sample 07; blue line with triangles is sample 03. C: Mg and Sr contents from all phases for sample 03. D: Mg and Sr contents from all phases for sample 07.

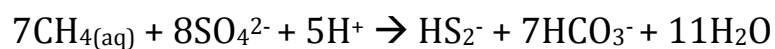
5. – Discussion

5.1 Implications of the paragenetic sequence

The process triggering carbonate precipitation at cold seeps is the sulfate dependent anaerobic oxidation of methane (AOM), proceeding according to the following net reaction (Devol and Ahmed 1981):



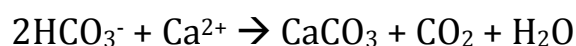
AOM is mediated by a consortium of anaerobic methanotrophic archaea (AMNE) and sulfate reducing bacteria (Deltaproteobacteria; *Desulfosarcina* and *Desulfococcus* clusters, Boetius et al., 2000; Knittel and Boetius, 2009; Milucka et al., 2012). ANME-2 accomplish AOM and the reduction of sulfate to disulfide or zero-valent sulfur compounds. The produced disulphide is then used by Deltaproteobacteria and disproportionated to sulfide and sulfate (Milucka et al., 2012):



When methane, which is primarily produced by archaeal methanogenesis in sulfate-depleted subsurface sediment, is transported upwards, it creates a steep methane gradient until it is oxidized in at the base of the sulfate reduction zone, where sulfate diffuses downward from seawater (Jørgensen and Kasten, 2006) or is provided by disproportionation from sulfate reducing bacteria (Milucka et al., 2012). This region in the sediment is also termed the sulfate methane transition zone (SMTZ).

Microcrystalline calcite (micrite) is the most common carbonate phase in most marine seep limestones (Beauchamp and Savard, 1992; Peckmann et al., 1999, 2002, 2003,

2011; Campbell et al., 2002; Kuechler et al., 2012) and it makes up the outer parts of the feeder pipes, representing the first phase of the paragenetic sequence. Micrite formation was primarily induced by AOM with possible contribution from the decomposition of organic matter by bacteria, which results in physicochemical changes of the microenvironment and leads to calcium carbonate precipitation (Flügel, 2004) according to the reaction (Baker and Burns, 1985):



The formation of authigenic pyrite within the matrix micrite is also linked to the activity of bacterial sulfate reduction and AOM, which produces reduced sulfur species such as bisulfide and hydrogen sulfide. These compounds have a high affinity for dissolved iron, which reacts to form iron monosulfides, which eventually transform into pyrite. The dependence of pyrite formation on the availability of reduced iron and sulfur species makes pyrite a valuable indicator for reducing, anoxic conditions in marine sediments (Berner, 1984; Raiswell and Berner, 1985; Peckmann et al., 2001; Neretin et al., 2004). The observed glauconite grains are possibly detrital, such as carbonate fragments, sponge spiculae, benthic foraminifera, pieces of wood and organic material, as well as quartz and feldspar. Glauconite authigenesis is in part dependent on the stability of pyrite and the redox potential within the sediment. Glauconite formation is thought to be favored by suboxic conditions, agreeing with the presence of both ferric and ferroan iron in its crystal lattice (Weaver and Pollard, 1973; Kelly and Webb, 1999). Thus, under partly reducing conditions, glauconite may form as long as iron sulfides are unstable (Kelly and Webb, 1999). In other words, iron sulfide precipitation is the limiting factor for glauconitization because of the competition for ferrous iron (Baldermann et al., 2013). However, as indicated by the presence of pyrite, feeder pipes formed under strongly reducing conditions making glauconite authigenesis unlikely. Petrographic observations reveal that pyrite grew at the expense of detrital glauconite grains. Fecal pellets observed in the matrix micrite were produced by organisms eating mud and digesting organic matter from it. The non-digested lime mud is excreted and the remains are characterized by the oval to spherically shaped pellets (Flügel, 2004). These

trace fossils were possibly produced by *Calianassa*, a marine thalassinid decapod crab (Peckmann et al., 2007), indicating macrofaunal activity at the seep. On-going micrite precipitation led to increased consolidation of the host sediment, providing a solid cast leading to the stabilization and subsequent preservation of feeder pipes (Campbell, 1992). The producers of the pipes are discussed afterwards.

Matrix micrite is followed by yellow aragonite cement, which is still an early diagenetic phase. Yellow aragonite, or yellow calcite, occurs in many ancient cold seep deposits (e.g. Beauchamp and Savard, 1992; Savard et al., 1996; Campbell et al., 2002; Peckmann et al., 2002, 2003; Himmler et al., 2008; Kuechler et al., 2012; Hagemann et al., 2012).

Trace element analyses and thin section staining confirmed that the yellow cement is in fact aragonite, due to significant enrichment in Sr and depletion in Mg (cf. Fig. 25).

Aragonite authigenesis was induced by AOM, which is reflected in the isotope patterns (negative $\delta^{13}\text{C}$ values). The occurrence of yellow aragonite in the vicinity of clear aragonite is noteworthy. The growth of yellow aragonite into veins and fracture surfaces of matrix micrite, its intrusion, penetration and overgrowth on clear aragonite implies highly dynamic and unusual growth patterns, which is interpreted to represent its formation within biofilms (cf. Hagemann et al., 2012). This scenario is supported by the intense fluorescence of this phase in comparison to all other phases in the sequence.

Isotope patterns and its relationship to yellow aragonite argue that clear aragonite is also an AOM related precipitate (cf. Beauchamp and Savard, 1992; Savard et al., 1996; Peckmann et al., 2002). Clear aragonite precipitated as a result of oversaturation due to AOM induced bicarbonate formation. The rhythmic precipitation of both cements indicated by crystal bands may reflect variations in the fluid flux regime. A possible scenario is that advective fluid flux supports growth conditions of microbial mats within the feeder pipes, and formation of larger clear aragonite bands is hindered due to rapid flushing of ions (including bicarbonate) from the pipes (cf. Luff et al., 2004). In periods of lower advective flux and higher local bicarbonate concentrations, the precipitation of broader aragonite bands is facilitated. Aragonite precipitation is favored over calcite due to the inhibiting effect of hydrated Mg^{2+} and sulfate ions on the calcite crystal lattice (Morse et al., 1997; Bots et al., 2011). Both yellow and clear aragonite probably precipitated in proximity to the seafloor, where seawater $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios and abundant sulfate inhibited calcite precipitation. Such reasoning is plausible since at modern seeps, aragonite appears to be the dominant carbonate mineral close to the sediment-water

interface (e.g. Bohrmann et al., 1998; Greinert et al., 2001; Luff et al., 2004).

The late diagenetic innermost phases including pipe-filling micrite, microspar and brownish calcite all formed in pore waters affected by archaeal methanogenesis, as revealed by their high $\delta^{13}\text{C}$ values compared to AOM related phases. Microspar crystals are larger than micrite crystals. The characteristic crystal morphology of brownish calcite has previously been observed by Peckmann et al. (2002). The dumbbell shaped crystal aggregates may possibly be induced by bacterial activity (cf. Warthmann et al., 2000), causing the required degree of supersaturation for this type of crystal aggregate (Fernandez-Diaz et al., 1996). As the XRD analysis revealed, this phase is a low Mg calcite with possible authigenic albite (Fig. 21). Observed fractures of some of the pipes are due to in situ brecciation caused by increased gas pressure or, maybe, gas hydrate dissociation (MacDonald et al., 2003). Horizontal lying tubes show a geopedal filling.

5.2 Implications of stable C and O isotope compositions of carbonate phases

Seep carbonates derived from biogenic methane are depleted in ^{13}C (e.g. Ritger et al., 1987; Peckmann et al., 2003; Peckmann and Thiel, 2004; Teichert et al., 2005). This signature is caused by the strong fractionation during archaeal methanogenesis, which may result in $\delta^{13}\text{C}$ values of methane as low as -110‰ (Whiticar et al., 1986). During anaerobic oxidation of methane, bicarbonate is produced that inherits this carbon isotope signature. Calcium finally reacts with carbonate ions, resulting in calcium carbonate precipitates depleted in ^{13}C (Teichert et al., 2005). The extent of ^{13}C depletion depends on the degree of mixing of carbonate ions from different sources (Peckmann and Thiel, 2004). Thermogenic methane, marine bicarbonate and bicarbonate resulting from the oxidation of higher hydrocarbons and organic matter all exhibit more positive $\delta^{13}\text{C}$ values than biogenic methane (Roberts and Aharon, 1994; Whiticar, 1999; Peckmann and Thiel, 2004). In the paragenetic sequence of the Lincoln Creek Formation feeder pipes, the early diagenetic carbonate cements, yellow and clear aragonite, show the lowest $\delta^{13}\text{C}$ values (-50.6 to -42.2‰). Such low values indicate an origin of these phases from anaerobic oxidation of methane. This interpretation is consistent with the tight association of these cements, suggesting that both phases precipitated under

similar conditions. The matrix micrite, the earliest phase, shows $\delta^{13}\text{C}$ values from -40.5 to -19.2‰ . The large scatter of values can be explained by the heterogeneity of this phase and the admixture of carbon from sources other than biogenic methane oxidation. The later diagenetic phases, pipe filling micrite and microspar, show $\delta^{13}\text{C}$ values from -2.3 to $+3.9\text{‰}$. Positive $\delta^{13}\text{C}$ values from methane seep carbonates have been related to methanogenesis rather than methane oxidation and seepage (Gaillard et al., 1992; Peckmann et al., 2002). The ^{13}C enrichment of pore fluids is caused by the preferential uptake of ^{12}C during archaeal methanogenesis, leaving the residual CO_2 pool enriched in ^{13}C (Irwin et al., 1977). During burial caused by on-going sedimentation, the feeder pipes entered the zone of methanogenesis, where the later carbonate phases precipitated from ^{13}C enriched pore waters. Brownish calcite is the only phase exhibiting exclusively positive $\delta^{13}\text{C}$ values, and has previously been suggested to reflect methanogenesis and reducing conditions (Peckmann et al., 2002).

Oxygen isotopes of seep carbonates are more difficult to interpret than carbon isotopes (Buggisch and Krumm, 2005). This is due to the ease of oxygen isotope exchange during diagenesis as the oxygen pool of the pore waters is much larger than that of carbon (Peckmann et al., 2003; Himmler et al., 2008). The early carbonate cements show slightly positive values. Such values at methane seeps have been ascribed to the dehydration of clay minerals (transformation of smectite to illite, cf. Han et al., 2004) and to the presence of gas hydrates, which incorporate the heavier oxygen isotope during formation and subsequently release it to the pore waters during dissociation (Bohrmann et al., 1998; Aloisi et al., 2000). Additionally, changes in pH also affect the oxygen isotopic composition of carbonates. Zeebe (1999) showed that a pH decrease of the solution by one unit leads to an increase of the $\delta^{18}\text{O}$ value of 1.42‰ . Finally, positive $\delta^{18}\text{O}$ values (between 0‰ SMOW (modern ocean water) and 1‰ SMOW (glacial ocean water)) indicate that carbonate precipitation occurred in close to the sediment water interface in equilibrium with seawater (Teichert et al., 2005; Himmler et al., 2010).

Considering the feeder pipes, precipitation from marine waters is favored over precipitation from fluids modified by gas hydrate dissociation, clay mineral dehydration and pH decrease to account for the oxygen isotopic composition of the early cements. Matrix micrite, early yellow and clear aragonite cements most likely precipitated close to the seafloor from fluids strongly influenced by seawater. During vigorous methane seepage through the conduits the enhanced methane flux shifts the AOM zone closer to

the seafloor (e.g. Luff et al., 2004). Later diagenetic phases, pipe-filling micrite, microspar and brownish calcite all show significant ^{18}O depletion. An enrichment in ^{16}O for later diagenetic phase of cold seep carbonates has been reported previously (Campbell et al., 2002; Peckmann et al., 2002, 2003; Himmler et al., 2008). The trend from positive towards more negative $\delta^{18}\text{O}$ values in seep carbonates has been attributed to progressive diagenesis, an increasing influence of meteoric waters and an increase in formation temperatures during burial (Campbell et al., 2002; Peckmann et al., 2002). Such a scenario is also feasible for the feeder pipes as the later, pipe-filling phases all exhibit lower $\delta^{18}\text{O}$ values.

5.3 Implications of rare earth element contents of carbonate phases

Ancient carbonates are thought to reliably inherit the rare earth element (REE) compositions of the pore waters from which they formed, and have therefore been used to track past changes in fluid chemistry (e.g. Zhong and Mucci, 1995; Webb and Kamber, 2000; Tanaka and Kawaba, 2006; Zhao and Jones, 2013). This approach has also been successfully applied for seep carbonates (Feng et al., 2009, 2010; Himmler 2010; Bayon et al., 2011; Rongemaille et al., 2011). Matrix micrite shows a slight enrichment of heavy rare earth elements (HREEs) relative to light rare earth elements (LREEs) and a slight positive Eu anomaly. HREE enrichment patterns have been interpreted to reflect the influence of oxygenated bottom waters, the degradation of organic carbon and increased HREE complexation by carbonate ions in carbonate rich sediments (Byrne and Kim, 1990; Himmler et al., 2010; Rongemaille et al., 2011). Haley et al. (2004) speculate that the HREEs are released during degradation of POC, whereby the LREE are adsorbed to residual POC which is not re-mineralized. The influence of oxygenated seawater is mostly accompanied by negative cerium anomalies and suprachondritic Y/Ho ratios (e.g. Feng et al., 2009; Himmler et al., 2010), both of which are absent in the REE patterns of the matrix micrite. Due to the absence of distinct Ce anomalies and rather low mean Y/Ho ratios of 25.8 (cf. Himmler et al., 2010), it is likely that the slight HREE enrichment in matrix micrite is linked to complexation by carbonate ions in solution. Positive Eu anomalies are characteristic for highly reducing hydrothermal fluids (Klinkhammer et al., 1983; Allen and Seyfried, 2005; Kim et al., 2012). This suggests that fluids with

positive Eu anomalies migrated from deeper sediments above the volcanic basement of the study area and influenced the REE composition of fluids from which the micrite precipitated. Clear aragonite shows very heterogeneous REE patterns and slight enrichments in HREEs just as matrix micrite and microspar. The higher Y/Ho ratios, twice as high than those of all other phases, indicate that seawater may have influenced the pore waters (Himmler et al., 2010). Furthermore, clear aragonite has by far the lowest total concentrations of REEs, indicating that this phase is a pure, authigenic carbonate (cf. Himmler et al., 2010). Microspar is more enriched in HREEs compared to LREEs than matrix micrite. Additionally, microspar shows a slight negative Ce anomaly, but no Eu anomaly. Since this phase is a product of later diagenesis, oxygenated seawater as a possible cause for the HREE enrichment is unlikely. This notion is further confirmed by the Y/Ho ratios of 27.7, which is much lower than that of oxygenated seawater. Interestingly, the REE pattern of microspar resembles patterns interpreted of carbonate phases that have been interpreted to reflect methanogenesis (Kim et al., 2012). The HREE enrichment can be explained the aforementioned processes, namely increased HREE complexation with carbonate ions in solution (Himmler et al., 2010; Kim et al., 2012). The origin of the negative Ce anomaly is difficult to interpret. In the case of microspar, a phase reflecting methanogenesis deeper within the sediment, an influence of seawater seems unlikely. Negative Ce anomalies can also be produced without the need for Ce oxidation under oxic conditions. Pourret et al. (2008) showed that at high CO_3^{2-} concentrations and alkaline pH, Ce-carbonate complexes may be readily adsorbed by organic particles such as humic substances, thus producing negative Ce anomalies in the residual waters. Cerium fractionation by organic particles during methanogenesis can explain the presence of negative Ce anomalies in seep carbonates precipitated from highly reducing pore waters (Himmler et al., 2010; Kim et al., 2012). Brownish calcite shows REE patterns very similar to that of microspar. This is in accord with the fact that this phase, like microspar, precipitated from a pore water pool affected by methanogenesis. However, the total amounts of REEs in brownish calcite vary considerably. All four phases, matrix micrite, clear aragonite, microspar and brownish calcite show a common enrichment pattern in HREEs over LREEs. The only phase deviating from these patterns is yellow aragonite. This phase shows enrichments of LREEs over HREEs as well as higher total REE concentrations than clear aragonite. Such a LREE enrichment pattern is unusual, and has not been previously observed for seep

carbonates. The preferential scavenging of LREEs over HREEs typifies particulate organic matter in seawater (Sholkovitz et al., 1994). Such preferred adsorption of LREEs to organic matter is reflected by the rare earth element pattern of yellow aragonite. This result is in agreement with the interpretation that yellow aragonite precipitated within biofilms covering the internal surfaces of the feeder pipes.

5.4 Origin of the feeder pipes

In contrast to the larger, tubular carbonate concretions described by Nyman et al. (2009) and De Boever et al. (2009, 2011), the much smaller feeder pipes (2-3 cm in diameter) from the Lincoln Creek Formation could have been produced by burrowing organisms, inhabiting the ancient cold seep site. Seep-endemic, megafaunal communities include sponges (Hexactinellida), anthozoa, bivalves, gastropods, cephalopods, decapods and others (cf. Peckmann et al., 2002). Among these, possible producers of the burrows that acted as fluid pathways are seep-endemic bivalves including *Calymene* sp. (e.g. Nobuhara, 2003; Campbell, 2006), *Acharax* sp. (Seike et al., 2012), *Lucinida* (Kiel, 2013) and *Thyasira* sp. (Zuschin et al., 2001; Kiel et al., 2008), and callianassid decapod crustaceans producing trace fossils such as *Spongeliomorpha*, *Ophiomorpha* and *Thalassinoides* (e.g. De Boever et al., 2009; Campbell et al., 2008; Chien et al., 2012; Wetzel, 2013). One option is that burrows were produced by bivalves via their extensible foot. Seep-endemic bivalves live in chemosymbiotic association with chemoautotrophic bacteria. The vesicomyid clam *Calymene* sp. and the solemyid *Acharax johnsoni* can extend their foot into the sediment to access reduced compounds (Childress and Girguis, 2010; Seike et al., 2012). This allows the bivalves to supply their symbiotic bacteria with reduced chemicals such as sulfide and methane while they still have access to oxygen (Levin, 2005; Childress and Girguis, 2010). *Acharax johnsoni* may reach shell lengths of up to 87 mm at seeps and produces burrows of up to 2 cm in diameter (Seike et al., 2012). Modern lucinid bivalves can extend their foot up to five times of their own shell lengths, *Thyasira* even up to fifteen times of their shell length (Dufour and Felbeck, 2003). Lucinid bivalves from ancient cold seeps may reach shell sizes from 60 to 200 mm (Kiel, 2013), *Thyasira* reach shell sizes from 5 to 15 mm (Kiel et al., 2008). Solemyid bivalves at ancient cold seeps may reach sizes to around 1.5 cm and

produces burrows of up to 20 cm in depth (Campbell, 1992). The shape of modern and ancient bivalve burrow structures range from straight (Dufour and Felbeck, 2003), to Y and U shaped (e.g. Campbell, 1992; Seike et al., 2012). Channeling of fluid flow at seeps due to the burrowing activity of bivalves has been suggested previously. Campbell (1992) reported fossilized *Solemya* burrows and invoked the possibility that the burrows serve as pathways for seeping fluids. In these conduits a mixing of carbon sources and fluids occurred, and was preceded by carbonate precipitation within the burrow after the organism died and active pumping had ceased (Campbell, 1992; Nobuhara, 2003). Likewise, Dufour and Felbeck (2003) showed that thyasirid and lucinid burrows act as conduits for sulfide. Nobuhara (2003) mentioned the effect of bioirrigation and pumping activity, producing a porous bioarchitecture possibly promoting upward fluid flow towards the sediment surface. Interestingly, also rims of aragonite cement on the inner walls of open burrows were mentioned, analogous to the feeder pipes in this study. However, the precipitation of the aragonite was linked to aerobic methane oxidation. Seike et al. (2012) proposed that modern *Acharax johnsoni* burrows actively enhanced methane discharge from sediments.

Another yet related option of feeder pipe generation is bioturbation by callianassid decapods. These crustaceans construct straight to branched and vertical to horizontal burrows within the subsurface sediment (Griffis and Suchanek, 1991; Papaspyrou et al., 2005) that may be preserved as trace fossils such as *Thalassinoides* or *Spongeliomorpha* (Neto de Carvalho et al., 2007; Peckmann et al., 2007). It has been suggested that the crustaceans inhabit sediments with anoxic pore waters (Bromley, 1996). They can tolerate anoxia for some time and are capable of ventilating parts of their burrow with oxygenated seawater (Forster and Graf, 1992; Anderson et al., 1994). Callianassid decapods feed on detritus and on burrow wall material, whereby excreted mucus used for the stabilization of the burrow walls acts as organic substrate for bacterial growth (Bertics et al., 2010). It has also been proposed that these invertebrates deliberately accumulate organic material to support microbial growth as an additional food source (bacterial gardening, Griffis and Suchanek, 1991). The functions of the burrow systems include protection and concealment from predators or disadvantageous environmental conditions, mating, fostering of juveniles or gardening (see above, Atkinson and Taylor, 1988; De Gibert and Ekdale, 2010). The burrow systems are built up by shafts and chambers, which measure 1 and 2 cm in diameter, respectively, and can extent up to 3

meters into the sediment (Bertics et al., 2010). *Spongiomorpha* burrows may reach up to 5 cm in diameter (De Gibert and Ekdale, 2010), showing that diameter and overall size of the burrows may vary considerably. *Thalassinoides*, unlike *Spongiomorpha*, do not exhibit bioglyphs on the inner walls of the burrows, but rather smooth and unlined to thinly lined walls (De Gibert and Ekdale, 2010). The occurrence of crustacean microcoprolites of the ichnogenus *Palaxius* in the feeder pipes provides evidence that decapod crustaceans lived at the cold seep site, and may have constructed the burrow systems that foster the formation of the feeder pipes. Interestingly, Peckmann et al. (2007) and Wetzel (2013) proposed that burrowing activity of crustaceans at seeps promotes the seepage of methane rich fluids. Both proposed producers could have constructed the feeder pipes as they all inhabited the ancient seep sites CR1 and SR4 (cf. Peckmann et al., 2002). However, it is beyond doubt that these pipes were caused by bioturbation, which regulates the uppermost plumbing system. It is difficult to decide which of these organisms produced the feeder pipes. Size and morphology of the pipes argue in favor of both producers and further investigations are required to make a more distinct statement.

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Assistenz bei dem Projekt „AIP – Austrian Interfacing Project: Paleoseismology of Temelin’s Near-Regional Faults“: Untersuchung einer seismischen Störung im Wiener Becken bei Markgrafneusiedl. Vorarbeiten zur Zugänglichmachung und Aufnahme eines sedimentologischen Profils.

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SPRACHKENNTNISSE

Deutsch: Muttersprache

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Software: Microsoft Office, Corel Draw, Adobe Photoshop

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Einführungskurse in:

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Zusammenfassung (Abstract)

Wege- und Kanalsysteme bilden komplexe Strukturen innerhalb mariner Sedimente. In kalten Methan Austritten sogenannten „methan seeps“ steigen Kohlenwasserstoff-angereicherte Fluide und Gase empor. In größeren Tiefen (mehrere hundert Meter) wird die Wegigkeit durch tektonische Brüche und Spalten (Störungen) ermöglicht. In seichteren Tiefen, einige Meter unterhalb der Sediment-Wasser Grenze findet der Fluid und Gastransport innerhalb von Kanälen statt, die oftmals durch Karbonatzemente verfüllt worden sind. Diese bilden dort mehrere Meter hohe und bis zu einem Meter im Durchmesser große Karbonat zementierte Röhren entlang derer Methan-angereicherte Fluide durchfließen. Diese Formationen wurden in den letzten Jahren intensiv diskutiert. Jedoch, den obersten Zentimetern der bioturbierten Sedimentzone wurde wenig Aufmerksamkeit geschenkt. Hier werden Röhren und Kanäle durch die Aktivität von Seep-endemischer Makrofauna angelegt. Diese Kanäle sind durch authigene Mineralfällungen verfüllt, die gekoppelt sind an die Sulfat-abhängige anaerobe Methanoxidation (AOM). AOM in marinen Sedimenten wird von einem Konsortium an anaeroben methanoxidierenden Archaea und sulfatreduzierenden Bakterien durchgeführt. Diese Arbeit beschreibt die Petrographie und Geochemie von Oligozänen Seep-Ablagerungen der Lincoln Creek Formation aus Washington State, USA. Die Arbeit enthält die Beschreibung der paragenetischen Sequenz authigener Minerale welche die Feeder Pipes verfüllen und geochemische Analysen der stabilen Kohlenstoff und Sauerstoffisotope, sowie der seltenen Erden und Spurenelementen. Zusätzlich wird diskutiert welche Organismen die Produzenten der Feeder Pipes sein können. Interessant und neu ist dass die Aktivität der grabenden Organismen Kanalsysteme anlegt, die anschließend den Austritt von Methan in die Wassersäule regulieren.